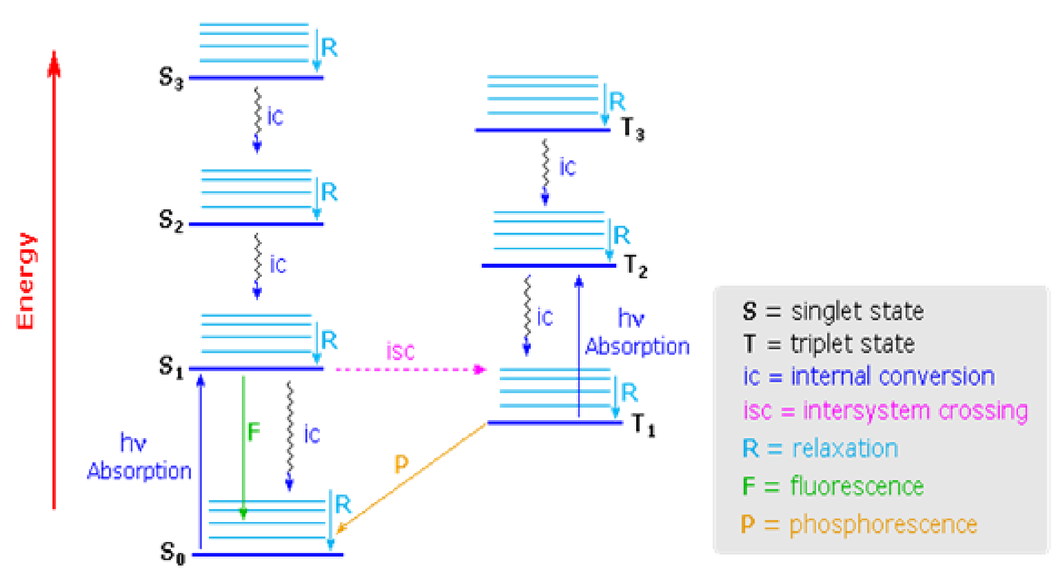
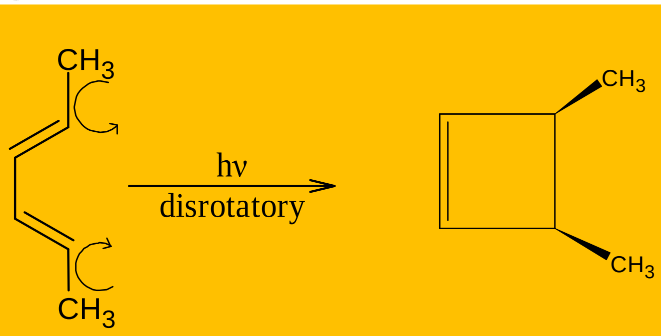
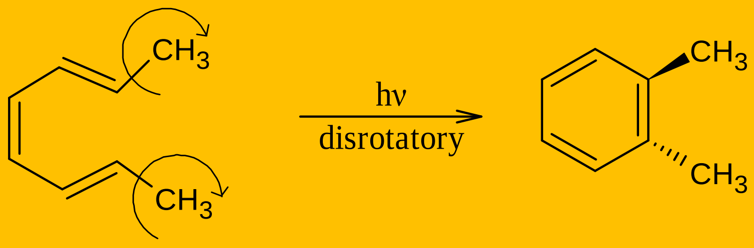
MSCCH-604

M.Sc. III Semester

PHOTO CHEMISTRY AND ALLIED CHEMISTRY







SCHOOL OF SCIENCES
DEPARTMENT OF CHEMISTRY
UTTARAKHAND OPEN UNIVERSITY

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CONTENTS

UNIT 1: BASICS OF PHOTOCHEMISTRY

CONTENTS:

1.1 INTRODUCTION

Photochemistry is the branch of chemistry in which study of chemical reactions take place by the absorption of electromagnetic radiation or by molecules absorb light radiation (electromagnetic radiation) particularly the visible (wavelength from (400-750) and ultra violet region (wavelength from 100-400nm), the molecules generally get activated due to electronic excitation. When electromagnetic radiation is absorb in the ultraviolet/visible region the molecules get excited to higher electronic state. This involves the promotion of an electron from bonding molecular orbital to antibonding molecular orbital.

According to the quantum theory, both matter and light are quantised, and only certain specific energies of light are absorbed by specific organic molecule for its excitation. The absorption or emission of light occurs by the transfer of energy as photons. These photons have both wave and particle-like properties and the energy E of a photon is given by Planck's law,

$E = h \upsilon$

Where h is Planck constant and is equal to 6.63×10^{-34}Js and υ is the frequency of oscillation of the photon in units of s^{-1} or Hertz (Hz).

$\upsilon = c / \lambda$

Where c is the velocity of light and λ is the wavelength of oscillation of photon. Thus, E

$E = h \upsilon = h c / \lambda$

Therefore, the energy of a photon is proportional to its frequency and inversely proportional to its wavelength. The energy of one mole of photons (6.02×10^{23} photons) is called an Einstein and is measured in units in kJ $mol^{-1.}$ It is equal to Nhc/λ.

The two main processes, therefore, studied under photochemistry are:

1. Photo physical process

2. Photochemical process

1. Photo physical process

In this process, the absorption of light does not result into any chemical reaction.

2. Photochemical process

In this process, the light that is absorbed by a system results into chemical change.

Difference between thermal and photochemical reactions

The main points of difference between thermal and photochemical reactions are as under:

Thermal Reactions	**Photochemical Reactions**
1. These reactions involve the absorption of heat	1. These reactions involve absorption of quantum of radiation. (UV/visible)
2. In these reactions, activation energy arises from the intermolecular collisions.	2. In these reactions, activation energy is acquired by absorption of quanta (hν)of radiation of suitable energy
3.When a reaction mixture is exposed to heat radiation, all the reactant molecules absorb these radiations and get excited almost to the same extent i.e., there is no selectivity	3. When a reaction mixture is exposed to light radiation, the molecules of a single selected species can be promoted to an excited state independent of the other species present in the mixture.
4. The presence of light is not necessary for the reaction to take place and can take place even in the dark.	4. The presence of light is an essential requirement for the reaction to take place.
5. Temperature has significant effect on the rate of a thermal reaction	5. Temperature has very little effect on the rate of a photochemical reaction. Intensity of light or electromagnetic radiations has a marked effect on the rate of a photochemical reaction
6. Rate of reactions of thermal reaction at a given concentrations can be change only by temperature change.	6. Rate of reactions, can be changed by change of intensity of radiations.

So, this unit mainly we study about of the chemical and physical changes that result from interactions between matter and visible or ultraviolet light.

1.2 OBJECTIVES

After studying this Unit, you should be able to:

- Absorption and excitation

- State the classical laws of photochemistry
- Electronic excited state –life times and measurement of times
- Flash photolysis, stopped and stopped flow techniques
- Energy dissipation by radiative and non radiative processes
- Franck-Codon Principle
- Absorption spectra
- Photochemical stages ie. Primary and secondary processes.
- This Unit familiarizes the reader with basic ideas relating to light and matter and the interaction between them.

1.3 ABSORPTION

All photochemical and photo physical processes are initiated by the absorption of a photon of visible or ultraviolet radiation leading to the formation of an electronically - excited state.

$R_{+} h\nu \rightarrow R^*$

For an effective interaction between the photon and the absorbing material:

- There should be a correspondence between the energy of the photon and the energy of a pair of electronic energy levels in the absorber.
- The strongest absorptions occur when the initial and final wave functions (ψ and ψ *) most closely resemble one another.

1.3.1 The Beer-Lambert’s law

The extent of absorption of light varies a great deal from one substance to another, with the probability of absorption being indicated by the molar absorption coefficient (ε). As light is absorbed, the intensity of light entering the substance, I in, is greater than the intensity of the emerging light, I out, and there is an exponential relationship between the relative absorption ($_{out}$ /I_{in}) and the concentration (c) and path length (l) of the absorbing substance:

$$I_{out} / I_{in} = 10^{-\varepsilon cl}$$

Taking logarithms to the base 10 gives us:

$$I_{out} / I_{in} = -\varepsilon cl$$

Thus,

$$I_{in} / I_{out} = \varepsilon cl$$

The left - hand - side quantity is the absorbance A, and the linear relationship between absorbance, concentration and path length is known as the Beer – **Lambert law.**

The Beer – Lambert law can generally be applied, except where very high - intensity light beams such as lasers are used. In such cases, a considerable proportion of the irradiated species will be in the excited state and not in the ground state.

The units of ε require some explanation here as they are generally expressed as non - SI units for historic reasons, having been used in spectroscopy for many years.

- Concentration, c, has units of moles per liter, (mol^{-1})
- Path length, l, has units of centimetres, (cm) .
- A has no units since it is a logarithmic quantity.

So the units of ε usually given are: $cm^{-1} x (mol^{-1})^{-1} = l\ mol^{-1}\ cm^{-1}$.

Molar absorptivity

The molar absorptivity (formerly called the extinction coefficient) of a compound constant that is characteristic of the compound at a particular wavelength. It is the absorbance that would be observed for a 1.00 M solution in a cell with a 1.00^{-cm} path length. The molar absorptivity of acetone, for example, is 9000 at 195 nm and 13.6 at 274 nm. The solvent in which the sample is dissolved when the spectrum is taken is reported because molar absorptivity is not exactly the same in all solvent so the UV spectrum of acetone in hexane would be reported as 195 nm (hexane); 274 nm (hexane). Because absorbance is proportional to concentration, the concentration of a solution can be determined if the absorbance and molar absorptivity at a particular wavelength are known.

$$\varepsilon = A/cl$$

So the units of ε usually given are**:**$cm^{-1} x (mol^{-1})^{-1} = l\ mol^{-1}\ cm^{-1}$.

1.3.2 PRESENTATION OF SPECTRA

The ultraviolet–visible spectrum is generally recorded as a plot of absorbance versus wavelength in nm (wave number) it is customary to then replot the data with either e or loge plotted on the ordinate and wavelength plotted on the abscissa. **Figure 1.1** the spectrum of acetone, is typical of the manner in which spectra are displayed.

The principal use of absorption spectra from the photo chemist's point of view is that they provide information as to what wavelength (λ max) a compound has at its maximum value of the molar absorption coefficient (ε_{max}). Thus, irradiation of the compound at λ_{max} allows optimum photo excitation of the compound to be carried out. In addition, the Beer-Lambert law is frequently used in the analytical determination of concentrations from absorbance measurements.

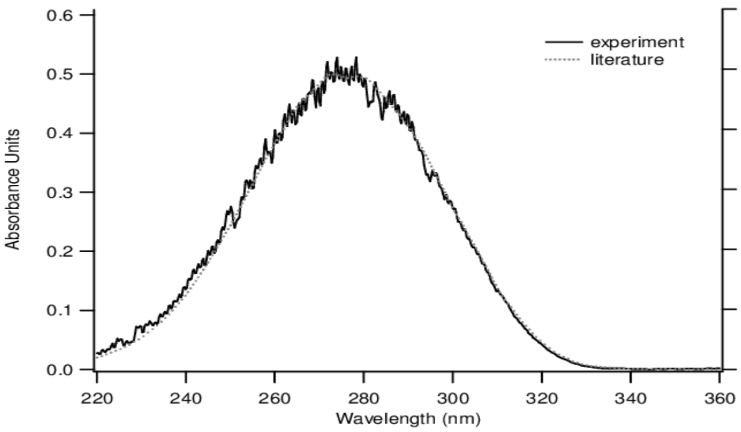


Figure 1.1 UV spectrum figure Absorption spectrum of acetone in hexane

1.3.3 The physical basis of light absorption by molecules

A group of atoms and electrons forming part of an organic molecule that causes it to be coloured. Are known as **chromophores** or **chromophoric groups**, which are responsible for the absorption of light. When the oscillating electromagnetic radiation encounters an appropriate chromophore, an electron in the chromophore can be promoted to a excited state (higher energy) provided there is an energy correspondence between the photon and the pair of quantised electronic energy levels involved in the electronic transition. When this electronic transition occurs, the absorbing chromophore undergoes an electric dipole transition and the energy of the photon becomes part of the total energy of the excited - state molecule. The transition dipole moment lasts only for the duration of the transition and arises because of the process of electron displacement during the transition. The intensity of the resulting absorption is proportional to the square of the transition dipole moment.

In considering absorption of light by molecules, we have been principally concerned with transitions between electronic states. Now, the total energy of molecules is made up of electronic energy and energy due to nuclear motion (vibrational and rotational):

$E\text{total} = E_{\text{electronic}} + E_{\text{vibrational}} + E_{\text{rotational}}$

Because of the large differences between electronic, vibrational and rotational energies, it is assumedby the Born-Oppenheimer approximation.

The energy gap between electronic states is much greater than that between vibrational states, which in turn is much greater than that between rotational states. As a result, we are able to describe the effects of electronic transitions within molecules by considering quantised electronic and vibrational states.

Absorption of ultraviolet and visible light by molecules results in electronic transitions in which changes in both electronic and vibrational states occur. Such transitions are called vibronic **transitions**. At thermal equilibrium the population of any series of energy levels is described by the Boltzmann **distribution law**. If the molecules are in the ground stateN_0, then the molecules are N_1 in any higher energy level is given the equation:

$N_1 / N_0 = \text{Exp} (-\Delta E / RT)$

Where, exp refers to the exponential function

Δ E is the energy difference between the two energy levels

R is the gas constant (which has a value 8.314J K^{-1} mol^{-1})

T is the absolute temperature.

The Boltzmann distribution law show that, at room temperature, most molecules will be in the

v = 0 vibrational state of the electronic ground state and so absorption almost always occurs from S_0 (v = 0) **(Figure 1.2).**

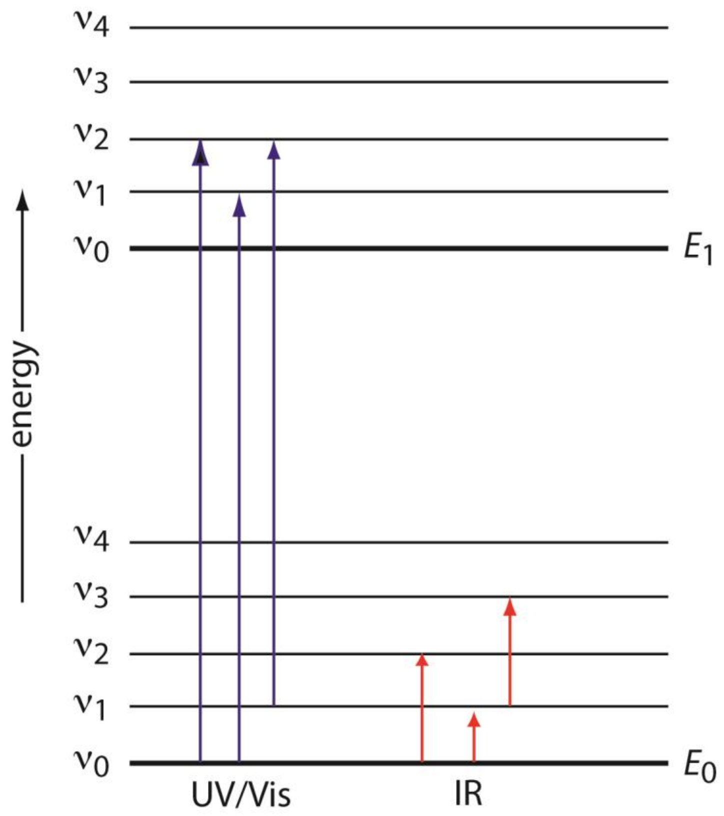


Figure 1.2 Vibrational states of the electronic transitions

1.3.4. Morse potential energy curve for diatomic molecules

In Morse potential curve, (Figure 1.3) the potential energy of the molecule changes with its bond length. At the points where the horizontal lines meet the Morse curve, the energy is wholly potential. In between, the energy is partly kinetic and partly potential.

Each vibrational energy level has an associated wave function, the square of which relates to the most probable internuclear distance for a given vibrational quantum number, v (Figure 1.4) shows the vibrational probability function for a series of vibrational quantum numbers. For the v = 0 level, the square of the wave function shows that the molecule spends most of its time in the region of the equilibrium configuration However, for an excited vibrational energy level, the magnitude of the ψ^2 function is greatest close to the turning points of the vibrational motion, which shows that the bond spends most of its time in the fully compressed or fully - extended configuration.

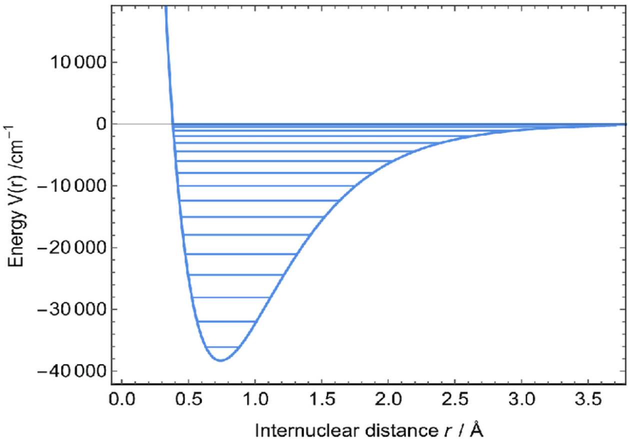


Figure 1.3 A Morse curve for a diatomic molecule, showing the quantised vibrational energy levels. The minimum on the curve represents the equilibrium bond distance

Nuclei move much more slowly than the much - lighter electrons so when a transition occurs from one electronic state to another, it takes place so rapidly that the nuclei of the vibrating molecule can be assumed to be fixed during the transition. This is called the Franck – Condon principle, and a consequence of it is that an electronic transition is represented by a verticalarrow that is, an electronic transition occurs within a ‘ stationary ’ nuclear framework.

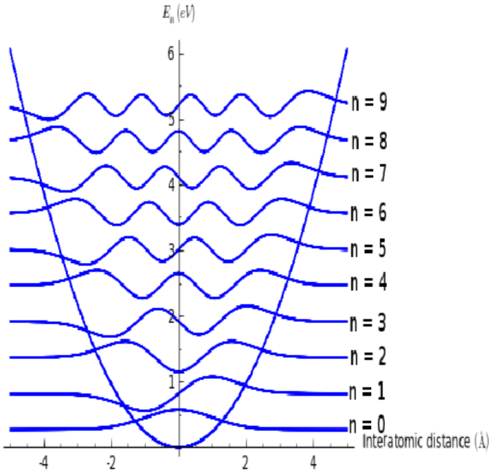


Figure 1.4: Vibrational probability functions for a series of vibrational quantum numbers Note that for the higher v there is a greater probability of the molecule having a bond length at the two limits shown by the Morse curve. Notice also that for each value of v, there are v +1 maxima.

Thus the electronic transition accompanying the absorption of a photon is often referred to as a vertical transition or Franck–Condon transition. Transitions between the vibrational levels in lower and upper electronic states will be most intense when the two states have similar internuclear separations that is, there will be a greater probability of an electronic transition when the ψ^2 functions for the upper and lower vibronic states have a greater overlap This overlap, called the Franck-Condon factor, is shown in Figure 1.5

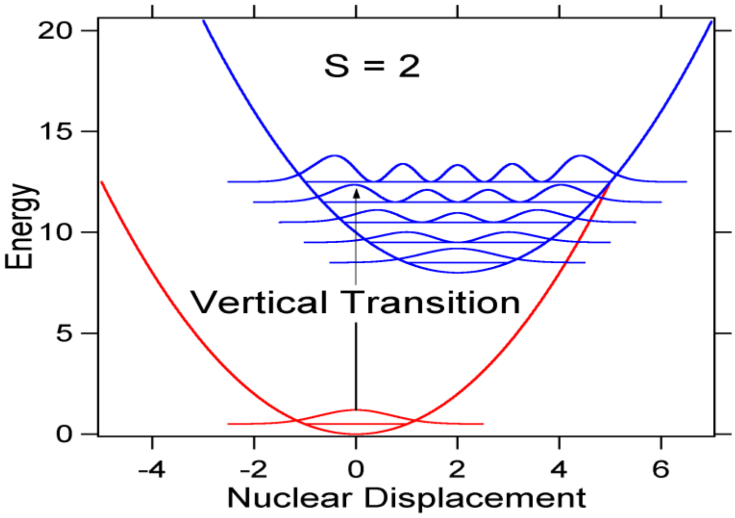
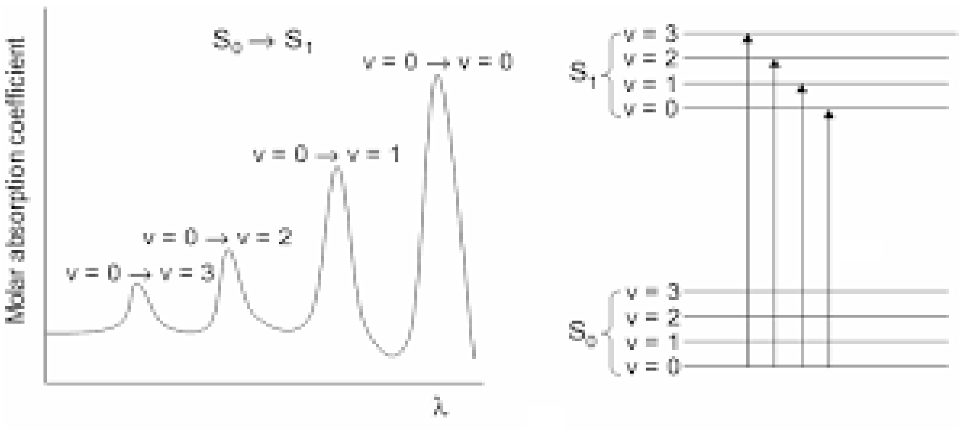


Figure 1.5 Electronic transitions with the greatest probability of absorption from S_0 (v=0): where the excited state has a larger internuclear distance than the ground state.

1.3.5 Example of absorption of light

The UV–visible spectrum of a very dilute solution of anthracene in benzene, which clearly shows small ‘fingers’ superimposed on a broader band (or envelope). These ‘fingers’ are called the vibrational fine structure and we can see that each ‘finger’ corresponds to a transition from the v = 0 of the ground electronic state to the v = 0, 1, 2, 3, etc. vibrational level of the excited electronic state different vibronic transitions vary. In the absorption spectrum of anthracene, the v = 0 → v = 0 transition gives rise to the most intense absorption band because for this transition the overlap of the vibrational probability functions for S 0 (v = 0) and S_1 (v = 0) is greatest; that is, the Franck –Condon factor for this transition is greatest.

The v = 0 → v = 0 transition gives rise to the 0–0 band .The absorption spectra of rigid hydrocarbons in nonpolar solvents may show vibrational fine structure, but absorption spectra of other organic molecules in solution tend to be broad, featureless bands with little or no vibrational structure .This is due to the very large number of vibrational levels in organic molecules and to blurring of any fine structure due to interaction between organic molecules and solvent molecules. The hypothetical spectrum shown in **Figure 1.6** shows the vibrational structure hidden by the enveloping absorption spectrum and the peak of the absorption curve does not correspond to the 0 – 0 band because the most probable vibronic transition here is the 0 →4 transition. The absorption bands in organic molecules result from transitions between molecular orbital’s.



Absorption spectrum of a solution of anthracene in benzene, and the vibronic transitions responsible for the vibrational fine structure

Figure 1.6 The hypothetical spectrum

1.4 EXCITATION

Photo excitation is the first step in a photochemical process where the reactant is elevated to a state of higher energy, an excited state. The photon can be absorbed directly by the reactant or by a photosensitize, which absorbs the photon and transfers the energy to the reactant. The opposite process is called quenching when a photo exited state is deactivated by a chemical reagent. Most photochemical transformations occur through a series of simple steps known as primary photochemical processes. One common example of these processes is the excited state proton transfer (ESPT).

1.4.1 Electronic excited state

According to Pauli Exclusion principle, two electrons in an atom cannot have the same four quantum numbers (n, l, m_l, m_s). Therefore, because two electrons can occupy each orbital, these two electrons must have opposite spin states. These opposite spin states are called spin pairing. Because of this spin pairing, most molecules are diamagnetic, and are not attracted or repelled by an external magnetic or electric field. Molecules that contain unpaired electrons do have magnetic moments that are attracted to an external magnetic or electric field.

In many diatomic molecules in ground state even number of electrons. Hence all the electrons are spin paired (two electrons with opposite spin) in ground state.

The quantity 2S + 1, where S is the total spin, is known as spin multiplicity of a state. When the spins are paired (↑↓) as shown in figure **(1.7, a)** below, the upward orientation of the spin is cancelled by the downward orientation. So that S = 0. This is illustrated as follows.

$S_1 = ½$ or $S_2 = – ½$

So that, $S = S_1 + S_2 = ½ - ½ = 0$

$2S + 1 = 2 (0) + 1 = 1$

Hence, the spin multiplicity of the molecules the molecule is said to be in the singlet ground state, denoted by S_0. Figure **(1.7, a)**

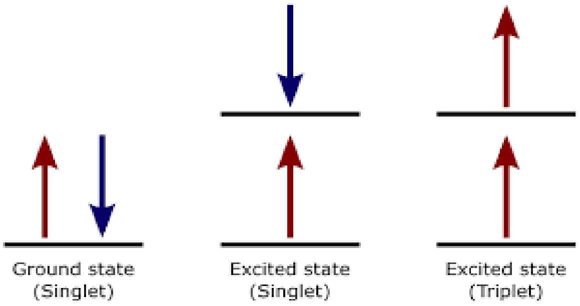


Figure 1.7 (a),(b),(c)

When by the absorption of a quantum (photon) of suitable energy "hυ",one of the electrons goes to a higher energy level (excited state), the spin orientation of the two single electrons may be either parallel as shown in. **figure (1.7 ,c)** or anti-parallel as shown in. **figure (1.7 b)**

If, the spin are parallel, as shown in **figure 1.7 (b)** then,

spin multiplicity = $2S + 1 = 2(s_1 + s_2) + 1$

So, $s_1 = ½ \quad s_2 = – ½$ (antiparallel)

$= 2 (½ - ½) + 1 = 2 (0) + 1 = 1$

The molecule is said to be in **singlet excited state**.

If , the spin are antiparallel , as shown in **Figure 1.7 (c)** , then ,

Then spin multiplicity = 2S + 1 = 2(s_1 + s_2) + 1

So, s_1 = ½ s_2 = ½ (parallel)

= 2 (½ + ½) +1

= 2 (1) + 1 = 3

The molecule is said to be in **Triplet excited state.**

In using the concept of molecular orbital theory to discuss the absorption of light by organic molecules, we concentrate on two molecular orbitals in particular. The highest occupied molecular orbital (HOMO) is the ground - state molecular orbital of highest energy with electrons in it and the lowest unoccupied molecular orbital (LUMO) is the ground state molecular orbital of lowest energy with no electrons in it. Thus, the lowest energy transition in an organic molecule will be the HOMO→LUMO transition. The absorption bands in organic molecules result from transitions between molecular orbitals as shown in **Figure 1.8**

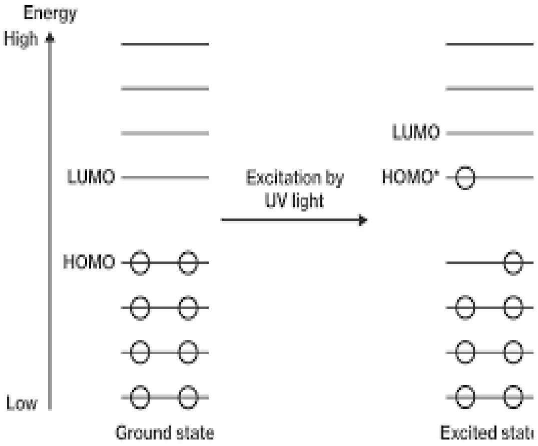


Figure 1.8

1.4.2 Jablonski diagram

Fate of the excited molecules can be explained by Jablonski diagram. The Jablonski diagram is a pictorial illustrated of different energy states which are absorbed by molecules. This partial energy diagram represents the energy of a photo luminescent molecule in its different energy states. The lowest and darkest horizontal line represents the ground-state electronic energy of the molecule ,which is the singlet state labeled as S_0 .The thicker lines on the left labeled S_1, S_2 , and S_3 represent the excited electronic states for the molecule in the singlet state. The thicker lines on the right labeled T_1, T_2, and T_3 represent excited triplet states.

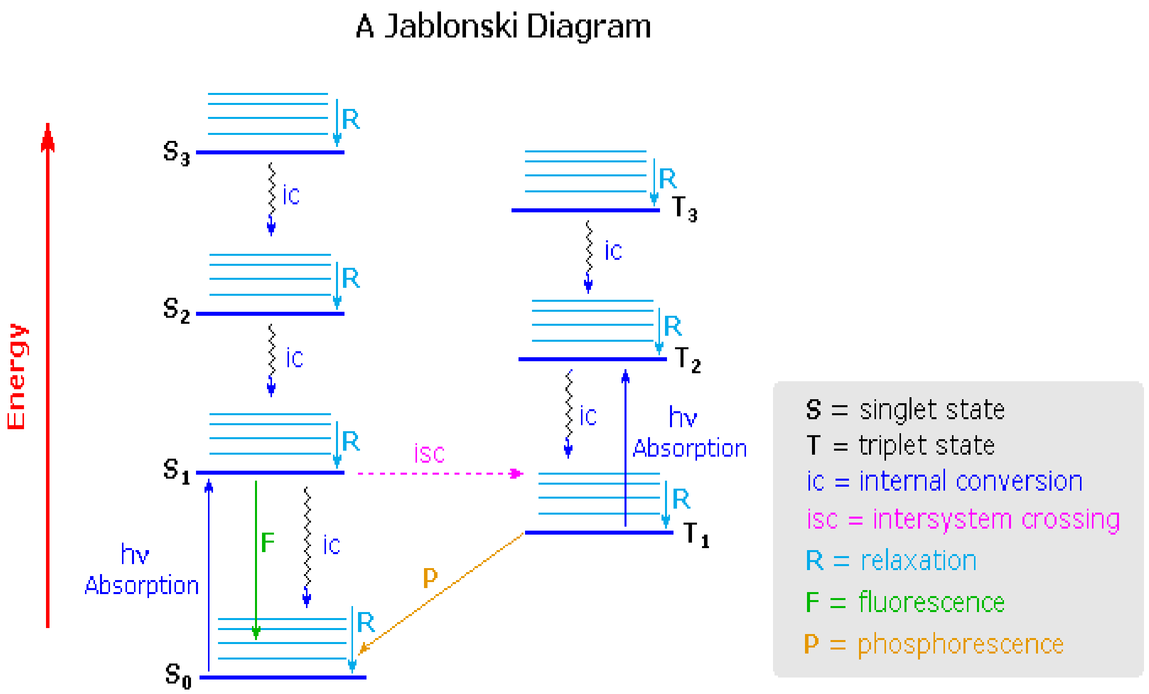


Figure 1.9: Jablonski Diagram, depicting various Photophysical Processes

There are numerous vibrational levels that can be associated with each electronic state as denoted by the thinner lines. Absorption transitions (solid up arrows in **Figure 1.9**) can occur from the ground singlet electronic state (S_o) to various vibrational levels in the singlet excited electronic states. It is unlikely that a transition from the ground singlet electronic state to a triplet electronic state because the electron spin is parallel to the spin in its ground state . This transition leads to a change in multiplicity and thus has a low probability of occurring and so is considered a **forbidden transition.**

Fate of the excited molecules can be explained by Jablonski diagram:

- When the molecule absorbs UV light radiations it get promotes to excited singlet state S_1, S_2 S_3. . In the above state molecules are collides and after 10^{-13} to 10^{-11}second it return back to the S_1, and release energy. Such process is called **energy cascade**.
- In a similar manner the initial excitation and the decay from higher singlet states initially populate many of the vibration levels of S_1, but these also cascade, down to the lowest vibrational level of S_1. This cascade is known as ***vibrational cascade*.** All these processes will occur in about 10^{-11} to 10^{-13} sec.
- The life time of singlet excited state S_1 is long hence in this state has done many physical and chemical processes. Molecules returns to its ground state, S_0 from excited singlet S_1,/ S_2 state by release energy as heat, but this is generally quite slow

because the amount of energy is large between S_0 and S_1. This process is called **internal conversion**.

- When molecules return to its ground state S_0 from excited state S_1,/ S_2 by giving off energy in the light form within 10^{-9} seconds. This process is known as **Fluorescence.**

  This pathway is not very common because it is relatively slow. For smaller, diatomic and rigid molecules (mainly aromatic compounds) show fluorescence. This is because emitted fluorescecent light is of lower energy than absorbance light.

- Most molecules in the S_1 state may drop to triplet state (T_1) ($S_1 \rightarrow T_1$). This is energetically slow process .However, if the singlet state S_1 is long lived, the $S_1 \rightarrow T_1$conversion occurs by a process called **intersystem crossing**. It is important phenomenon in photochemistry. For every excited singlet state there exist corresponding triplet states. Since transition from ground state singlet (S_0) to triplet state (T_1) is forbidden, intersystem crossing is the main source of excited triplet state. This is one way of populating the triplet state. The efficiency in intersystem crossing depends on the $S_1 \rightarrow T_1$ energy gap. When this energy difference is small their intersystem crossing is efficient, if energy difference is large, spin forbiddenessis quite important and efficiency is low or zero.
- When molecule in the T_1 state may return to the S_o state by giving up heat or light this is called **Phosphorescence**. Intersystem crossing and phosphorescence are very slow process (10^{-3} to 10^{1} sec). This means that T_1 state generally have much longer lifetime than S_1 states (lifetime of S_1 s 10^{-9} to10^{-15} sec, lifetime of T_1 is 10^{-5} to 10^{-3} sec).
- When fluorescence and phosphorescence occur in same molecule, phosphorescence is found at lower frequencies than fluorescence. This is because of the higher difference in energy between S_1 and S_0 than between $T_1$and S_o and is longer-lived.
- For many molecules intersystem crossing ($S_1 \rightarrow T_1$) is not very efficient. If this is the only way to produce T_1 then T_1 would be rather very-very limited.

1.4.3 Electronic transitions and their nomenclature

The absorption of electronic transition by organic compounds in the UV and Visible region occurs due to extinction of electrons from bonding or non-bonding molecular orbitals (ground state) to the antibonding moleculer orbital's (excited state) which are usually vacant in the ground state of the molecule.

The electronic transitions that occur in UV and visibile region are of following six types:

$\sigma \rightarrow \sigma^*$, $\sigma \rightarrow \pi^*$, $\pi \rightarrow \pi^*$, $\pi \rightarrow \sigma^*$, $n \rightarrow \sigma^*$,and $n \rightarrow \pi^*$ are possible **(Figure 1.9).**

The $\sigma \rightarrow \sigma^*$ transition corresponds to absorption in the in accessible far-UV (100–200 nm) and both $\sigma \rightarrow \pi^*$ and $\pi \rightarrow \sigma^*$ are obscured by much stronger $\pi \rightarrow \pi^*$absorptions, and $n \rightarrow \sigma^*$ transition occurs by vacuum UV light (below 200 nm).

The usual order of energy required for various electronic transitions is as follows: (**Figure 1.9)**

$\sigma \rightarrow \sigma^* > n \rightarrow \sigma^* > \pi \rightarrow \pi^* > n \rightarrow \pi^*$.

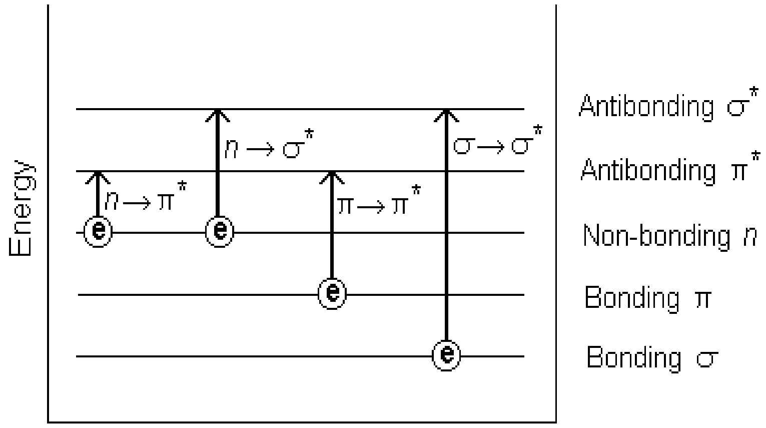


Figure 1.9 Generalised ordering of molecular orbital energies for organic molecules and electronic transitions with light.

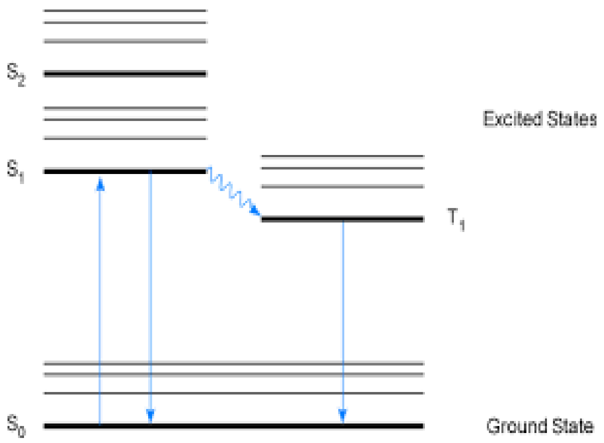


Figure 1.10 Electronic states of molecular orbitals of an organic compound

In a molecule, the singlet electronic states are denoted by S_0, S_1, S_2, etc., of increasing energy and triplet electronic states as T_1, T_2, etc. S_0 indicates the ground state of singlet electron, whereas S_1, S_2, etc., and T_1, T_2, etc., are excited singlet and triplet states, respectively. The n → π* transition is the lowest energy transition for most of saturated carbonyl compounds and this transition is known as $S_0 \rightarrow S_1$ and T_1. These transitions occur from the promotion of an electron from n molecular orbital to the π* molecular orbital and these transitions are referred as 1(n, π*) and 3(n, π*) states, respectively. Similarly, S_2 and T_2 excited states arise from the promotion of an electron from its π molecular orbital to its π* antiboding orbital and are referred to as 1(π, π*) and 3(π, π*) states, respectively. These transitions are represented in **Figure 1.10**

1.4.4 Electronic transitions by excitation with light

The possible electronic transitions of p, s, and n electrons are as in **(Figure 1.9)**

1. **σ —σ*Transitions** :In which an electron is excited from sigma bonding MO to sigma star antibonding MO are called σ —σ* transitions. These transitions are shown by only those compounds which all the electrons are involved in σ—bond formation i.e, in saturated hydrocarbons. These require very high energy. Therefore, these transitions occur at short wavelengths or high frequency and are usually found in vacuum or far ultraviolet region. For example, methane which has only C-H bonds, and can only undergo σ —σ* transitions ,shows an absorbance maximum at 125 nm. Absorption maxima due to σ —σ* transitions are not seen in typical UV-Visible spectra (200 - 700 nm).
2. **n—σ*Transitions** : In which a non—bonding electron is excited to σ* antibonding MO are called n—σ* transitions. These transitions occur in those compounds which contain heteroatoms such as oxygen, nitrogen, sulphur, halogensetc. These transitions require comparatively less energy than the σ —σ* transition. For example amines, alcohol, ethers, alkyl halides, carbonyls compounds, show this type of transition. In These transitions absorption bands appears at occur longer wavelengths in near UV region. Infact the energy required for these transitions depends up on the electronegativity of the hetero atom. In saturated alkyl halides, the energy required for n to sigma star transition (n—σ*) decreases with the increase in the size of the halogen atom or decrease in electronegativity of the atom. Due to the greater electronegativity of chlorine than iodine, the n electron on the chlorine atom is comparatively difficult to excite. The n electrons on the iodine atom are loosely bound.

3. **π— π *Transitions**:In which a π-electron is excited to a antibonding orbital π *MO are called π— π *.This type of transition occurs in those molecules having a π electron system or containing double bonds(compounds with unsaturated centres). For example Alkenes, carbonyl compounds .Aromatic compounds etc. shown π—π * transitions . It requires lesser energy than n to sigma star transition (n → σ∗). In simple alkenes several transitions are available but n → π∗ transition required the lowest energy. In saturated aldehydes and ketones the π—π * transition produces a n absorption band of high intensity at about 285nm.

4. **n— π * transitions:**In which an electron is excited from the non bonding atomic orbital to the π *MO are called n— π * transitions. The energy gap for an n→π∗ transition is smaller than that of a π - π* transition – and thus the n - π* peak is at a longer wavelength. In general, n - π* transitions are weaker (less light absorbed) than those due to π - π* transitions. In saturated ketones, n → π* transitions around 280 nm are the lowest energy transition. n → π* is forbidden by symmetry consideration. Thus the intensity of the band due to this transition is low, although the wavelength is long.

Absorptions due to π → π* and n → π* transitions differ from one another in several important aspects as shown in given Table:

Absorptions due to π → π * transitions	**Absorptions due to n → π* transitions**
1. Occur at shorter wavelengths than do absorptions due to n → π* transitions	**1.** Occur at longer wavelengths than do absorptions due to π → π * transitions
2. Relatively strong absorptions with ε max values of ~ 10^3 to ~ 10^5 l mol^{-1}cm^{-1}	**2**.Relatively weak absorptions with ε max values of ~ 1 to ~10^2l mol^{-1}cm^{-1}
3. Substitution moves the absorption to longer wavelength	**3**. Substitution moves the absorption to shorter wavelength
4. The absorption band occurs at longer wavelength in a polar solvent than in a nonpolar solvent (the absorption shows a red shift or bathochromic shift)	**4**. The absorption band occurs at shorter wavelength in a polar solvent than in a nonpolar solvent (the absorption shows a blue shift or hypsochromic shift).

1.5 PHOTOCHEMICAL LAWS

There are two basic laws governing photochemical reactions:

1.5.1. Grotthuss –Draper Law

When light falls on a cell containing a reaction mixture, some light is absorbed and the remaining light is transmitted. Obviously, it is the absorbed component of light that is capable of producing the reaction. The transmitted light is ineffective chemically. Early in the 19th century, Grotthuss and Draper studied a number of photochemical reactions and enunciated a generalization. This is known as Grotthuss-Draper law and may be stated as follows.

"It is only the absorbed light radiations that are effective in producing a chemical reaction. However, it does not mean that the absorption of radiation must necessarily be followed by a chemical reaction. When the conditions are not favourable for the molecules to react, the light energy remains unused. It may be re-emitted as heat or light." The Grotthuss-Draper law is so simple and self-evident. But it is purely qualitative in nature. It gives no idea of the relation between the absorbed radiation and the molecules undergoing change.

1.5.2. Stark-Einstein Law of Photochemical Equivalence

Stark and Einstein (1905) studied the quantitative aspect of photochemical reactions by application of Quantum theory of light. They noted that "Each molecule taking part in the reaction absorbs only a single quantum or photon of light. The molecule that gains one photon-equivalent energy is activated and enters into reaction". Stark and Einstein thus proposed a basic law of photochemistry which is named after them. The Stark-Einstein law of photochemical equivalence may be stated as.

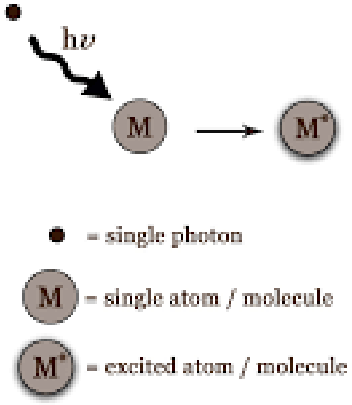


Figure 1.11 Stark-Einstein law of photochemical equivalence

In a photochemical reaction, each molecule of the reacting substance absorbs a single photon of radiation causing the reaction and is activated to form the products. The law of photochemical equivalence is illustrated in **(Figure 1.11)** where a molecule 'M' absorbs a photon of radiation and gets activated. The activated molecule (M*) then decomposes to yield B. We could say the same thing in equational form as:

$$M + hv \rightarrow M^*$$

$$M^* \rightarrow B$$

$$\text{Overall} \quad M + hv \rightarrow B$$

In practice, we use molar quantities. That is, one mole of M absorbs one mole of photons or one einstein of energy, E. The value of E can be calculated by using the expression given below:

$$E = \frac{2.859 X 10^4}{\lambda} \text{ kcal mol}^{-1}$$

1.6 ELECTRONICALLY EXITED STATE - LIFE TIME

1.6.1 Lifetimes of electronic excited states

The lifetime of a system in an excited state is usually short: spontaneous or induced emission of a quantum of energy (such as a photon) usually occurs shortly after the system is promoted to the excited state, returning the system to a state with lower energy (a less excited state or the ground state).The rapid nature of vibration relaxation and internal conversion between excited states an electronically excited molecule will usually relax to the lowest vibrational level

of the lowest excited singlet state. It is from the S_1 (v = 0) state that any subsequent photo physical or photochemical changes will generally occur by Kasha's rule.

Lifetime of radiative S1 state is given by:

$$\tau_0 = 10^{-4} / \varepsilon_{max}$$

Where τ_0 has units of s and ε_{max} has units of l mol^{-1} cm^{-1}. Thus, for (π, π^*) transitions, τ_0 is $10–^{9}$ to 10^{-6} s, whereas for (n, π^*) transitions, τ_0 is 10^{-6} to10^{-3} s. Lifetime of radiative T_1 state is relatively long. In general, (π, π^*) states have long lifetimes (1–10^2 s), whereas (n, π^*) states have short lifetimes (10^{-4} to 10^{2} s).

1.6.2 Kasha's Rule

Kasha's rule is a principle in the photochemistry of electronically excited molecules. The rule states that photon emission (fluorescence or phosphorescence) occurs in appreciable yield only from the lowest excited state of a given multiplicity. It is named for American spectroscopist Michael Kasha, who proposed it in 1950.

Kasha' Rule, therefore, states that fluorescence will always originate from the vibrational ground state of the lowest excited singlet level, the $\mathbf{S_1}$, while phosphorescence will originate from the vibrational ground state of the lowest excited triplet level, the $\mathbf{T_1}$, regardless of which initial level the molecule is excited too.

Kasha's Rule is a consequence of the fact that in complex molecules the rate constant of internal conversion and vibrational relaxation from the higher lying electronic levels is significantly greater than the emission rate constant back to the ground state from those levels . The rate of internal conversion between two electronic levels is inversely proportional to the energy splitting between those levels (energy gap law). The $\mathbf{S_0}$ and the $\mathbf{S_1}$ have the largest energy splitting and the rate constant of internal conversion is comparable to that of fluorescence, and the $\mathbf{S_1} \rightarrow \mathbf{S_0}$ fluorescence emission is therefore observed. The higher-lying electronic excited states are closer in energy and therefore undergo faster internal conversion that outcompetes the fluorescence. As a result, when a molecule is excited to a higher excited singlet state, $\mathbf{S_n}$, it will rapidly undergo internal conversion and vibrational relaxation to the vibrational ground state of the $\mathbf{S_1}$ before fluorescing, and only $\mathbf{S_1} \rightarrow \mathbf{S_0}$ fluorescence will be observed.

Kasha's Rule is obeyed by nearly all molecules in solution, but like most scientific 'rules' there are exceptions. The most famous exception is azulene which has an $\mathbf{S_2} \rightarrow \mathbf{S_0}$ fluorescence emission. This is a consequence of the unusually high energy gap between the $\mathbf{S_2}$ and $\mathbf{S_1}$ in azulene, which results in slow internal conversion between these levels.

1.6.3 Vavilov's Rule for Fluorescence

Vavilov rule states that the fluorescence quantum yield is independent of the wavelength of the exciting light. If a molecule in S_1 ($v = 0$) undergoes fluorescence emission and has fluorescence, intersystem crossing and internal conversion having rate quantum yields k_f, kisc, kic respectively, then

$$k_f + k_{isc} + k_{ic} = 1$$

Since k_{ic} is much smaller than Ψ_f and k_{isc} ,

$$k_f + k_{isc} \approx 1$$

This mathematical expression is known as **Ermolev rule.**

1.6.4 Excited singlet - state lifetime

The competing intramolecular photophysical processes that can occur fromS_1 (v = 0) undergoes fluorescence, intersystem crossing and internal conversion, with first - order rate constants of,k_f, k_{isc} ,k_{ic}respectively **(Figure 1.12)**.

Applying a standard treatment of first - order chemical kinetics, the rate of disappearance of the excited molecules, S_1 , J_{total} , is given by:

$$J_{total} = -\frac{d(S1)}{dt} = (k_f + k_{isc} + k_{ic})[S_1] = k_{total}[S_1]$$

(the− sign shows that the excited state S_1 decays with time; that is, its concentration decreases with time).

Solution of this equation gives the exponential decay form of the transient excited S_1molecule:

$$[S_1]_t = [S_1]_0 \exp(-t/\tau)$$

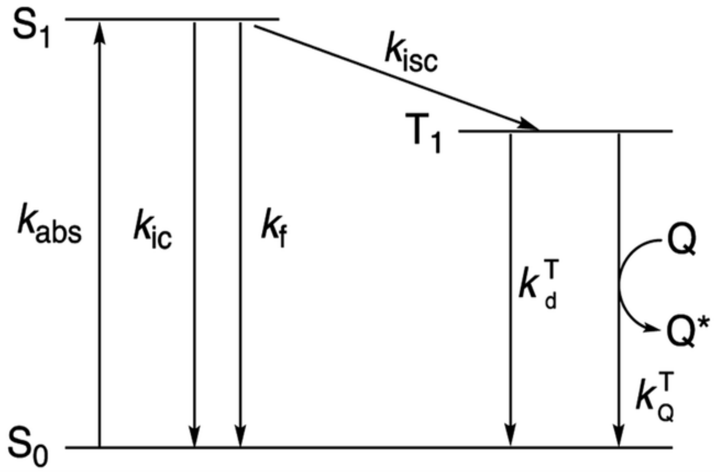
where $[S_1]_0$ is the concentration of excited S_1molecules at time t = 0 resulting from the initial exciting pulse, $[S_1]_t$ is the concentration of excited S_1molecules at time t and τ is the excited singlet - state lifetime of the S_1 excited state.

Where, $t = \tau$

$$[S_1]_t = [S_1]_0 \exp(-1) = [S_1]_0 / e$$

Thus τ is given by the time for the concentration ofS_1 to decrease to 1/e of its original value, where, $1/e = 1/2.718 = 0.3679$

The excited singlet - state lifetime, τ, is the time taken for the concentration of S_1 to decrease to 1/e of its initial value.



Label	Name	Time scale ($\tau_{process} = 1/k_{process}$) (s)
k_{abs}	Absorption	10^{-15}
k_{IC}	Internal conversion	$10^{-12} – 10^{-6}$
k_{ISC}	Intersystem crossing (S → T)	$10^{-12} – 10^{-6}$
k_{vr}	Vibrational relaxation	$10^{-13} – 10^{-12}$
k_f	Fluorescence	$10^{-9} – 10^{-7}$

Figure 1.12 Excited Singlet - State Lifetime

1.6.5 The Technique of time - correlated single - photon counting

The technique of time-correlated single - photon counting **(Figure 1.13)** is used to measure an excited singlet -state lifetime, 1 τ. The sample is irradiated with a very short - duration light pulse (<< 1 ns) to ensure any given molecule will only be excited once during the pulse. As soon as he population of molecules is excited, the molecules randomly begin to relax to the ground state by fluorescence.

When the pulsed source produces its pulse of light to irradiate the sample, the START photomultiplier sends a signal to the TAC, which then linearly builds up a voltage until a signal is received from the STOP photomultiplier. When the STOP signal is received, the magnitude of the voltage (linearly proportional to the detection time) is measured and stored in a multichannel analyser.

The multichannel analyser divides the voltage range into a sequence of several hundred channels, each channel building up the count of the number of times a certain voltage level is detected. The electronics of the system allows the process to be repeated millions of times a second, building up a histogram representing the time distribution of the emission events.

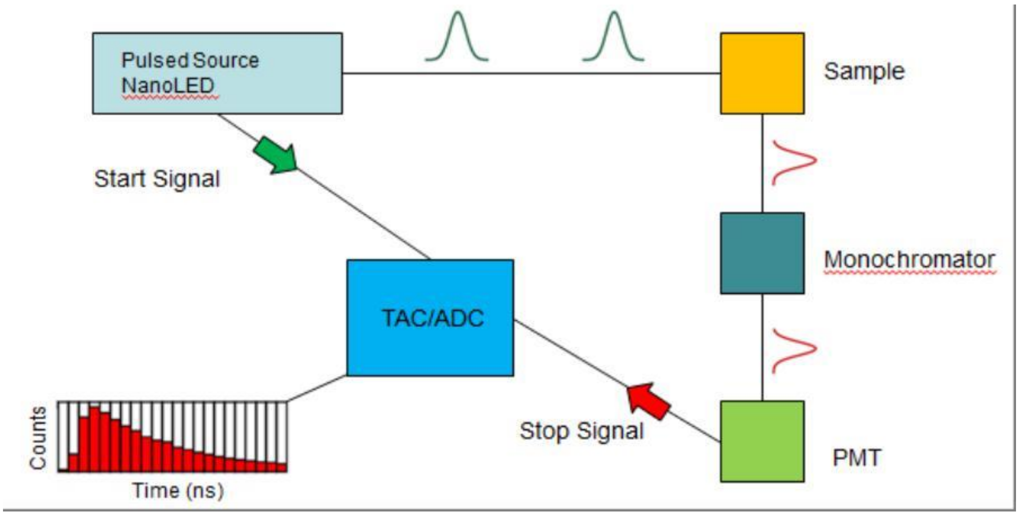


Figure 1.13 Schematic diagrams of the principal components of a time - correlated single - photon counting apparatus

1.6.6 Excited singlet - state radiative lifetime

The excited singlet - state radiative lifetime, τ_0, of S_1 is the lifetime of S_1 in the absence of any radiationless transitions; that is, the onlydeactivation process is fluorescence τ_0 is the reciprocal of the rate constant for fluorescence, k_f

$$\tau_0 = 1/k_f$$

Similarly, for the excited singlet - state lifetime:

$$k_{total} = k_f + k_{isc} + k_{ic}$$

Since $k_{tota\ l}$is greater than kf, the observed excited singlet - state lifetime is less than the excited singlet - state radiative lifetime τ only approaches τ_0 as intersystem crossing and internal conversion from S_1 become much slower processes than fluorescence.

Now, the fluorescence quantum yield, ϕ_f is the fraction of excited molecules that fluoresce. This is given by the rate of fluorescence, J_f , divided by the rate of absorption J_{abs}

$$\phi_f = J_f / J_{abs}$$

Under conditions of steady illumination, a steady state will be reached, where the rate of formation of excited molecules, R*, is equal to the rate of deactivation by the intramolecular processes:

$$J_{abs} = J_{total}$$

Therefore ;

$$\phi_f = J_f / J_{abs}$$

$$\phi_f = J_f / J_{total}$$

$$\phi_f = k_f[S_1] / k_{total}[S_1]$$

$$\phi_f = k_f / k_{total}$$

Now,

$$\tau_0 = 1 / k_f$$

or, $k_f = 1 / \tau_0$

Similarly,

$$\tau = 1 / k_{total}$$

so,

or, $k_{total} = 1 / \tau$

Thus: $\phi_f = \tau / \tau_0$

An order - of - magnitude estimate of the radiative lifetime of S_1 is given by:

$$\tau_0 \approx 10^{-4} / \varepsilon_{max}$$

Where τ_0 has units of s and ε_{max} has units of l mol^{-1} cm^{-1} .

Thus, $\pi \rightarrow \pi^*$ transitions with ε_{max} of the order of $10^3 – 10^5$ $mol^{-1}cm^{-1}$ give τ_0 of the order of ns – μs. For $n \rightarrow \pi^*$ transitions, ε_{max} has values of the order $10^0 – 10^2$ $mol^{-1}cm^{-1}$ give τ_0 of the orde of μ s–ms.

1.6.7 Lifetimes of the T_1 excited state

Similar considerations apply to the T_1 triplet state as to the S_1 singlet state. By analogy with the expressions for the lifetimes of S_1, the values for T_1 are given by:

$$\tau = 1/k_P$$

$$\tau = 1/k_{total} = 1/k_P + k_{ISC}$$

An order - of - magnitude estimate of the radiative lifetime of T_1 is given by:

$$\tau_0 \approx 10^{-4} / \varepsilon_{max}$$

Where τ_0 has units of s and ε_{max} have units of l mol^{-1} cm^{-1}.

The molar - absorption coefficients for such transitions will be very small and so T_1states will have a longer lifetime than S_1 states .In general (π, π *) states have longer radioactive lifetimes ($10 – 10^2$) than (n , π *) states ($10^{-4} – 10^{-2}$ s) .

Because excited triplet states decay more slowly than excited singlet states, it is much easier to determine the excited triplet - state lifetime $^3\tau$ than $^1\tau$. Phosphorescence emission from a degassed sample at low temperature (77 K) lasts for longer than 1 ms and may even be several seconds. The molecules in the sample are irradiated with a short (∼ 1 μs) flash and the decay of the phosphorescence signal is monitored using an oscilloscope. Any accompanying fluorescence signal will decay too rapidly to be observed. The excited triplet - state lifetime is obtained as the time taken for the emission intensity to fall to 1/e of its initial value.

1.7 FLASH PHOTOLYSIS

The technique of **flash photolysis** employed by Norrishand Porter in 1949 revolutionized the of generating and analysing chemical species.

Flash photolysis is **a pump-probe laboratory technique**, in which a sample is first excited by a strong pulse of light from a pulsed laser of nanosecond, picoseconds, or femtosecond pulse width or by another short-pulse light source such as a flash lamp. In this technique spectrometer typically **monitors the change in absorption as a function of time**, utilizing a second light source (probe) besides the excitation (pump) pulse going through the sample. This technique is also known as transient absorption (TA).

The basis of flash photolysis is to irradiate the system with a very short, intense pulse of light and then, as soon as the pulse is over, to monitor the changes in the system with time by some spectroscopic method. The high - intensity photolysis pulse produces a large number of photons, which in turn produce a large electronically - excited – state population, the time evolution of which can be monitored by absorption or emission spectroscopy. The monitoring device must have a time resolution fast enough to observe the transient state before it decays. The development of millisecond and microsecond flash photolysis allowed.

With the invention of the laser in 1960 and the subsequent development of pulsed lasers using Q - switching, monochromatic and highly - collimated light sources became available with pulse durations in the nanosecond timescale. These Q - switched pulsed lasers allow the study of photo - induced processes that occurs some 10^3 times faster than events measured by flash lamp - based flash photolysis.

By the late 1960s the development of mode locking allowed the study of picoseconds laser techniques. Excited - state processes carried out in the picoseconds domain allow such processes as intersystem crossing, energy transfer, electron transfer and many photo induced unimolecular reactions to be investigated .

According to the Beer – Lambert law, when a beam of light of wavelength λ is incident on an absorber, the logarithm of the ratio of incident light intensity, I_0 , to that of the transmitted light intensity, is termed the absorbance, $A_{\lambda,}$ of the sample. $A_{\lambda,}$ is related to the molar concentration, c, of the absorbing species according to:

$$A_\lambda = \log (I_0 / I) = \varepsilon cl$$

where,

ε = The molar absorption coefficient

λ = wavelength and lies the optical path length of the sample.

Now the concentration of a ransient absorbing species varies with time, c (t), and so A is a function of two variables, namely time and wavelength:

$A (\lambda t) = \log (I_0 / I) = \varepsilon c (t) l$

The wavelength - dependent data provide spectral information, useful for assignment or structural purposes, while the time - dependent data lead to information relating to the kinetics of the processes that occur in the sample.

1.7.1 Experimental technique used to generate A (λ, t)

There are two distinct types of experiment have been employed to generate A (λ, t) data for transient species:

1. The **spectroscopic technique** involves measurement of a complete absorption spectrum at a specific time after excitation. The spectrally- resolved absorption kinetics can be obtained by stepping the delay through a predetermined time range and digitally storing the data. Details of the transient absorption kinetics are obtained by measuring the point on each curve corresponding to the light absorbed at a particular wavelength from a large number of such experiments.

2. The **kinetic technique** measures the decay of the transient species as a function of time at a single wavelength. The transient decays digitally stored and the experiment repeated over a range of wavelengths. By measuring the point on each curve corresponding to the light absorbed at a particular delay time from a large number of such experiments it is possible to generate the absorption spectrum of the transient species at different times after the initial excitation. **Figure 1.1 4** shows a nanosecond kinetic flash photolysis apparatus. The absorbance of the sample is monitored, using a photo multiplier, by the change in the transmittance of the sample to the xenon arc lamp continuous light source. The electronic devices used in nanosecond flash photolysis are at the limit of their time responses to the signals they receive. In order to investigate reactions occurring in the sub - nanosecond timescale it is necessary to overcome this problem.

1.7.2 Methods to study kinetics of fast reactions

In several cases flash is so powerful about all the molecules of the sample are excited and due to which most of the molecules are broke into free radicals. Powers of the order of 50 megawatt can be obtained for a few microseconds. In recent years, high intense pulsed laser light sources have been utilized in flash photolysis. The concentration of the intermediated formed by flash photolysis is followed as a function of time by absorption photometry From **Figure1.14**,

a condenser of high microfarad capacity is charged to 10,000 volt-by a high voltage supply. Through the trigger signal, a spark is created in the spark gap which allows quick passage of current via the flash lamp. The condenser discharges in a few microseconds. The lasers can create a flash of the period of a few nanoseconds. Immediately after the capacitor discharges, the flash lamp is spontaneously triggered off. The rate of the fading of excited molecules or free radicals is followed by the rate of increase in the monochromatic transmitted light as calculated with an oscilloscope and photomultiplier. The spectrometer is fixed such that the light moving via the illuminated cell is of the wavelength that is absorbed by the excited molecule or free radical. This technique is known as kinetic spectroscopy.

Flash photolysis has been used for deducing the absorption spectra of free radicals such as CH_3 ,NH_2, and ClO, whose concentration may be as small as 10^{-6} M.

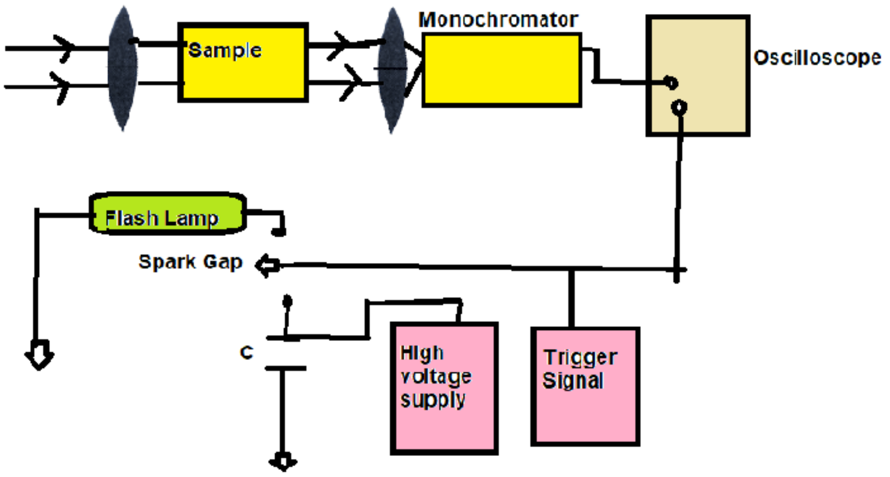


Figure1.14 Experimental Techniques: Flash Photolysis.

1.8 STOPPED FLOW TECHNIQUES

Stopped-flow is an experimental technique for studying chemical reactions with a half time of the order of 1m, introduced by Britton Chance and extended by Quentin Gibson. The most popular flow method is the stopped- flow method. The schematic diagram of its experimental set up is shown in Figure 1.15

Two syringes contain distinct reactant and are fixed with proper valves. The common drive mechanism consists of an air-driven piston by which the solution is forced into the mixing chamber. Another syringe on the right receives the effluent solution and is arranged to establish the time origin. The time scale is provided by the sweep frequency of the oscilloscope, which displays a plot of the transmitted light intensity against time. In this arrangement the distance between the mixing region and the observation point which monitored the light of absorption. The method of detection operates the ultraviolet/ visible spectrophotometer Kinetic data are acquired by determining the values of a suitable physical property as determined at several times after mixing with the aid of an appropriate technique, kinetic date are obtained.

In this method, measurements are made at different distances down the flow tube **(i.e. Fig.1.15).** There is no utilization of stopping syringe. The principle of this procedure uses the information that the measurements along the flow stream amount in effect to determination at different times. With a known and constant flow rate, the time corresponding to each reading is known. By placing several detectors alongside the tub or moving a single detector to different positions the measurement can be made. There is a minor perfection in time resolution in the continuous-flow method as compared with the stopped flow

This method is best appropriate to the study of exchange reactions which takes place too fast for the typical sampling techniques.

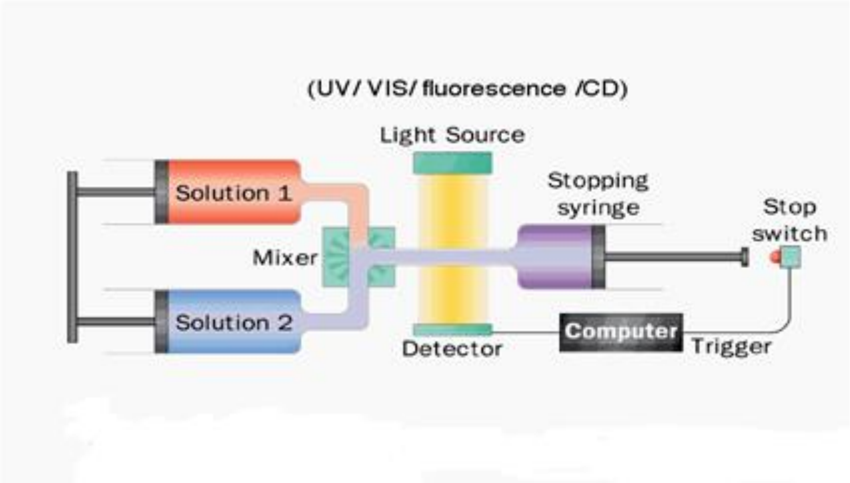


Figure 1.15 Stopped flow techniques

1.9 ENERGY DISSIPATION

On absorption of a quantum of energy, the electron of the absorbing molecule may jump from S_0 to S_1, S_2, S_3 ………. Singlet excited states depending upon the energy of the quantum absorbed, as shown in the Jablonski diagram (**Figure 1.9**)

For each singlet excited state S_1, S_2, S_3 ……. there is a corresponding triplet excited state T_1 ,T_2 T_3…… The molecule in singlet or triplet excited state is said to be activated.

Thus; $A_0 + h\nu \rightarrow A^*$

Where, A_0, is the molecule in the ground state

A*, is the molecule in the excited state

The activated molecule returns to the ground state by dissipating its energy through the following types of processes:

1.9.1 Non radiativeprocesses

These transitions involve the return of the activated molecule from the higher (activated states) excited state (S_3 S_2 or T_3, T2) to the first excited state (S_1 or T_1). These transitions do not involve the emission of any radiations and are thus referred to as non radiative or radiation less transitions. The energy of the activated molecule is dissipated in the form of heat through molecular collisions. The process is called internal conversion (IC) and occurs in less than about 10^{-11} second.

The other type of non-radioactive transition, in which transition take place higher singlet state to another singlet state at this time it's shown same spine multiplicity. This process called internal conversion (IC).

When the molecules loss energy by another process called Inter system crossing (ISC). In this process involves transitions between lowest excited singlet state (S_1 , S_2) to corresponding lowest triplet state,(T_1 ,T_2) i.e. S_1 to T_1 or S_2 or T_2 .This process transition between states of different spins shown different multiplicity and Spectroscopically, forbidden .Such transitions are also non-radiative or radiation less. However, they do occur though at relatively slow rates.

It is clear from **Figure 1.16** this transition take place near the cross over point of two potential energy curves. If any molecules jump from singlet state to triplet state cannot return back to singlet state .S_0 it reached to triplet state vibrational level $\nu' = 0$. From this stage it return back singlet. S_0 state through producing **Phosphorescence**. **(Figure 1.16)**

1.9.2. Radiative processes

A radiative transition is one in which the energy is released as a photon. The nature of the emission depends on the nature of the initial and final states and the route to the excited state. These transitions involve the return of the activated molecule from the singlet excited state S_1 and triplet excited state T_1 to S_0. These transitions are of two types:

a) When molecules produce fluorescence

When by the absorbing radiation transition take place from S_0 to S_1, S_2 then excited molecules due to collision S_1 to S_2 lose some energy. In this way some parts of vibrational energy by internal conversion process change to heat. .By releasing energy in the form of heat molecules reached to the $\nu' = 0$ state. From this point in S_1 excited state the molecules may return back to ground state S_0. When the molecules return back to ground state S_0 it emits radiations. It is called fluorescence or fluorescence spectrum. Spectroscopically, the transition from S_1 to S_0 is allowed transition and occurs in about 10^{-8} second.

It is clear from figure that the substance absorbs high energy radiation to become excited and after 10^{-8} second they emit radiation having shorter wavelength. These substances are called fluorescence matters and the process of emission of radiation is known as **fluorescence (Figure 1.16).**

b) When Molecules produce Phosphorescence

When active molecules return back to ground state S_0 from first triplet excited state. It is clear that when the transition from lowest vibrational energy level $\nu' = 0$ to ground state S_0 is Spectroscopically forbidden because the selection rule ΔS is not applicable , but this transition occur in slower rate than allowed electronic transition .

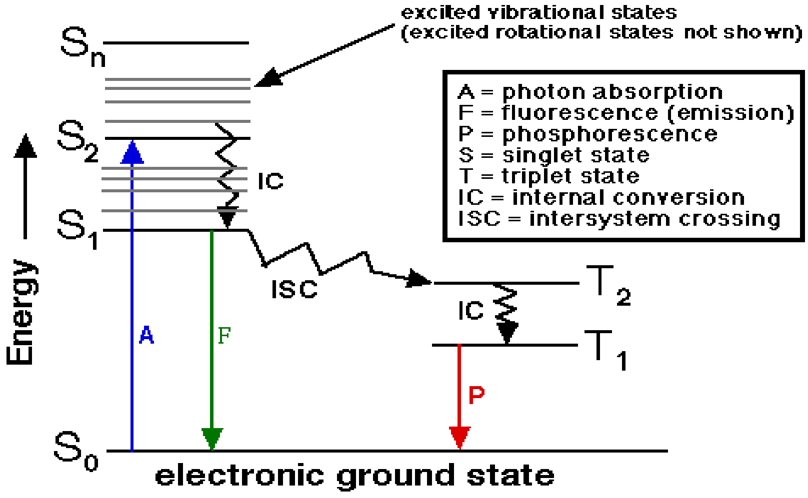


Figure 1.16 Phosphorescence

The emission of this transition is called Phosphorescenc.The time period of Phosphorescenc are much longer being in the order of 10^{-3} second or more, since the transition involves spin inversion which need time for its occurrence.

In both fluorescent and phosphorescent radiations are of shorter frequencies than the exciting radiation. This is because; some part of the absorbed energy by the molecules is dissipated in the form of heat during non-radiative transitions. **(Figure 1.16)**

1.10. ABSORPTION SPECTRA

A material's absorption spectrum is the fraction of incident radiation absorbed by the material over a range of frequencies of Electromagnetic Radiation. The absorption spectrum is primarily determined by the atomic and molecular composition of the material. Spectroscopy is mainly concerned with the interaction of electromagnetic radiation with matter. After interaction there may occur variation in intensity of electromagnetic radiation with frequency (or wavelength).

When molecules absorbs photon of electromagnetic radiation in the visible light and ultraviolet radiation in electronic energy increase , and electron move to new orbital s of higher energy. Thus for electronic transitions a broad absorption spectrum is observed. Let's know how absorption spectra are formed.**(Figure 1.17)**

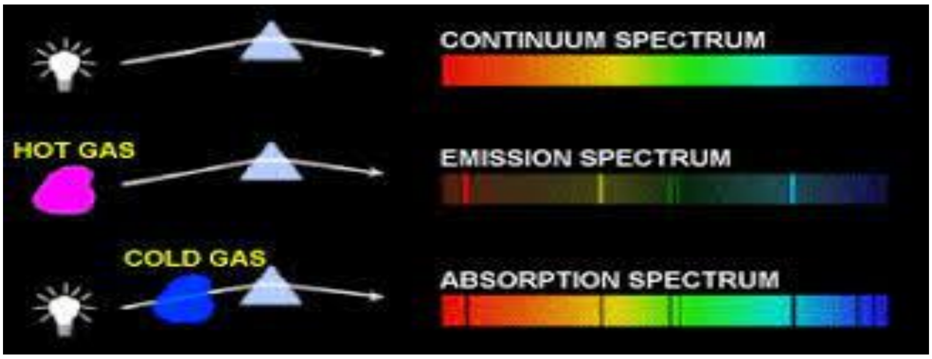


Figure 1.17 absorption spectra

1.10.1Absorption spectrophotometer

Absorption spectrum of a given sample is obtained experimentally with the help of an apparatus called absorption spectrophotometer. Shown in. **(Figure 1.18).** When light from any source is passed through the sample. The wavelengths corresponding to allowed molecular transitions are absorbed. The transmitted light passes through a prism which resolved it into various wavelengths. It is then reflected from the mirror into a detector. The prism is orated so that light of each gives wavelength is focused on the detector. The response of the detector is recorded on a chart by mean a motor- driven pen synchronized with the prism movement. The recorder records the intensity of radiation as a function of frequency and gives the absorption spectrum of the sample.

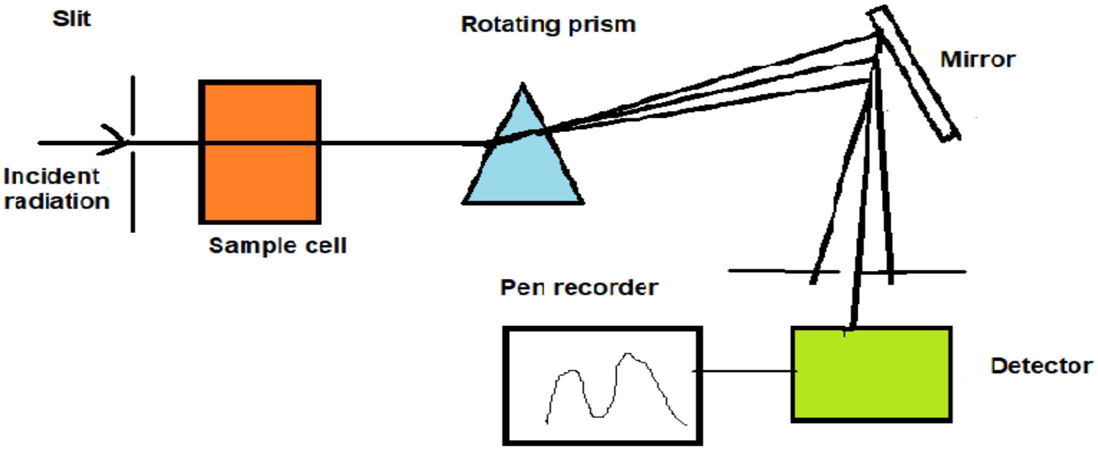


Figure 1.18 Absorption spectrophotometer

1.10.2 Application of absorption spectra

(a) Chemical analysis

Absorption spectra quantitative in nature so it is used in chemical analysis. The specificity of absorption spectra allows compounds to be distinguished from one another in a mixture, making absorption spectroscopy useful in wide variety of application. Infra red gas analyzer can be used to identify the presence of pollutant in air, distinguishing the pollutant from nitrogen, oxygen, water etc. In many cases, it is possible to determine qualitative information about a sample even if it is not in a library. Infrared spectra, for instance, have characteristics absorption bands that indicate if carbon-hydrogen or carbon-oxygen bonds are present.

Absorption spectra can be quantitatively related to the amount of material present using Bee – Lambert Law. Demanding the absolute concentration of a compound requires knowledge of the compound's absorption coefficient. The absorption coefficient for some compounds is available from reference sources, and it can also be determined by measuring the spectrum of a calibration standard with a known concentration of the target.

(b) Atomic and molecular Physics

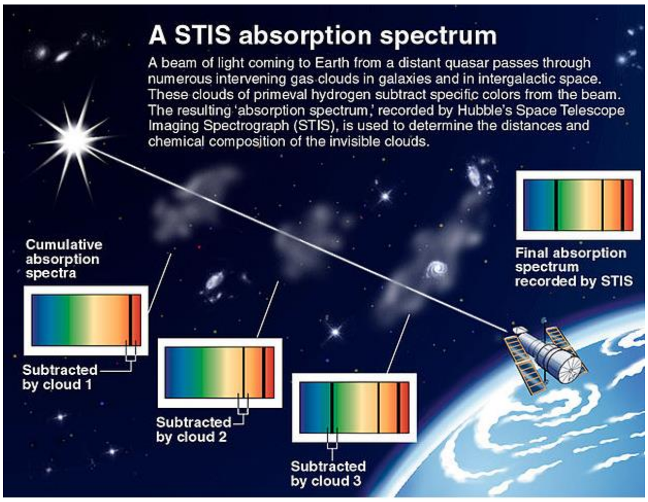
Theoretical models, principally quantum mechanical models, allow for the absorption spectra of atoms and molecules to be related to other physical a properties such as atomic or molecular mass a electronic structure, and molecular geometry**.** Therefore, measurements of the absorption spectrum are used to determine these other properties. In addition, spectral measurements can be used to determine the accuracy of theoretical predictions. For example, the Lamb shift measured in the hydrogen absorption spectrum was not expected to exist at the time it was measured. Its discovery spurred and guided the development of quantum electrodynamics, and measurement of the Lamb shift is now used to determine the fine – structure constant.

(c) Remote sensing

One of the unique advantages of spectroscopy as an analytical technique is that measurements can be made without bringing the instrument and sample into contact. Radiation that travels between a sample and an instrument will contain the spectral information, so the measurement can be made remotely. Remote spectral sensing is valuable in many situations. For example, measurements can be made in toxic or hazardous environments without placing an operator or instrument at risk. Also, sample material does not have to be brought into contact with the instrument—preventing possible cross contamination. Remote spectral measurements present several challenges compared to laboratory measurements .The space in between the sample of interest and the instrument may also have spectral absorptions. These absorptions can mask or confound the absorption spectrum of the sample. These background interferences may also vary over time. The source of radiation in remote measurements is often an environmental source, such as sunlight or the thermal radiation from a warm object, and this makes it necessary to distinguish spectral absorption from changes in the source spectrum.

(d) Astronomy

Astronomical spectroscopy s a particularly significant type of remote spectral sensing. In this case, the objects and samples of interest are so distant from earth that electromagnetic radiation is the only means available to measure them. Astronomical spectra contain both absorption and emission spectral information. Absorption spectroscopy has been particularly important for understanding interstellar clouds and determining that some of them contain molecules. Absorption spectroscopy is also employed in the study of extra solar planets. Detection of extra solar planets by the transit method also measures their absorption spectrum and allows for the determination of the planet's atmospheric composition , pressure , temperature and scale height, due to which determined the planet's mass.



A beam of light coming to Earth from a distant quasar passes through numerous intervening gas clouds in galaxies and in intergalactic space. These clouds of primeval hydrogen subtract specific colors from the beam. The resulting 'absorption spectrum,' recorded by Hubble's Space Telescope Imaging Spectrograph (STIS), is used to determine the distances and chemical composition of the invisible clouds.

Figure 1.17 Absorption spectra observed by Hubble space telescope

1.11. THE FRANCK-CONDON PRINCIPLE

The Franck–Condon principle is a statement on allowed vibrational transitions between two different electronic states without changed its internuclear distance**.** It can be explained with the help of potential energy diagram **(Figure 1.18)**

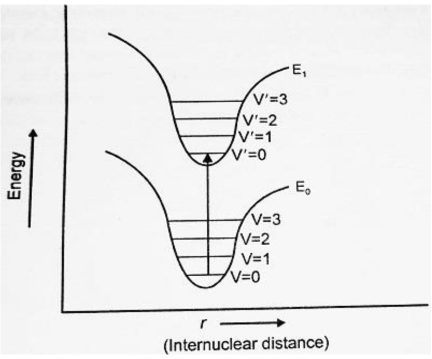


Figure 1.18 Potential energy diagram

In this diagram where E_0 is the energy of the ground state and E_1 of the excited electronic state. The two curves show the variation in electronic energy with internuclear separation in the two states. The vibrational energy levels are shown as horizontal lines. If a molecule absorbs quantum in the ground state E_0, then its transition to excited state must occur along a straight line. Because nuclei are heavy and slow as compared to electrons. An electron undergoes a transition in about 10^{-16} sec, which is very short as compared to the period of vibration of atomic nuclei. So the internuclear distance in the excited electronic state remains the same as it was in the initial ground state before the time of electronic transition. This transition is represented by a vertical line.

Transition in diatomic molecules can be explained easily by Franck condon principal. It can also be explained that why is change take place in vibrational quantum number during electronic transition. But the intensity of band line become high and low resultant continuous spectrum is obtained. The molecules may have dissociation due to transition in between stable electronic state. Frank condon principle is able to explain all these process. Suppose any diatomic molecule goes to first excited electronic energy state after absorbing energy. **Now there are four types of possibilities transitions with respect to the internuclear distance.**

(a) First Possibility- In this case upper electronic state (E_1) has the same internuclear distance as the lower electronic state (E_0). Now according to Franck Condon Principle transition occurs vertically along a straight line. If the molecule is in V = 0 vibrational level of lower electronic state E_0, then the strongest spectral line will be obtained if the molecule undergoes a transition to $V' = 0$ of upper electronic state (E_1).It is called (0,0) transition. The spectral lines this transition have intensity. These transition starts from V = 0 to $V' = 1, 2, 3$….. So the spectral line of decreasing intensity may be obtained from (1, 0) (2,0) (3,0) transition. **Figure 1.19**

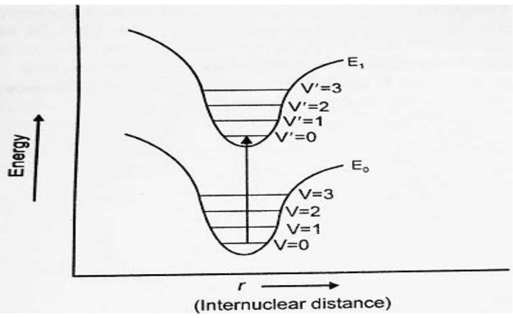


Figure 1.19

(b) Second Possibility- In this case, the upper excited electronic state has a slightly smaller internuclear distance than the lower electronic state (E_0). In such a case a vertical transition from V = 0 vibrational energy level vibration V' = 1. V' = 2, 3…… the possibility of transition is least. The resulting transitions and spectrum are similar as above. **Figure 1.20**

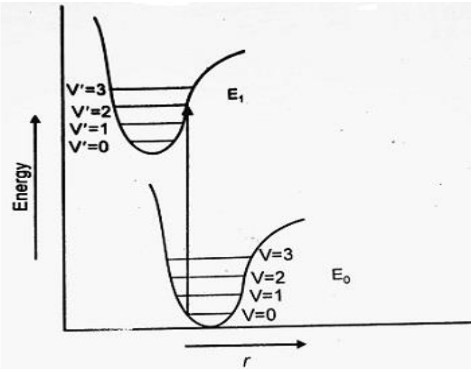


Figure 1.20

(c) Third Possibility- In this case, the upper excited electronic state has considerably greater than that in the lower electronic state. In such a case transition taking place from V'=0 to V'. (The upper electronic state (E_1) from the lower electronic state (E_0). In such condition transition taking place and the excited molecules has absorb energy greater than dissociation energy of molecules**. Figure 1.21**

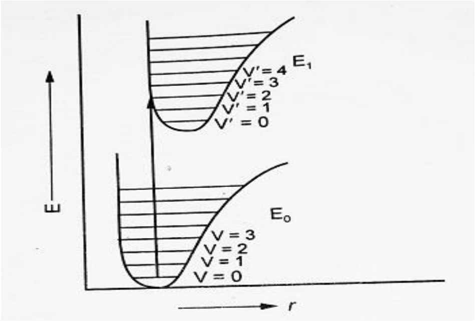


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Figure 1.21

From such states, the molecule will dissociate into atoms, and without any vibration continuous spectrum will be obtained.

1.12 PHOTOCHEMICAL STAGES

In photochemical process, an atom or molecule must absorb a quantum of visible or ultraviolet light, the energy of the atom or molecule increases its normal level, they get excited into a higher energy state. . If infrared radiation is absorbed by a molecule, then the excitation energy affects the motions of the nuclei in the molecule. After the initial absorption of a quantum of energy, the excited molecule can undergo a number of primary photochemical processes. A secondary process may occur after the primary processes.

M. Bodenstein proposed two photochemical processes these are mainly:

1.12.1. Primary process

In which light quantum hν is absorbed by a molecule A resulting in the formation of an excited molecule A*. Thus,

$$A + h\nu \rightarrow A^*$$

In this process:

1. The molecules which absorb light may get dissociated yielding excited state atoms or free radicals. In this process molecules energy emitted by luminescent radiation through fluorescence or phosphorescence.
2. It may transfer its energy to some other molecule, C, with which it collides, without emitting light. The latter energy transfer process results in a normal molecule, A, and an excited molecule, C^*. As a result of the initial light absorption step, an electron in the atom or molecule may absorb so much energy that it may escape from the atom or molecule, leaving behind the positive M^+ ion. This process is called photoionization.
3. If the excited A^* molecule (or atom) does react, then it may undergo any of the following chemical processes: photo dissociation, intramolecular (or internal) rearrangement, and reaction with another molecule C. Photo dissociation may result when the excited molecule breaks apart into atomic and/or molecular fragments A and B. A rearrangement (or photo isomerization) reaction involves the conversion of molecule A into its isomer.

1.12.2. Secondary processes

Secondary Photochemical Processes may occur upon completion of the primary step. In which the excited atoms, or free radicals produced in the primary stage react further giving rise to higher quantum yields.

1.12.3. Quantum Yield (or) Quantum Efficiency (ϕ)

To express the relationship between the numbers of molecules reacting with the number of photons absorbed, the concept of quantum yield or quantum efficiency (ϕ) is introduced. Quantum yield is defined as “the number of molecules of the substance undergoing photochemical change per quantum of radiation absorbed. Thus Number of molecules reacting in a given time

$$\phi = \frac{\text{Number of molecules reacting in a given time}}{\text{Number of quanta of light absorbed in the same time}}$$

In certain photochemical reaction, λ = wavelength of light in Ǻ; q = amount of radiation absorbed in certain interval of t s. & n = number of moles of substance reacted in the same time interval (t), then Number of einsteins absorbed = $q / (Nhc/ \lambda) = q \lambda / Nhc$

Quantum yield, $\phi = n/(q \lambda /Nhc) = nNhc/q \lambda$

In CGS units, $\phi = n/q \times [1.196 \times 1016/ \lambda \text{ (in Ǻ)}]$

1.12.4 Cause of high quantum yield

- Absorption of radiations in the first step involves production of atoms or free radicals, which initiate a series of chain reactions.
- If the reactions are exothermic, the heat evolved may activate other molecules without absorbing the additional quanta of radiation
- Formation of intermediate products will act as a catalyst.
- The active molecules, produced after absorption of radiation, may collide with other molecules and activate them which in turn activate other reacting molecules

1.12.5 Examples of high quantum yield

Formation of HCl

1) In the primary step, one Cl_2 molecule absorbs a photon and discussed into two Cl atoms.

2) This is followed by the secondary reaction,

$Cl_2 + h\nu \rightarrow 2\,Cl^*$ …………. Primary reaction

$Cl + H_2 \rightarrow HCl + H^*$

$H^* + Cl_2 \rightarrow HCl + Cl^*$ ……. Secondary reaction

The Cl atom consumed in step 2 is regenerated in step 3; this will propagate the chain reaction. The chain reaction gets terminated when the Cl atoms recombine at the walls of the vessel, where they lose their excess energy.

$$2\,Cl \rightarrow Cl_2$$

Thus the quantum yield varies from 10^4 to 10^6, ie . ($\phi > 1$) quantum yield > 1 .

1.12.6 Cause of low quantum yields

1. Excited molecules may get deactivated before they form products.
2. The Collisions of excited molecules with non-excited molecules may cause the former to lose energy.
3. The broken molecules may combine with each other resulting in the formation of the original molecule.
4. Quantum yield will also be affected by the intensity of light energy.

1.12.7 Examples of high quantum yield:

Dimerization of anthracene to di-anthracene

$$2C_{14}H_{10} + h\nu \rightarrow C_{28}H_{20}$$

The quantum yield ($\phi < 1 = 2$), quantum yield< 1) = 2 but actually it is found to be = 0.5, the reason is the above reaction is reversible.

$2C_{14}H_{10} \rightarrow C_{28}H_{20}$

The law of photochemical equivalence can be applied only to primary process because in which each molecule capable of entering into chemical reaction absorbs one quantum of radiation. The secondary processes take place of themselves quite independent of the light radiation. It may also be noted that if reactions in the secondary processes that are responsible for the formation of products are endothermic in nature, their rate of occurrence is extremely slow at ordinary temperatures.

1.13 SAQ's TYPES QUESTIONS

A. Multiple Choice Questions:

1) Calculate the Frequency for a radiation of 5000 A^0

a) $6 \times 10^{14} sec^{-1}$ b) $6 \times 10^{4} sec^{-1}$

c) $2 \times 10^{14} sec^{-1}$ d) $6 \times 10^{14} sec$

2) Which of the following are the reactions in which molecules absorbing light do not themselves react but induce other molecules to react?

a) Free radical reactions b) Chain reactions

c) Reversible reactions d) Photosensitized reactions

3) Decomposition of HI quantum yield is:

a). 1 b). 2 c). 4 d). 0

4) Quantum efficiency is given by:

a) nNhc / q λ b) nq / Nhc

c) n λ / nNhc d) nc λ / hc

5). in atomic emission spectroscopy the emission due to the electronic transition of

a) Singlet ground state to singlet exited state

b) Singlet exited state to singlet ground state.

c) Singlet ground state to triplet exited state

d) Triplet exited state to Singlet ground state

6). The fact that the fluorescence wavelength is often much longer than the irradiation wavelength is a consequence of which phenomenon:

a) The frank condon principal b) Vertical transition (Kasha's rule)

c) Low extinction (Lambert beer rule) d) High ISC rate

7). Which of the following is the example of photo chemical reaction:

a) Decomposition of ammonia b) Formation of NaOH

c) Photosynthesis d) Decomposition of HCl

8). Beer-Lambert law is applicable if

a) Temperature changes b) Temperature varies linearly

c) Non-monochromatic radiation is used d) Dilute solution is used

9). The different types of energy associated with the molecules are:

a) Electronic energy b) Rotational energy

c) Vibrationl energy d) All of the mentioned

10). The necessary condition of absorption spectra is that:

a) hν should be greater than the energy difference

b) hν should be smaller than the energy difference

c) hν should be equal than the energy difference

d) None of the mentioned

B) Fill in the blanks:

1. A reaction which is caused by heat and in absence of light is called ………..
2. In photochemical reaction absorption of ………………. Radiation takes place.
3. When a beam of light is allowed to pass through a transparent medium, the rate of decrease of intensity with the thickness of medium is …………….. to the intensity of the light.
4. . ……… …… is also known as Principle of Quantum Activation.
5. Energy of photon is given by ……………….
6. **Carbonyl compound shows, which transition……….**
7. A substance absorbs 2.0 x 10^{16} quanta or radiations per second and 0.002 mole of it reacts in 1200 seconds, the quantum yield of the reaction …………… (N = 6.02 x 10^{23})
8. **Which state electron is in pair but opposite spin …………..**

Answer Key: A)

1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
a	**d**	**b**	**a**	**b**	**a**	**c**	**d**	**d**	**c**

B)

	2	3	4	5	6	7	8
Dark reaction	Uv and visible	directly proportional	Stark-Einstein law	$h\nu$	$n \Rightarrow \pi *$	50	Singlet ground state

1.14. REFERENCES

1. Principles and Applications of PhotochemistryBrian Wardle Manchester Metropolitan University, Manchester, UK
2. Physical chemistry-III (classical Thermodynamics, Non-EquilibriumThermodynamics, Surface Chemistry, Fast Kinetics) Module No and Title 32: Reactions in Flow Systems and Kinetics of Fast Reaction.
3. Photochemistry – Wikipedia https://en.wikipedia.org › wiki › Photochemistry.
4. Biswanath Dinda Essentials of Pericyclic and Photochemical Reactions. Biswanath Dinda Department of Chemistry Tripura University Agartala, Tripura India and Department of Chemistry NIT Agartala Jirania India
5. https://en.wikipedia.org/wiki/Franck%E2%80%93Condon_principle.
6. https://www.sciencedirect.com/topics/chemistry/franck-condon-principle#
7. https://en.wikipedia.org › wiki › Absorption spectroscopy.
8. Photochemistry and Pericyclic Reactions (third edition) Jagdamba singh and Jaya singh.

1.15. SUGGESTED *READINGS*

1. Principles and Applications of Photochemistry Brian Wardle Manchester Metropolitan University, Manchester, UK

2. Biswanath Dinda Essentials of Pericyclic and Photochemical Reactions. Biswanath Dinda Department of Chemistry Tripura University Agartala, Tripura India and Department of Chemistry NIT Agartala Jirania India
3. Photochemistry and Pericyclic Reactions (third edition) Jagdamba singh and Jaya singh
4. Hand book of Photochemistry (3rd edition) Macro Montalti, Alberto Credi, Luca Prodi, M. Teresa Gandolfi

1.16 TERMINAL QUESTIONS

1. Define Morse potential energy curve for diatomic molecules?
2. What does the Jablonski diagram show? Give reason that the fluorescence spectrum observed always at lower wavelength than the phosphorescence?
3. Write a short notes on : (a) Kasha's Rule (b) Vavilov's Rule
4. Explain the flash photolysis process?
5. What is the Laws of Photochemistry?
6. What are the possible electronic transitions of p, s, and n electrons by excitation with light?
7. Give Qualitative Description of Frank – Condon Principle?
8. Define Primary process, Secondary process in photochemical stages?
9. What are absorption spectra? Name the apparatus which used in absorption spectra? Write down the application of absorption spectra.
10. Write short note on: (a) singlet and triplet excited states. (b) internal conversion (c) florescence and phosphorescence (d) photosensitizer (e) quenchers

UNIT 2: PHOTO-PHYSICAL REACTIONS

CONTENTS:

2.1 INTRODUCTION

A chemist has most difficult challenge is determining the chemical structure of an unknown substance. There are many methods for identifying the unknown material. To establish the structure of a compound, one can utilise physical methods such as boiling point, melting point, and spectroscopy, as well as chemical procedures such as functional group testing and others. Spectroscopy, which includes UV, IR, NMR, Raman, and other techniques, is one of the finest ways to identify a chemical. In this unit, we will go through the many aspects of electronic transitions and their phenomenon.

The electromagnetic spectrum contains a broad variety of electromagnetic radiations, from gamma-rays with wavelengths on the order of a fraction of an angstrom to radio waves with wavelengths measured in metres or kilometres. The electromagnetic (EM) spectrum is the organisation of all forms of radiations in order of increasing wavelength or decreasing frequency. As shown in Figure 1, the electromagnetic spectrum includes radio and television waves, microwaves, infrared, visible light, ultraviolet, X-rays,gamma -rays, and cosmic rays. In photochemistry, reactions started by electronically stimulated molecules are the center. Such molecules are produced when energy in the visible and near ultraviolet regions of the spectrum is absorbed. Since the sun is the main source of light in our universe, photochemistry must have played some role in the beginning of life. Complex organic molecules like proteins and nucleic acids must have been created by photochemical reactions between simple gaseous molecules like methane, ammonia, and carbon dioxide.

The relevance of photochemistry also stems from its numerous scientific and technological applications. Many substances that could not be created by dark reactions can now be made via synthetic organic photochemistry. Certain commercially feasible photochemical synthesis processes include the production of some antioxidants, the synthesis of vitamin D2 from yeast-derived ergosterol, and the synthesis of caprolactum, the monomer for nylon 6. Photography, lithoprinting, and the creation of printed circuit boards for the electrical sector all involve photoinitiated polymerization and photopolymerization. Fluorescent tube lights, TV screens, luminous watch dials, "optical brighteners" in white garment materials, paints in billboard advertisements, and other products have all used the photophysical phenomena of flourescence and phosphorescence. Laser technology is yet another breakthrough use of electrically stimulated molecular systems.

The two main processes, therefore, studied under photochemistry are:

1. Photophysical process
2. Photochemical process
3. Photophysical process:- In this process, the absorption of light does not result into any chemical reaction.

4. Photochemical process:-In this process, the light that is absorbed by a system results in to chemical change.

2.2 OBJECTIVES

After studying this Unit, you shall be able to know:

- We will understand the difference of photochemical and photophysical process.
- How the photochemical reactions undergo in the presence of light.
- We will know about laws of photochemistry.
- How to calculate the quantum yield.
- We will learn the phenomenon of Jablonskii diagram.

2.3 ENERGY OF A MOLECULE

The sum of electronic energy, vibrational energy, rotational energy and translational energy is the total energy of a molecule.

$E_{Total} = E_{elec} + E_{vib} + E_{rot} + E_{trans}$

Except translational energy all other three energies are quantised and furthermore Eelec>>Evib>>Erot>>Etrans. Translational energy is (only 4% of the total energy) negligible. Thus, the energy of molecule is $E_{Total} = E_{elec} + E_{vib} + E_{rot}$. These energies related with the property of the molecule that is size, shape, flexibility as well as on the type of motion.

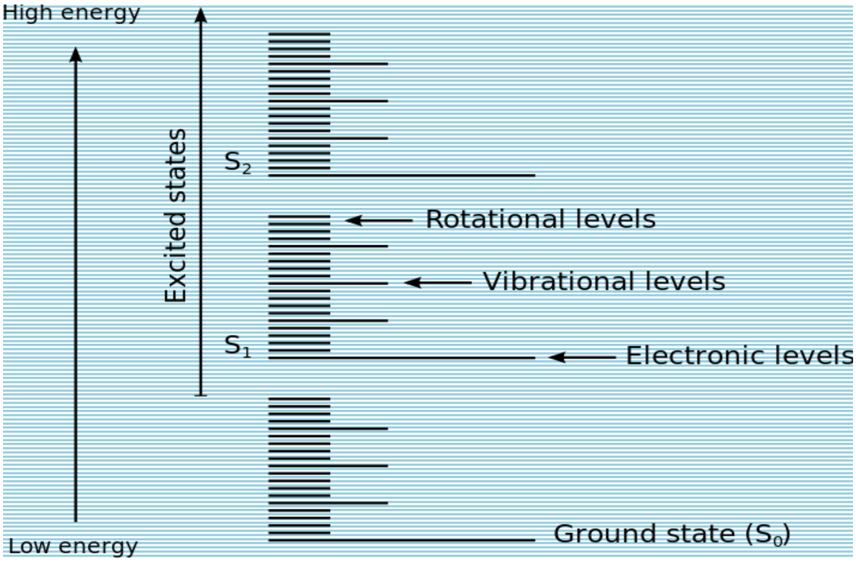


Figure 2.1: Different energy levels of the molecule

2.3.1 Process of photochemistry

The two main processes studied under photochemistry are:

i. Photophysical process

ii. Photochemical process and photochemical reactions

2.3.1.1 Photophysical processes (LUMINESCENCE)

Photophysical processes*are those which takes place in the presence of light but do not result into any chemical reaction.* When a solid body e.g. a piece of iron is heated, it first becomes 'red hot' and then becomes 'white hot' and hence it begins to glow. The glow can be produced by methods other than. the action of heat, eg. when the excited electrons jump back to the inner levels, light is emitted. The light thus produced is called "cold light ". The glow produced in a body by methods other than the action of heat i.e. the production of cold light is called luminescence. The body emitting the cold light is called luminescent.

Luminescence may be any one of the following three types:

(a) Fluorescence (b) Phosphorescence (c) Chemiluminescence

2.3.1.1.1. Chemiluminescence

When a photochemical reaction takes place, light is absorbed. However, there are certain reactions (taking place at ordinary temperature) in which light is produced, the emission of light in chemical reactions at ordinary temperatures is called chemiluminescence. Thus, chemiluminescence is just the reverse of a photochemical reaction. A few examples of chemiluminescence are as under:

i. The light emitted by glow-worms (fire-flies) is due to the oxidation of the protein, luciferin, present in the glow-worms by atmospheric oxygen in the presence of the enzyme, luciferase.

ii. The oxidation of yellow phosphorus in oxygen or air to give P-205 at ordinary temperatures (-10 ^{o}C to 40 ^{0}C) is accompanied by the emission of visible greenish-white luminescence.

iii. Oxidation of decaying wood containing certain forms of bacteria also produces luminescence. In all the above cases, a part or whole of the energy emitted during the reaction, instead of appearing as heat, is used up for the excitation of electrons which when jump back to the inner orbits result into the emission of light.

Figure 2.2: Chemiluminescence of fireflies and luminol

2.3.1.1.2. Fluorescence

There are certain substances which when exposed to light or certain other radiations absorb the energy and then immediately or instantaneously start re-emitting the energy. Such substances are called fluorescent substances and the phenomenon is called fluorescence. Obviously, the absorption of-the energy results into the excitation of the electrons (present in the atoms or the molecules of the substance) followed immediately by the jumping back of the excited electrons to the lower levels. As a result, the absorbed energy is emitted back

The word 'instantaneous' used above implies that the time between the absorption of the energy and the re-emission of the absorbed energy is not more 10-8 sec. Thus, fluorescence starts as soon as the substance is exposed to light and the fluorescence stops as soon as the light is cut off.

A few examples of the substances showing the phenomenon of fluorescence are

(a) a solution of quinine sulphate on exposure to visible light, exhibits blue fluorescence.

(b) a solution of chlorophyll in ether shows blood red fluorescence.

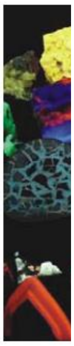


Figure 2.3: Fluorescent minerals, shown under ultraviolet light.

Figure 2.4: (a) tonic water is clear under normal light, but vividly fluorescent under ultraviolet light, due to the presence of the quinine used as flavouring; **(b)** A solution of chlorophyll in ether solution shown blood red fluorescence.

Explanation: When a molecule absorbs high energy radiation, it is excited to higher energy states. Then it emits excess energy through several transitions to the ground state. Thus the excited molecule emits light of longer frequency. The colour of fluorescence depends on the wavelength of light emitted

1. Fluorite, CaF_2 (from which the name of the phenomenon is derived)
2. Certain organic dyes such as eosin, fluorescein etc.
3. Vapour of sodium, mercury, iodine etc.,
4. Certain inorganic compounds such as uranyl sulphate, UO_2SO_4

It is interesting to observe that in the phenomenon of fluorescence, the wavelength of the emitted light is usually greater than that of the absorbed light. This is explained on the basis that the energy absorbed raises the electron to a sufficiently higher level but the return of the excited electron to the original level takes place in steps, through the intermediate levels. The energy thus produced in every jump is smaller and hence the wavelength of the light emitted is large as $E = h\nu$ than that of the absorbed light.

In case of mercury vapour, the emitted light has the same wavelength as that of the absorbed light. This phenomenon is called resonance fluorescence. In certain cases, light of shorter wavelength (i.e. of higher energy) is emitted. This is explained by suggesting that the emitted light contains the absorbed energy as well as some energy present in the system before absorption.

2.3.1.1.3. Phosphorescence

In case of fluorescent materials, the florescence stops as soon as the external light is cut off However, there are certain substances which continue to glow for some time even after the external light is cut of such substances arc called phosphors or phosphorescent substances and the phenomenon is called phosphorescence. Thus, in a way, phosphorescence is a slow fluorescence. It is found mostly in solids, as might be expected because in solid, the molecules have least freedom of motion. The excited electrons thus keep on jumping back slowly for quite some time.Phosphorescence is chiefly caused by ultraviolet and visible light. It is generally shown by solids.

Examples

(a) Sulphates of calcium, barium and strontium exhibit phosphorescence.

(b) Fluorescein in boric acid shows phosphorescence in the blue region at 5700 Å wavelength.

Explanation: As in fluorescence, a molecule absorbs light radiation and gets excited. While returning to the ground state, it emits light energy of longer wavelength. In doing so the excited molecule passes from one series of electronic states to another and gets trapped. This shows the emission of light which persists even after the removal of light source. Thus phosphorescence could be designated as delayed fluorescence.

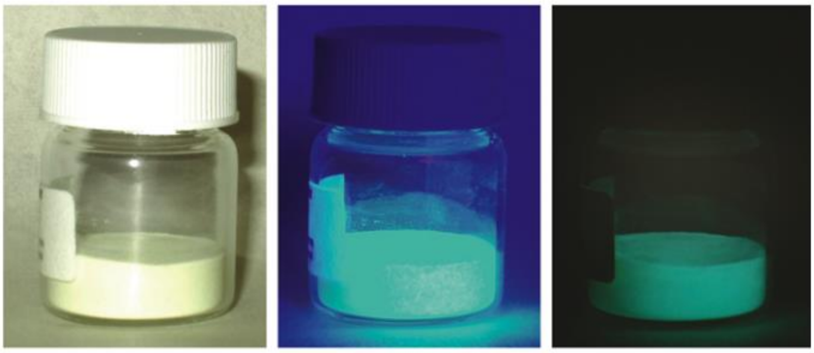


Figure 2.5 Phosphorescent powder under visible light, ultraviolet light, and total darkness

The other examples of the substances exhibiting phosphorescence include zinc sulphide and sulphides of the alkaline earth metals. Usually, a trace of heavy metal is added (in the form of its sulphide) which intensifies the light emitted by the phosphorescent substance. Further, it has been found that the fluorescent substances become phosphorescent if fixed by suitable methods, e.g. by fusion with other substances etc. For example, many dyes (which show fluorescence) when dissolved in fused boric acid or glycerol and then cooled to get rigid mass become phosphorescent.

2.4 JABLONSKII DIAGRAM

When particular molecules are exposed to light, some of the electrons within them absorb energy and jump to the outer orbitals. The molecules are said to be in an excited state at this point. The majority of excited species have extremely brief life spans, often less than 10-6 seconds. They can either alter chemically or return to their original state.

The excitation of an electron occurs so quickly (10-13 seconds) that it is thought that there isn't enough time for the orientation of the electron's spin to change, i.e., the one that was clockwise after the excitation remains clockwise and the one that was anti-clockwise after the excitation remains anti-clockwise**.**

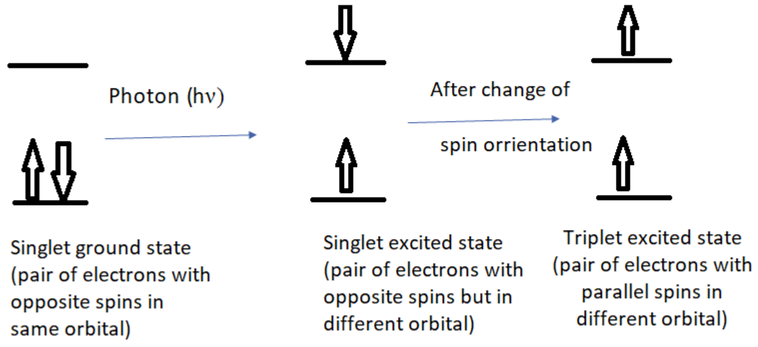


Figure 2.6 Excitation of electron in photochemical process

The spin multiplicity of these states is 2S + I, where S is the total electron spin. S = 0 for a molecule with all paired electrons, and so its spin multiplicity is l. The molecule is considered to be in the ground state of a singlet. When the molecule is in the excited state with opposite spins after absorbing a photon, S = 1/2-1/2=0, resulting in a spin multiplicity of l. When this happens, the molecule is considered to be in a singlet excited state. The electrons are present in distinct orbitals but spin in the same direction in the excited state, S = 1/2+1/2=1 and spin multiplicity = 2S + 1 = 3. The molecule is considered to be in a triplet excited state at this point. Depending upon the energy absorbed, electrons may jump to any of the higher excited state and we have a number of singlet excited states called first, second, third singlet excited states represented by S_1, S_2, S_3 etc. The singlet ground state is represented by S_o. The corresponding triplet excited states arecalled first, second, third triplet excited states and are represented by T_1, T_2, T_3 etc. Any singlet state is found to have higher energy than the corresponding triplet state i.e. $ES_1>ET_1$, $ES_2>ET_2$.

In all these paths, however the first step is the transitions from higher excited states to the lowest excited singlet state S_1. This is called **internal conversion** (IC). The energy is lost only in the form of heat (shown by wavy line in the diagram) due to collision with other molecules. As it does not result into the emission of any radiation, it is therefore, called **non-radiative** or **radiation less** transition. It is a very fast process and occurs in less than about 10-11 second. Now from the first excited singlet state, the molecules return to the ground state by any one of the following paths

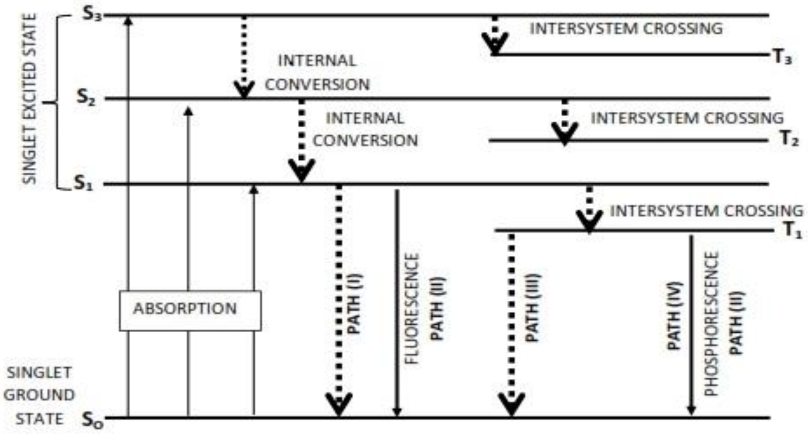


Figure 2.7 Jablonski diagram showing excitation of molecules and their decay process to the ground state by different paths..

Path I. The molecule may lose rest of the energy also in the form of heat so that the complete path is non-radiative.

Path II. The molecule may release the energy in the form oflight or ultraviolet radiation in returning to the ground state from the first excited singlet state (shown by straight line in the diagram). Hence it is a radiative transition. This is called fluorescence. It occurs for about 10-8 second after absorption so that a substance fluoresces only in the presence of absorbed radiation.

Path III. Some energy may first be lost in transition from first excited singlet state to the first excited triplet state i.e. between states of different multiplicity i.e. S_1 to T_1 (or similarly S_2 to T_2,S_3 to T_3 etc., in the form of heat so that it is again a radiation lesstransition. It is also called intersystem crossing (ISC). Such transitions are normally forbidden but whenever they occur, their rate is very slow. In further transition from first excited triplet state to the ground state, the rest of the energy may again be lost in the

Path IV. After intersystem crossing, the molecule may lose the rest of the energy in the form of light in going from the excited triplet state to the ground state. This is called phosphorescence. As triplet states have much longer life times than singlet states, some as long as an hour, phosphorescence persists even after the removal of absorbed radiation. This may also be attributed to the fact that the transitions from excited triplet states to ground singlet state are forbidden. Note that fluorescence involves a radiative transition between two states of the same multiplicity (usually two singlets) whereas phosphorescence arises due to a radiative transition between two states of different multiplicity (usually triplet to singlet). It may be observed that the energy emitted during fluorescence as well as phosphorescence is less than the energy absorbed during excitation, as a part of the energy is dissipated as heat in the internal conversion and intersystem crossing. Hence the frequencies emitted during fluorescence and phosphorescence are smaller or wavelengths are longer than those of the light absorbed for excitation Further, the energy is lost not only as heat but also in undergoing a chemical reaction. As singlet excited states return quickly to the ground state, there is no chance for a chemical reaction. However, if the molecules are in the triplet excited states, they return to the ground state slowly and thus get sufficient time to undergo a chemical reaction. Thus, molecules undergoing chemical reaction are those which are first in the excited triplet state. The paths followed as explained above may be compared with a two-floor building having steps, ramps and windows. Firststep ofall paths is like a ball falling from second floor to the first floor by bouncing on steps going from second floor to first floor. If the ball now falls on the ramp going from first floor to ground floor, it is like path I. If the ball after coming to first floor falls out of the window, it is like path Il. If after coming to first floor, the ball moves on some steps and then falls on the ramp going fromfirst floor to ground floor, it is like path Ill. If the ball after having come to first floor, moves on some steps going from first floor to ground floor and then jumps out of the window, it is like path IV.

2.5 PHOTOSENSITIZATION

There are many substances which do not react directly when exposed to light. However, if another substance is added, the photochemical reaction starts. Substance thus added itself does not undergo any chemical change; It merely absorbs the light energy and then passes it on to one of the reactants. Such a substance which when added to a reaction mixture helps to start the photochemical reaction but itself does not undergo any chemical change is called a photosensitizer and the process is called photosensitization. Thus, a photosensitizer simply acts as a carrier of energy. At the first instance it appears that a photosensitizer is similar to a catalyst, however, this is not so as they act by different mechanism.

2.6 LAWS OF PHOTOCHEMISTRY

There are two basic laws governing photochemical reactions:

a. The Grothus-Draper law

b. The Stark-Einstein law of Photochemical Equivalence

2.6.1 Grothus–Draper law

When light falls on a cell containing a reaction mixture, some light is absorbed and the remaining light is transmitted. Obviously, it is the absorbed component of light that is capable of producing the reaction. The transmitted light is ineffective chemically. Early in the 19th century, Grothus and Draper studied a number of photochemical reactions and enunciated a generalisation. This is known as Grothus-Draper law and may be stated as follows:

- It is only the absorbed light radiations that are effective in producing a chemical reaction. However, it does not mean that the absorption of radiation must necessarily be followed by a chemical reaction.
- When the conditions are not favourable for the molecules to react, the light energy remains unused. It may be re-emitted as heat or light. The Grothus-Draper law is so simple and self-evident. But it is purely qualitative in nature.
- It gives no idea of the relation between the absorbed radiation and the molecules undergoing change.

2.6.2. Stark-Einstein law of photochemical equivalence

Stark and Einstein (1905) studied the quantitative aspect of photochemical reactions by application of Quantum theory of light. They noted that each molecule taking part in the reaction absorbs only a single quantum or photon of light. The molecule that gains one photon-equivalent energy is activated and enters into reaction. Stark and Einstein thus proposed a basic law of photochemistry which is named after them. The Stark-Einstein law of photochemical equivalence may be stated as:

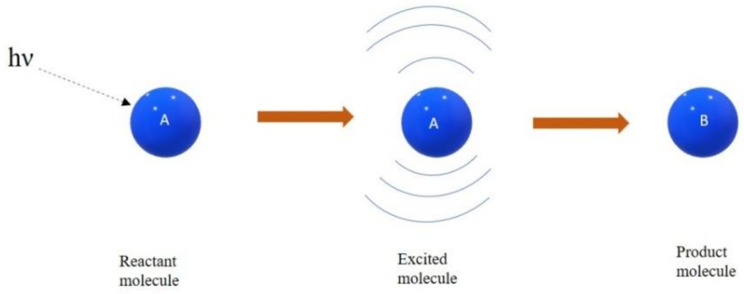


Figure 2.8 Illustration of Law of Photochemical equivalence; absorption of one photon decomposes one molecule

“In a photochemical reaction, each molecule of the reacting substance absorbs a single photon of radiation causing the reaction and is activated to form the products.”

Processes of photochemical reactions: The overall photochemical reaction consists of

(a) *Primary reaction*.

i. In the primary reaction, the quantum of light is absorbed by a molecule ‘A’ resulting in the formation of an excited molecule A*.

$$A + h\gamma \rightarrow A^*$$

(b) *Secondary reaction*

ii. In the secondary reaction, the excited molecules react further to give the product of higher quantum yield.

$$A^* \rightarrow B$$

2.7 QUANTUM YIELD (OR) QUANTUM EFFICIENCY (Φ)

The term "quantum yield" or "quantum efficiency" is used to describe the relationship between the number of molecules responding and the number of photons absorbed.

The number of molecules of the substance undergoing photochemical change per quantum of radiation absorbed is referred to as quantum yield. Thus,

$$\phi = \frac{\text{Number of molecules reacting in a given time}}{\text{Number of quanta of light absorbed in the same time}}$$

In certain photochemical reaction, λ = wavelength of light in Å; q = amount of radiation absorbed in certain interval of t s. & n = number of moles of substance reacted in the same time interval (t), then

$$\text{Number of Einstein's absorbed} = q/(Nhc/\lambda) = q\lambda/Nhc$$

$$\text{Quantum yield } \phi = n/(q\lambda/Nhc) = nNhc/q\lambda$$

$$\text{In CGS units, } \phi = n/q \times [1.196 \times 10/\lambda \text{ (in Å)}]$$

2.7.1 High (or) low quantum yield

From zero to ten, the quantum efficiency ranges. The quantum yield is equal to one if the Einstein law is followed and one molecule is broken down for every photon.

***High Quantum Yield*: ** A high quantum yield reaction has a quantum yield $\phi > 1$ when two or more molecules are broken down per photon.

***Low Quantum Yield*: ** When the number of molecules decomposed is less than one per photon, the quantum yield $\phi < 1$ and the reaction has a low quantum yield.

Conditions for high and low quantum yield: The reacting molecules should full-fill the following conditions:

1. All the reactant molecules should be initially in the same energy state and hence equally reactive.

2. The reactivity of the molecules should be temperature independent.

3. The molecules in the activated state should be largely unstable and decompose to form the products.

Causes (or) Reasons for high quantum yield

1. Absorption of radiations in the first step involves production of atoms or free radicals, which initiate a series of chain reactions.
2. Formation of intermediate products will act as a catalyst.
3. If the reactions are exothermic, the heat evolved may activate other molecules without absorbing the additional quanta of radiation.
4. The active molecules, produced after absorption of radiation, may collide with other molecules and activate them which in turn activate other reacting molecules.

Examples:

Decomposition of HI: In the primary reaction, one HI molecule absorbs a photon anddissociated to produce one H and one I. This is followed by the second reaction as shown below:

$HI + h\gamma \rightarrow H^* + I^*$ Primary reaction

$H^* + HI \rightarrow H_2 + I^*$ Secondary reaction

$I^* + I^* \rightarrow I_2$

Overall reaction: $2HI + h\gamma \rightarrow H_2 + I_2$

The overall reaction shows that the two HI are decomposed for one photon (hγ). Thus, the quantum yield (ϕ) = 2

1. **Formation of HCl:** In the primary step, one Cl2molecule absorbs a photon anddiscussed into two Cl atoms. This is followed by the secondary reaction as shown below:

$Cl_2 + h\gamma \rightarrow 2Cl^*$ Primary reaction

$Cl^* + H_2 \rightarrow HCl + H^*$

$H^* + Cl_2 \rightarrow HCl + Cl^*$ Secondary reaction

The Cl atom consumed in step 2 is regenerated in step 3, this will propagate the chain reaction. The chain reaction gets terminated when the Cl atoms recombine at the walls of the vessel, where they lose their excess energy.

$2Cl^* \rightarrow Cl_2$

Thus the quantum yield varies from 10^4 to 10^6.

***Causes (or) Reasons for low quantum yield*:**

1. Excited molecules may get deactivated before they form products.
2. Excited molecules may lose their energy by collisions with non-excited molecules.
3. Molecules may not receive sufficient energy to enable them to react.
4. The primary photochemical reaction may be reversed.
5. Recombination of dissociated fragments will give low quantum yield.

Example: Dimerization of anthracene to dianthracene

$2C_{14}H_{10} + h\gamma \rightarrow C_{28}H_{20}$

The quantum yield = 2, but actually it is found to be = 0.5 ; the reason is the above reaction is reversible.

2.7.2 Classification of photochemical reaction based on quantum yield

Based on quantumyield, the various photochemical reactions can be divided into three categories.

1. The reaction in which the quantum yield is a small integer like 1, 2.

   Examples: a) Dissociation of HI & HBr;

   b) Combination of SO_2+Cl_2

   c) Ozonisation of O_2.

2. The reaction in which the quantum yield is less than 1.

   Eaxmples: a) Dissociation of NH_3, CH_3COCH_3& NO_2

   b) Transformation of maleic acid into fumaric acid.

2. The reaction in which the quantum yield is extremely high.

   Examples: a) Combination of CO + Cl_2

   b) Combination of H_2 + Cl_2.

2.8. SUMMARY

- We have understanded about photophysical and photochemical process with suitable examples.
- How to calculate the quantum yield of any photochemical reaction.
- We have learnt about the laws of photochemistry.
- We have known about Different examples of photophysical reactions.
- How the different decay process mechanisms undergo in photochemical process.

2.9 TERMINAL QUESTIONS

A. Solved problems

1. When a substance A was exposed to light, 0.002 mole of it reacted in 20 minutes and 4 seconds. In the same time A absorbed 2.0×10^6 photons of light per second. Calculate the quantum yield of the reaction. (Avogadro number $N = 6.02 \times 10^{23}$)

SOLUTION:

Number of molecules of A reacting = $0.002 \times N = 0.002 \times 6.02 \times 10^{23}$

Number of photons absorbed per second = 2.0×10^6

Number of photons absorbed in 20 minutes and 4 seconds = $2.0 \times 10^6 \times 1204$

Quantum yield $\varphi = \frac{\text{No.of molecules reacted}}{\text{No.of photons absorbed}}$

$$= \frac{0.002 \times 6.02 \times 10^{23}}{1204 \times 2.0 \times 10^6}$$

$$= 5.00 \times 10^{11}$$

2. When irradiated with light of 5000 Å wavelength, 1×10^{-4} mole of a substance is decomposed. How many photons are absorbed during the reaction if its quantum efficiency is 10.00. (Avogadro number $N = 6.02 \times 10^{23}$).

SOLUTION

Quantum efficiency of the reaction = 10.00

No. of moles decomposed = 1×10^{-4}

No. of molecules decomposed = $1 \times 10^{-4} \times 6.02 \times 10^{23}$

$= 6.02 \times 10^{19}$

we know that,

$$\varphi = \frac{\text{No. of molecules decomposed}}{\text{No. of photons absorbed}}$$

$$10 = \frac{6.02 \times 10^{19}}{\text{No. of photons absorbed}}$$

$$\text{No. of photons absorbed} = \frac{6.02 \times 10^{19}}{10}$$

$$\text{No. of photons absorbed} = 6.02 \times 10^{18}$$

3. When propionaldehyde is irradiated with light of λ = 3020 Å, it is decomposed to form carbon monoxide.

$CH_3CH_2CHO + h\nu \rightarrow CH_3CH_3 + CO$

The quantum yield for the reaction is 0.54. The light energy absorbed is 15000 erg mol in a given time. Find the amount of carbon monoxide formed in moles in the same time.

SOLUTION

we have one einstein (E) = 1.196 10^{16} erg mol

one einstein (E) $= \frac{1.196 \times 10^{16}}{\lambda}$ erg mol

when λ = 3020 Å, one Einstein=$\frac{1.196 \times 10^{16}}{3020}$erg mol

or 15000 erg mol of energy=$\frac{15000 \times 3020}{1.196 \times 10^{16}}$ erg mol

$$\varphi = \frac{\text{No.of molecules decomposed}}{\text{No.of photons absorbed}} = 0.54$$

Hence the amount of CO formed = $0.54 \times 3.78 \times 10^{-9} = 2.04 \times 10^{-9}$ mole

B. UNSOLVED QUESTION

Q.1 Define or explain the following terms :

A) Photochemical reaction

B) Grothus-Draper law

C) Stark Einstein law

D) Quantum yield

E) Quantum Efficiency

Q.2 Distinguish between photochemical and thermal reactions.

Q.3 A radiation of 2530 Å incident on HI results in the decomposition of 1.85×10^{-2} mole per 1000 cal. of radiant energy. Calculate the quantum efficiency. ($h = 6.62 \times 10^{-27}$; $N = 6.023 \times 10^{23}$; $c = 3 \times 10^{10}$ cm/sec.

Answer: 2.09

Q.4 What is meant by quantum energy and Einstein energy? State Einstein law of photochemical equivalence.

Q.5 In the photochemical reaction B → C, 1.00×10^{-5} mole of C is formed as a result of the absorption of 6.00×10^{7} ergs at 3600 Å. Calculate the Quantum yield.

Answer. 0.553

Q.6 How would you explain very high and very low quantum efficiencies of some photochemical reactions.

Q.7 For the photochemical reaction A → B, 1.0×10^{-5} moles of B were formed on absorption of 6.0×10^{7} ergs at 3600 Å. Calculate the quantum efficiency of the reaction. (N = 6.02 × 1023; h = 6.0×10^{-27} erg/sec)

Answer: 90.92%

Q.8 A certain system absorbs 3.0 × 1016 quantum of light per second on irradiation for 10 minutes. 0.002 mole of the reactant was found to have reacted. Calculate the quantum efficiency of the process. (N = 6.023 × 1023).

Answer: 66.92

Q.9 Distinguish between fluorescence and phosphorescence. Draw energy level diagrams to explain these processes and discuss them briefly.

Q.10 State and explain the law of photochemistry. What do you mean by quantum yield? How is it determined experimentally?

C. Multiple choice questions

1. A photochemical reaction takes place by the absorption of

   (a) visible and ultraviolet radiations

   (b) Infrared radiations

   (c) heat energy

   (d) none of these

   Answer. (a)

2. Photochemistry deals with the study of

   (a) photons

   (b) photos

(c) reactions which proceed with absorptions of UV light

(d) reactions which proceed with absorption of IR light

Answer. (c)

3. The wavelength of ultraviolet and visible regions of electromagnetic spectrum is:

(a) less than 2000 Å

(b) more than 8000 Å

(c) 2000° to 8000 Å

(d) none of these

Answer. (c)

4. Which of the following statements about the photochemical reactions is true?

(a) the presence of light is the primary requirement for reactions to take place

(b) temperature has a very little effect on the rate of photochemical reactions

(c) ΔG for photochemical spontaneous reactions may +ve or –ve

(d) all of the above

Answer. (d)

5. The number of photons that pass through a unit area in a unit time is called

(a) amplitude of light

(b) frequency of light

(c) intensity of light

(d) wavelength of light

Answer. (c)

6. “Only the fraction of incident light that is absorbed by the substance can bring about a chemical change”. is

(a) First law of photochemistry

(b) Second law of photochemistry

(c) Third law of photochemistry

(d) none of these

Answer. (a)

7. The energy of an einstein of radiation of wavelength 400 nm is _______ than that of radiation of 300 nm

(a) lesser

(b) greater

(c) equal to

(d) none of these

Answer. (a)

8. Photochemical decomposition of a substance is called

(a) thermal dissociation

(b) thermolysis

(c) photolysis

(d) none of the above

Answer. (c)

9. Out of the photons corresponding to light of wavelengths 200 nm, 400nm, 600nm and 800 nm, the one with highest energy will be

(a) photon of light with 200 nm wavelength

(b) photon of light with 400 nm wavelength

(c) photon of light with 600 nm wavelength

(d) photon of light with 800 nm wavelength

Answer. (a)

10. The substances which initiate a photochemical reaction but itself does not undergo any chemical change is called

(a) catalysis

(b) fluorescent

(c) sensitizer

(d) none of these

Answer. (c)

11. Organic dyes like eosin, chlorophyll, ultrarine etc. show _______ in the visible or UV region

(a) fluorescence

(b) phosphorescence

(c) chemiluminescence

(d) none of these

Answer. (a)

12. In photochemical reactions, the absorption of light takes place in

(a) primary processes only

(b) secondary processes only

(c) either primary or secondary process

(d) both primary and secondary processes

Answer. (a)

13. _______ stops as soon as the incident radiation is cut off

(a) fluorescence

(b) phosphorescence

(d) chemiluminescence

(d) none of these

Answer. (a)

14. The emission of light as a result of chemical action is called _______

(a) phosphorescence

(b) fluorescence

(c) chemiluminescence

(d) none of these

Answer. (c)

15. The light emitted in a chemiluminescent reaction is also called

(a) cold light

(b) hot light

(c) bright light

(d) none of these

Answer. (a)

2.10 REFERENCES

1. Arun Bahl, B.S. Bahl and G.D. Tuli; Essentials of Physical Chemistry, 2014.
2. Jagdamba Singh and Jaya Singh; Photochemistry and Pericyclic Reactions, New Academic Science New Academic Science Limited (Third Edition), 2012.
3. D.O. Crown and R.L. Drisko, Elements of Organic Photochemistry, Plenum, New York, 1976. William M. Horspool, Aspects of Organic Photochemistry, Academic Press, New York, 1976. 3. Jan. Kopecky, Organic Photochemistry, VCH, New York, 1991

UNIT 3: PHOTOCHEMISTRY OF ORGANIC COMPOUNDS

CONTENTS:

3.1 INTRODUCTION

When an organic molecule absorbs radiation, it transitions from its ground state to an excited state, which is followed by changes in electrical distribution, shape, and electron spin uncoupling. Although electronically stimulated molecules have a limited lifetime, their high reactivity allows photochemical reactions to occur often. Alkenes' electrical conductivity can be explained in terms of and bonding Orbital's, with matching anit-bonding orbitals π* and σ* There are a few generally; there are two types of transitions:

- With a maximum absorption of around 180nm (10^4 Mol^{-1} dm^3 cm^{-1}), the π - π* transition (π - π* excited state) is the more intense.
- The π - σ* transition (π - σ*excited state) is weak.

Gas phase spectra, on either side, show signs of Rydberg absorption, which leads to a Rydberg state (π, 3s).

Simple alkenes absorb UV light with a maximum wavelength of around 180nm, whereas conjugated systems like dienes and polyenes, as well as aryl-substituted alkenes, absorb at a maximum wavelength of around >200nm, with a 35-nm rise for each succeeding double bond. As a result, direct irradiation with vacuum UV sources is required for simple alkenes. For strongly substituted alkenes with wavelengths greater than 200 nm, a medium-pressure mercury lamp with a quartz filter can be used.

The singlet and triplet state reactions are more distinguishable in alkenes photochemistry. Because the singlet (π, π*) and equivalent triplet states for alkenes have a substantial energy difference, intersystem crossing is difficult.

In order to populate the triplet state, a triplet sensitizer is required. As a result of the substantial energy difference between the singlet and triplet states, as well as differing spin properties, many alkenes have different reactions in the singlet (direct irradiation) and triplet (sensitizer irradiation) states. Geometrical isomerization around the carbon-carbon double bond, concerted reactions like electrocyclic, shifts (typically hydrogen) along the -system, di-methane reactions, and photoaddition reactions are the reactions of alkenes and dienes. Organic chemists' go-to tool is resonance structures.

To qualitatively describe the electron distribution of molecules Spin-coupled electron pairs localized in bonds or lone pairs are shown by lines in resonance structures. To represent the electron distribution when electrons are delocalized in a molecule, many resonance structures are required. The resonance hybrid for a molecule is a manifold of resonance structures. In general, different weights of resonance structures emerge in the resonance hybrid. Those with big weights are the typical qualitative notation for electron distribution in molecules and their reactivity in organic chemistry. As a result, understanding the resonance structures that enter the resonance hybrid with big weights is critical. Those weights were determined extensively using valence-bond theory in the early days of quantum chemistry. Cooper's spin-coupled valence-bond approach, which creates compact valence-bond functions, is an appealing recent variation. Shaik et al. support an effective modern curve-crossing model for chemical reactivity.

Large-weight resonance structures are written by organic chemists using qualitative rules and a wealth of acquired chemical knowledge; this works well for mole cules in the electronic ground state and associated thermal reactions. Photochemical processes, on the other hand, begin with electrically excited states, making large-weight resonance structures photochemically relevant far more difficult to envision. Nonetheless, resonance structures based on valence bond theory are a useful tool for interpreting photochemical reactivity qualitatively. For key two-electron situations, Michl and Bonancic-Koutecky fully define the transformation between molecular orbital (MO) and valence-bond wave functions, and both MO and valence-bond schemes are used to discuss the electronic properties of two-electron s and p bonds.

In the past, this type of transformation was commonly used to interpret calculated MO wave functions in the context of valence-bond theory. Hiberty et al. were the first to come up with and implement a general technique for expanding a delocalized MO wave function into the set of valence-bond functions. Karafiloglou et al. devised a poly-electron population analysis in recent years to interpret a delocalized MO wave function in terms of strictly local poly-electron distributions. The Moffitts theorem, which allows the expansion of a delocalized MO Slater determinant into AO (atomic orbital) Slater determinants with atomic orbitals localized at the atoms of the molecule, is at the heart of this approach. Many Karafiloglous technique applications demonstrate that sophisticated delocalized MO.

3.2 OBJECTIVES

This unit you will be able to:-

- This unit covers geometrical isomerism, electrocyclic reactions, and the rearrangement of 1,4- and 1,5-dienes, as well as many other photochemical reactions of alkenes and dienes.

- Photochemical reactions could be beneficial in the production of a certain product from a synthetic perspective. These reactions play an important role in biological processes as well.
- Photochemistry of alkenes

3.3 PHOTOCHEMISTRY OF ALKENES

Simple alkenes have an intense broad band of absorption from 140 nm to 190 nm (for ethylene), with an absorption threshold of 200 nm (for ethylene) to 240 nm (for 2, 3-dimethyl-2-butene). A π to π* transition is responsible for the diffuse bands in the ethylene spectrum. The first singlet Rydberg transition for ethylene occurs at 174 nm. The 2p3s excitation is responsible for this Rydberg transition.Because different electronic states have distinct electronic configurations, alkene excited states are complicated. Although the nature of the majority of alkene electronic states is unknown, some are clearly understood.

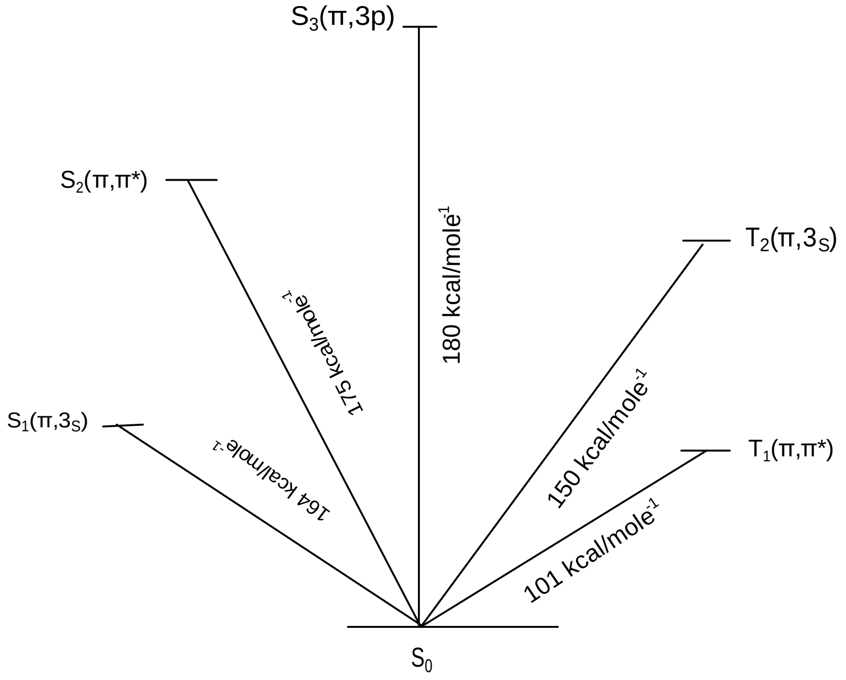


Fig. 3.1 different electronic state of ethylene

There are two low-lying excited singlet states in alkenes: The Rydberg state 1[2p, 3s] and the valence state 1[π, π*]. According to calculations, there is an additional state, namely the (2p, 3p) Rydberg state. T2 is basically a pure Rydberg 3[2p, 3s] state (Fig. 3.1), while the lowest triplet state is practically pure 3(π, π*).

Alkenes have a substantial singlet-triplet splitting (S-T splitting) (ethylene 70 kcal/mole^{-1}). As a result, ISC is inefficient and slow. As a result, singlet excited state reactions are induced by direct irradiation of alkenes, while triplet state reactions require sensitisation. According to the Franck-Condon principle, when a planar alkene like ethylene is excited, it first forms a planar excited state molecule. The first created planar excited state, species, wherever as a singlet or triplet, relaxes by rotating the terminal group-methylene in the case of ethylene- through 90 degrees around the central bond to yield the lowest energy conformation feasible. As a result, the molecule can rotate away from the planar structure created by the Frank-Condon excitation to achieve an energy minimum. This energy minimum is reached by rotating the central bond such that the methylene groups are at right angles to one another, easing the unfavourable interactions between the carbon atoms' singly-filled orbitals.

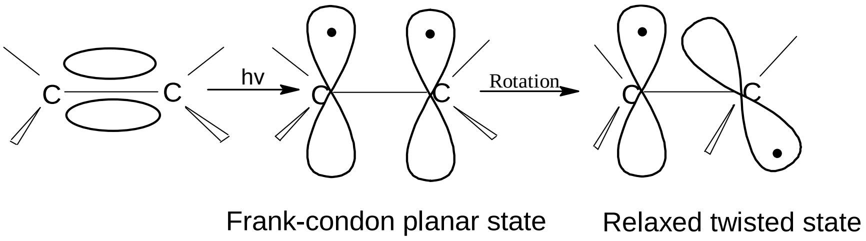


Fig. 3.2 Formation of relaxed twisted state

Spectroscopic evidence has been acquired which suggests that there is extra distortion of the methylene groups from planarity when the carbon atoms trend towards tetrahedral (sp3) hybridisation. In this energy minimum there is essentially no π (pi) bond, the electronic interaction is at a minimum and the terminal carbon atoms are orthogonal.This orthogonal model may anticipate several forms of reactions from the excited state olefin. Cis-trans isomerisation via rotation around the central bond, hydrogen abstraction via the half-filled orbitals on carbon, addition to other alkenes, and rearrangement are some of them.

Cis-trans isomerisation is the most straightforward photochemical reaction for alkenes.

3.4 Cis-Trans ISOMERISATION IN ALKENES

The most common photochemical reaction of alkenes in solution is cis-trans isomerisation, which can be triggered by both direct and sensitized irradiation. π, π* excited states are commonly connected with this isomerisation process.

3.4.1 Cis-Trans isomerisation of alkenes by direct irradiation

Because of the large energy absorptions, direct irradiation of the simplest alkenes (whose λ_{max} is below 200 nm) is difficult to achieve. With more substituted alkenes, however, UV absorptions are pushed above 200 nm, allowing for easier direct excitation. The stilbenes are the most common substrate for isomerization. When cis- or trans- stilbenes are irradiated at

313 nm, 93% of the cis- and 7% of the trans- stilbenes are formed. The ratio of products does not change no matter how long the irradiation is prolonged within reason, and this is referred to as a photostationary state. The excitation co-efficient of the two isomers at the stimulating wavelength determines the composition of the photostationary state. For most alkenes (ε_{max}) trans is greater than (ε_{max}) cis for most alkenes. As a result, more molecules of the trans isomer will achieve the excited singlet state in an equilibrium mixture than the cis isomer, followed by quick relaxation to S_0. When the rate of cis-trans and trans cis-isomerisation equalises at photostationary state, there is no change in the composition of the reaction mixture after further irradiation.

As previously mentioned, the energy of a $\pi \rightarrow \pi^*$ excited species is a function of the angle twist around the carbon-carbon (sigma) bond, and trans-to-cis-isomerisation is thought to be effected by distortion of the trans- excited state initially produced, to an excited state common to both cis- and trans isomers. A phantom state is the name given to this aroused state.In terms of the sample model, the cis-trans isomerisation is triggered by the excitation of an electron to a planar excited state, which then relaxes to the twisted state. Figure 3.3 shows a simplified representation. Twisting the planar trans singlet to the twisted singlet state requires a low activation energy of 2 kcal/mole. This twisted form can decompose into either cis or trans stilbene. However, as previously stated, the trans form absorbs more light at the exciting wavelength (ε_{max} trans = 16300) than the cis form (max cis = 2880), and as a result, the trans isomer is almost fully transformed to the cis isomer.

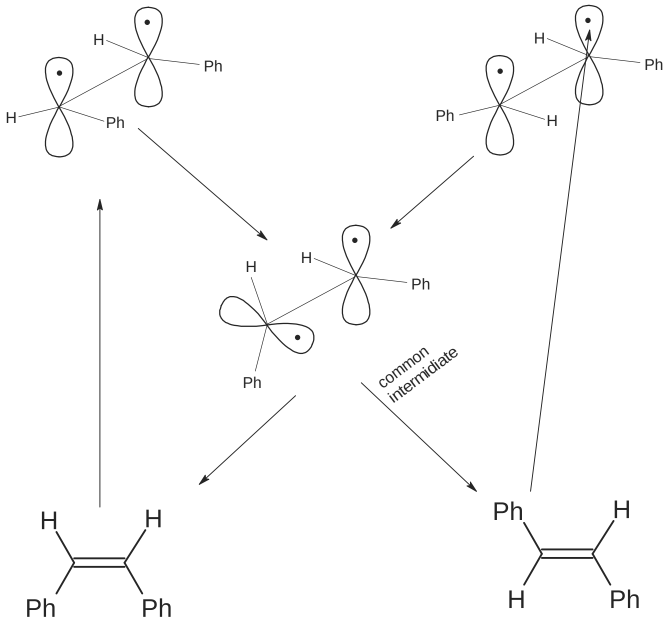
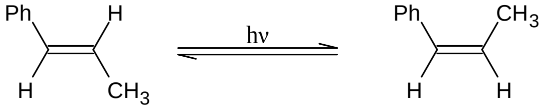
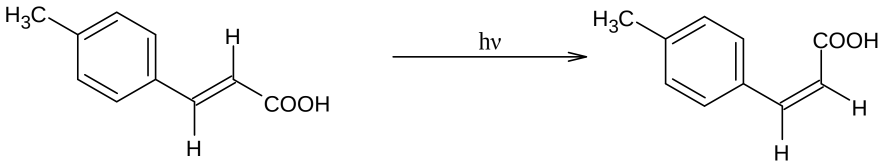
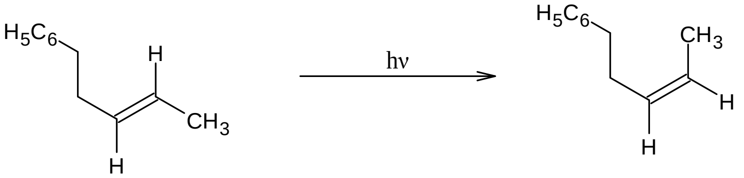


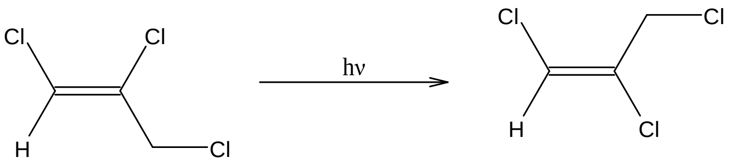
Fig. 3.3 Cis-Trans isomerisation of alkenes by direct irradiation

The synthetic utility value of trans-cis isomerisation comes from the ease with which the more stable alkene can be transformed to the less stable alkene. The following are some instances of the results of direct irradiation of alkenes:





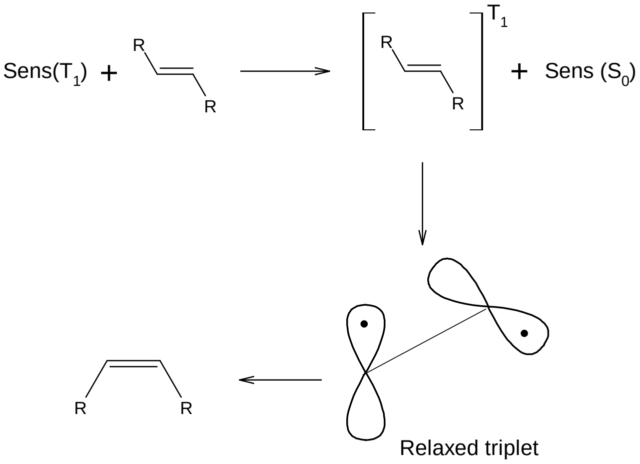




3.4.2 Sensitised cis-trans isomarisation

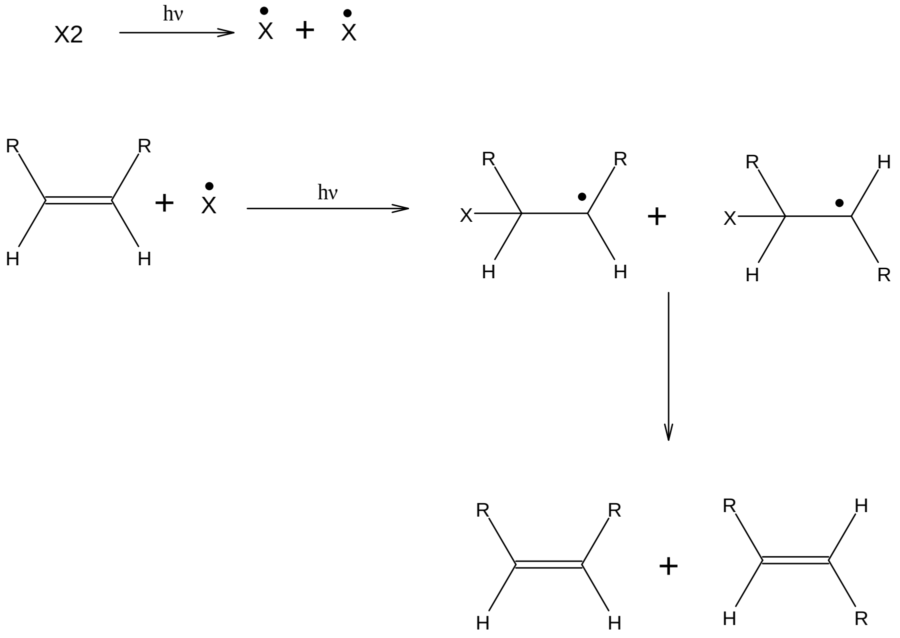
A triplet sensitiser, such as ketone, can be used to achieve sensitised cis-trans isomerisation of an alkene. A good example is the sensitized isomerisation of stilbene. The photostationary state of the sensitized isomerisation has a different composition depending on the energy of the sensitizer used. If the donor species meets the criteria for successful sensitization and has triplet energy greater than either of the geometrical isomers, triplet energy is transferred to both cis and trans isomers, resulting in isomerisation. When the cis and trans triplet excited species collapse to the ground state (S_0), they form a mixture of isomers. The proportion of cis-trans isomer in the photostationary state obtained from a sensitized reaction is lower than that obtained from direct irradiation because the sensitizer can excite both isomers. In contrast to the unsensitized isomerization, this is the case. High-energy sensitizers produce photostationary states with roughly the same isomer composition (55% cis), but direct photolysis in the instance of stilbene produces a higher proportion of cis isomer (93%). As the energy of sensitization Anomaly results have been minimized.

$$\text{Sens }(S_0) \xrightarrow{h\nu} \text{Sens }(S_1) \xrightarrow{\text{ISC}} \text{Sens}(T_1)$$



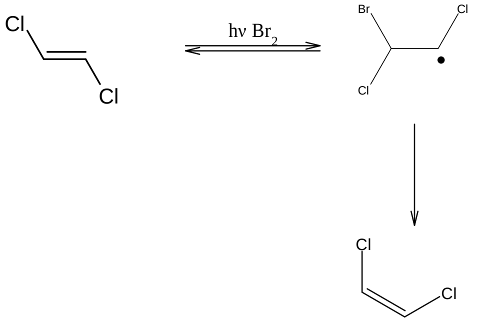
The triplet energy sensitiser has a big influence on the composition of the photostationary state. The cis-trans ratio is tighter than one for sensitizers with triplet energies over 60 kcal/mole, while a range of sensitizers with triplet energies of 52 to 58 kcal/mole offered a substantially higher cis-trans ratio in the photostationary state. The fact that the energy required for excitation of the trans isomer is less than that required for excitation of the cis isomer leads in a larger cis-trans ratio in this location. The trans isomer is selectively excited by the sensitizer, which has triplet energies in the range of 52 to 58 kcal/mole. Because the rate of trans-cis conversion is increased, the photostationary state's composition is richer in the cis isomer. In the presence of halogens, photochemical cis-trans isomerisation can also occur. Under these conditions, it appears that a photochemical product of halogen atoms attaches to the alkene, resulting in a radical. When halogen is removed from this radical, the ratio of cis and trans isomers remains constant.

(i)



3.4.3 Catalyzed method

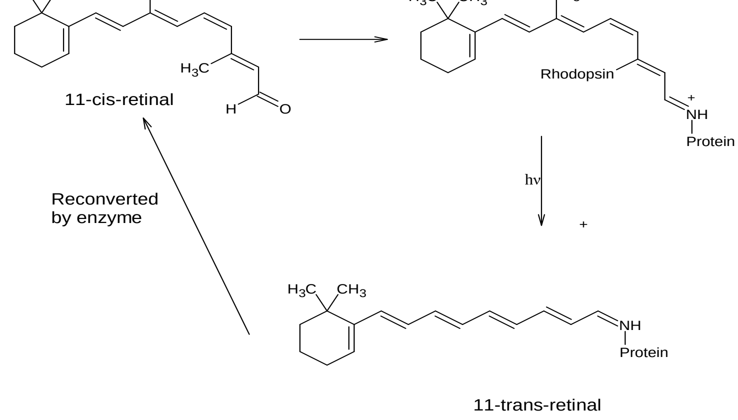
Photoiosmerization of alkenes are also achieved in the presence of catalysis, e.g., Bromine. Halogen atom absorbs the photon and gives radical, and then radical added to alkene forming the intermediate radical where bonds can rotate. So that the alkene excited state does not take part. In the presence of catalysts, such as bromine, photoiosmerization of alkenes is also possible. The photon is absorbed by the halogen atom, which produces a radical, which then reacts with the alkene to form an intermediate radical in which bonds can rotate. As a result, the alkene excited state is not involved.



3.4.4 Biological importance

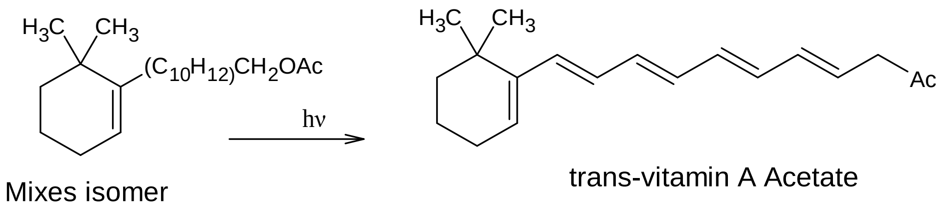
Photochemcial geometrical isomerization is impotent in biological system, for example,

1. A multitude of photoreceptor cells make up the retina of the eye.11-cis rhodopsin is a visual pigment that is derived from 11-cis rhodopsin. The reaction of an aldehyde group with an amino substituent in a protein produces retinal. The trans-rhodopsin is formed when the cis-rhodopsin absorbs photons in the visible area and the double bond is isomerized. This change in bound retinal geometry causes changes in protein structure, which causes a nerve impulse to be sent to the brain, resulting in vision. An enzyme in the eye converts the trans form of retinal to the cis form, and the visual cycle begins a new.



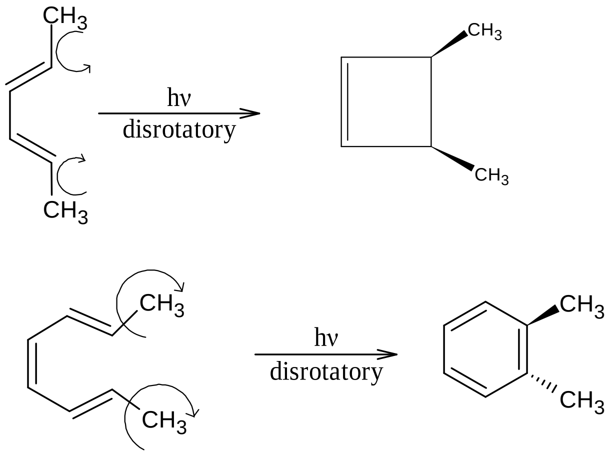
2. The chlorophyll-sensitized isomerization vitamin A acetate, which is commercially utilised to acquire the requisite all trans isomer from the synthesis's mixture of isomers. Unlike the triplet sensitised process, photoinduced electron transfer and rotation of the Carbon-Carbon bond happens in the most stable isomer.

3.

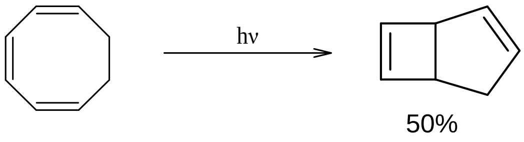


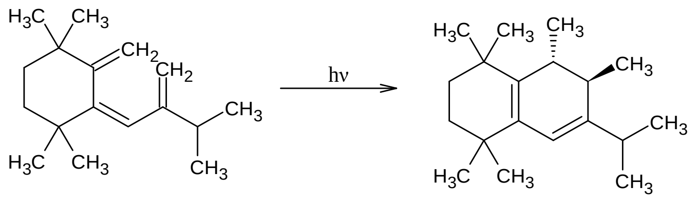
3.5 CYCLISATION REACTIONS

In a cyclic transition state, these reactions involve a change in the position of the bond and bond locations within a conjugated system. The 4n electron systems in the excited state react in a disrotatory mode, according to the Woodward– Hoffmann orbital symmetry principles, in which rotations along the axes of double bonds occur in the same direction (clockwise or anticlockwise). Reactions with 4n+2 electrons, on the other hand, follow a conrotatory route, in which rotations along these axes occur in opposite directions (one clockwise, the other anticlockwise).

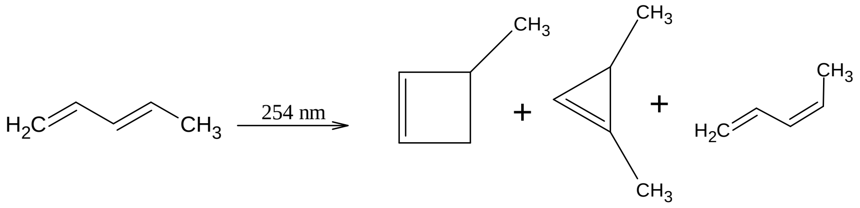


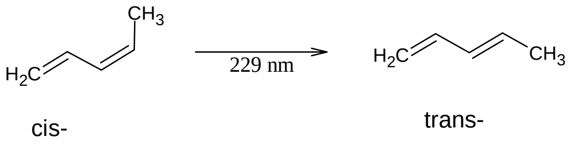
Example:



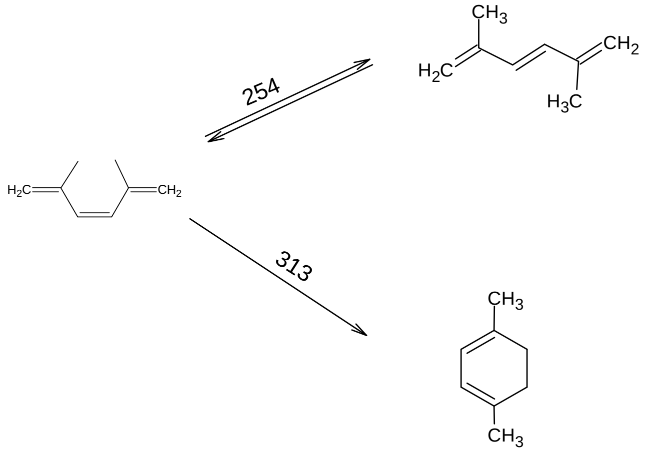


Conjugated dienes undergo electrocyclic reactions in the vertical singlet state. In most cases, the triplet state is not involved in this process. Two major aspects influence electro cyclization: I simultaneous geometrical isomerization along the double bond reduces reaction efficiency, and (ii) cis-diene conformation must be obtained before cyclization can occur. Direct irradiation of dienes can lead to the creation of wavelength-dependent photoproducts, which are connected to the absorption properties of the diene conformers. For example, when trans-penta-1,3-diene is irradiated at 254 nm, it produces a cyclic product with two additional products at low quantum yield. When irradiated at 229 nm, however, where the trans-conformation absorbs the greatest, primarily trans–cis isomerization is observed.

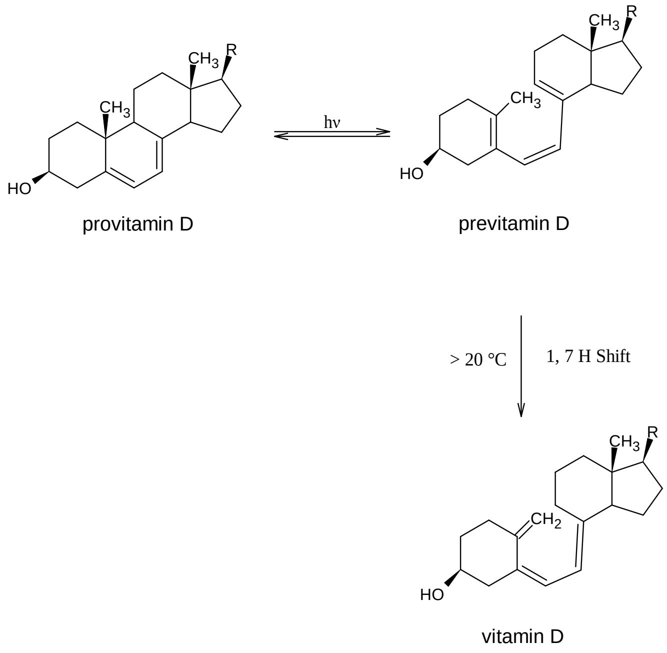




At 254 nm, the conjugated triene 2,5-dimethylhexa-1,3,5-trine exhibits effective cis-trans isomerization, but at 313 nm, it cyclizes to a cyclohexadiene.



The electrocyclic process is a crucial step in the production of vitamin-D. Bone development, immune system responses, cell defenses, and antitumor activity are all aided by this compound. Vitamin-D is found in two forms: ergocalciferol (ergocalciferol) and cholecalciferol (cholecalciferol), as well as its metabolites. Some foods contain both vitamin D_2 and vitamin D3. Vitamin D3 can also be made in keratinocytes from 7-dehydrocholesterol (provitamin D), which undergoes a photochemical six electron conrotatory electrocyclic ring opening at 280 nm to previtamin D3, which then spontaneously isomerizes to vitamin D in a thermal antarafacial hydride [1,7]- sigmatropic shift.



3.6 SOME RELATED QUESTIONS

Question 1

A. Multiple Choice

1. The photochemical reactions of alkenes are initiated by-

a) n-Л* transition

b) b) Л$^{-}$ Л* transition

C) σ- σ* transition

d) n- σ* transition

2. The irradiation of either cis- or trans- stilbene occurs at-

a) 313 nm

b) b) 350 nm

c) 390 nm

d) d)300 nm

3. Sensitised cis-trans isomerisation of an alkene can be brought about by the use of-

a) Triplet sensitizer

b) b) Singlet sensitizer

c) Both (a) & (b)

d) None above

4. Direct irradiation for the simplest alkenes whose λmax is below

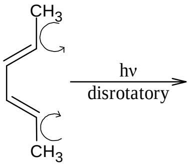
a) 150 nm.

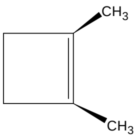
b) b) 170 nm.

c) 200 nm.

d) None above.

5. Product of reaction-



(a)


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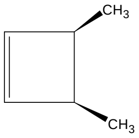

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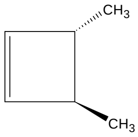
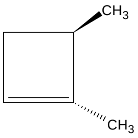
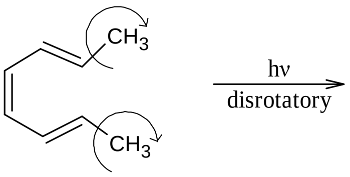
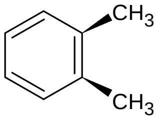


(d)


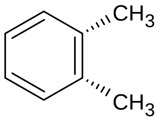
6. Product of following reaction-



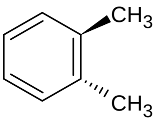
(a)



(b)

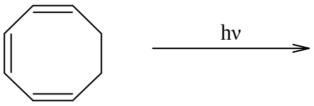


(c)

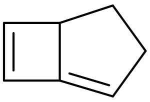


(d) None

7. Product of the given reaction will be-



(a)



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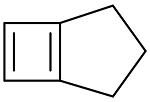

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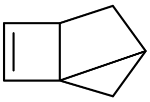
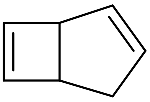
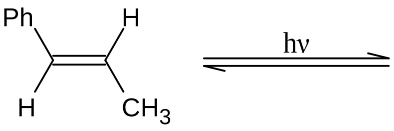
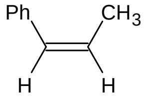


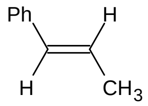
(d)



8. Product will be-



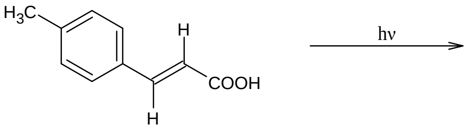
(a) 

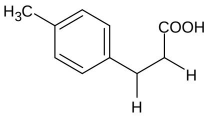
(b) 

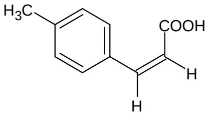
(c) Both

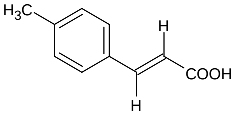
(d) None

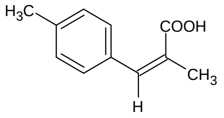
9. Product will be-



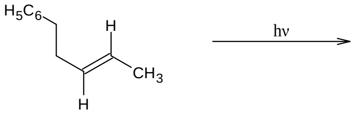
(a) 

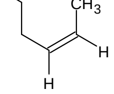
(b) 

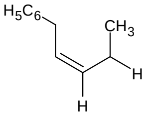
(c) 

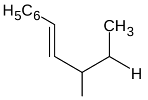
(d) 

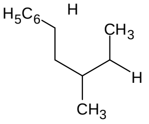
10. Product will be-



(a) 

(b) 

(c) 

(d) 

B. Fill in the blanks:

a. The most common substrate for isomerisation is the…………

b. The relaxed, non-vertical excited state of the conjugated system may have an angle of twist less than …………..

c. Electronic absorption spectra of simple alkenes consist of an intense broad band from ……… nm to ………. nm.

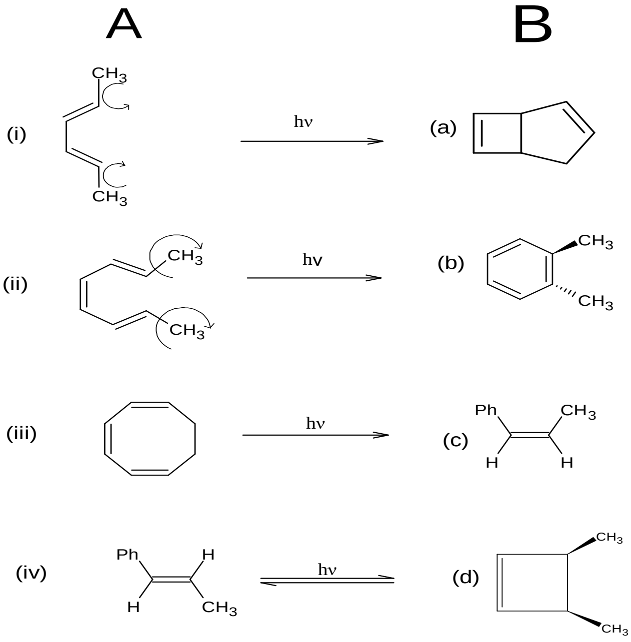
C. True / False:

a. According to the Franck-Condon principle excitation of a planar alkene like ethylene results initially in the formation of planar excited state molecule. (True / False)

b. The composition of photostationary state depends very much on the singlet energy sensitizer. (True / False)

c. The absorption at 174 nm for ethylene is the first singlet Rydberg transition. **(**True / False)

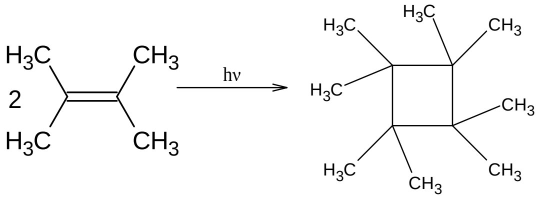
D. Match the following:



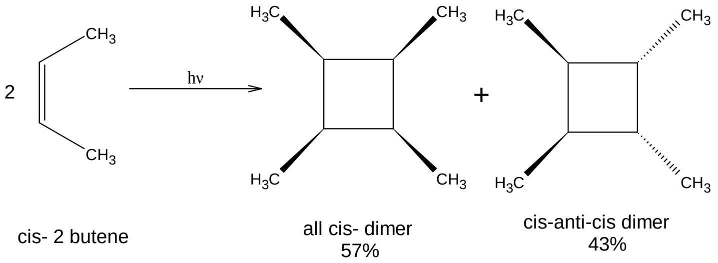
3.7 DIMERISATION OF ALKENE

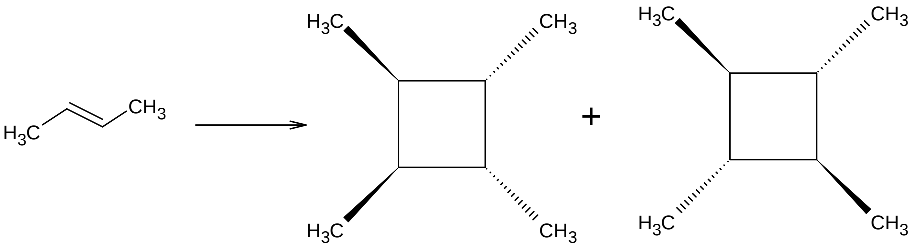
Photocycloaddition reactions are reactions that compete with cis-trans isomerisation at higher concentrations of the alkene(s). To make a cyclobutane derivative, an alkene in its S_1 or T_1 state reacts with either the same (photodimerisation) or a different (photocycloaddition) alkene in the ground state.

Increased alkyl substitution of ethene causes a bathochromic shift of the absorption band, so that direct irradiation (abs = 224 nm) of neat 2, 3-dimethyl-2-butene gives the corresponding dimers, despite the fact that dimerisation of simple alkenes (whose max is equal or less than 200 nm) is technically difficult.



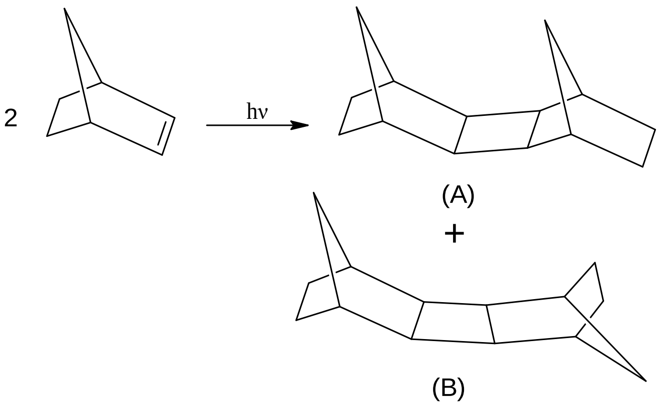
Irradiation of cis-2-butene gives all cis dimers and the cis-anti-cis dimer, whereas irradiation of trans-2-butene yields the cis-anti-cis dimer and the trans-anti-trans dimer.



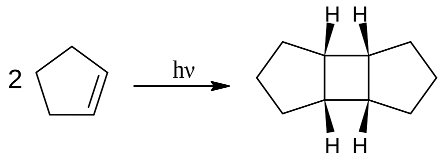


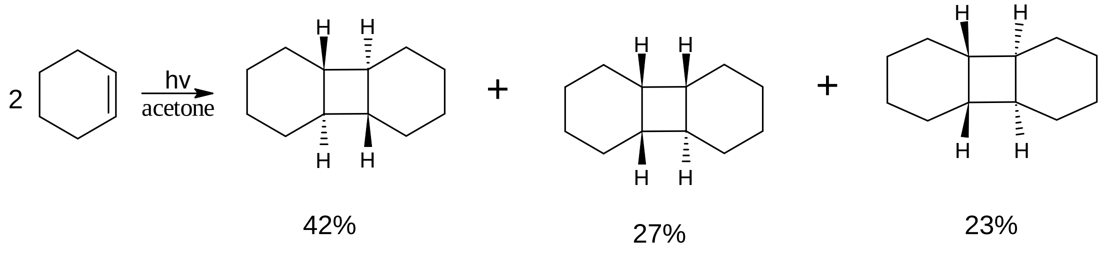
trans-2-butene **cis-anti-cis dimer 39%** **trans-anti-trans dimer60%**

Cyclohexene dimerises as well, generating a variety of dimeric products, whereas norbornene dimerises into two dimers (A) and (B) with a 1: > 10 ratio.

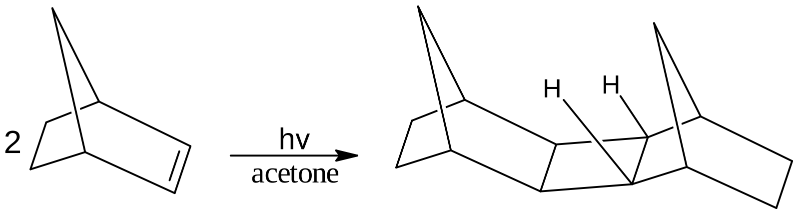


Because cycloalkenes cannot undergo cis-trans isomerisation, photosensitised dimerisation (triplet state dimerisation) is a common occurrence; especially with tiny ring alkenes.The development of a cis-trans-cis ring configuration in the dimer appears to be favored by dimerization. There have been reports of cyclopropenes, cyclobutenes, cyclopentenes, and cyclohexenes dimerizing.Aliphatic ketones are the most sensitive to the dimerization of alkenes and cycloalkenes. Aromatic ketones are used to make oxitane.

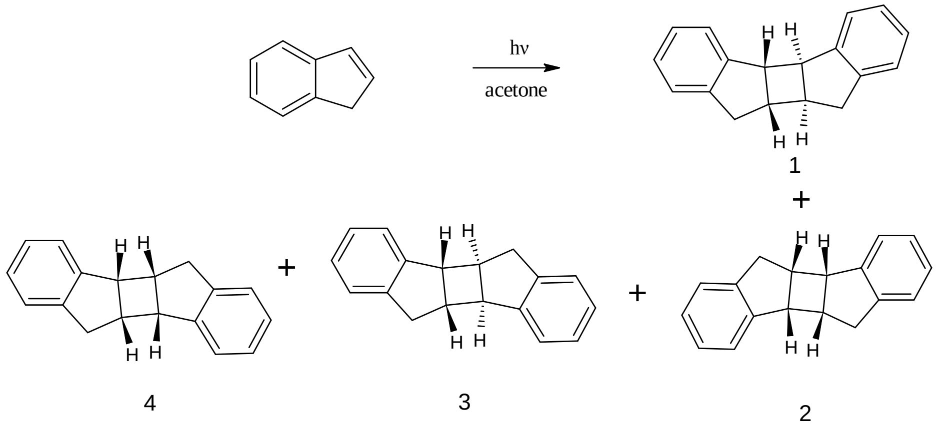




On sensitisation, norbornene can also dimerise, which is preferable for the creation of the exo-trans-endo dimer.

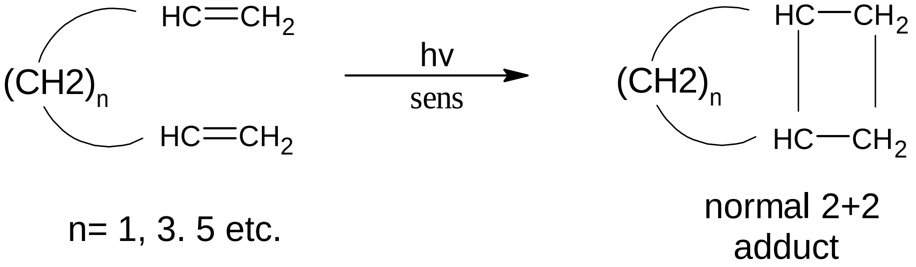


Photodimerisation of indene produces four dimers with different regio and stereochemistry. The dimer ratio is determined by the irradiation settings. As a stepwise bond formation process, triplet sensitized dimerisation develops the thermodynamically more stable exo products from the more stable 1, 4-biradical intermediate (head-to- head).

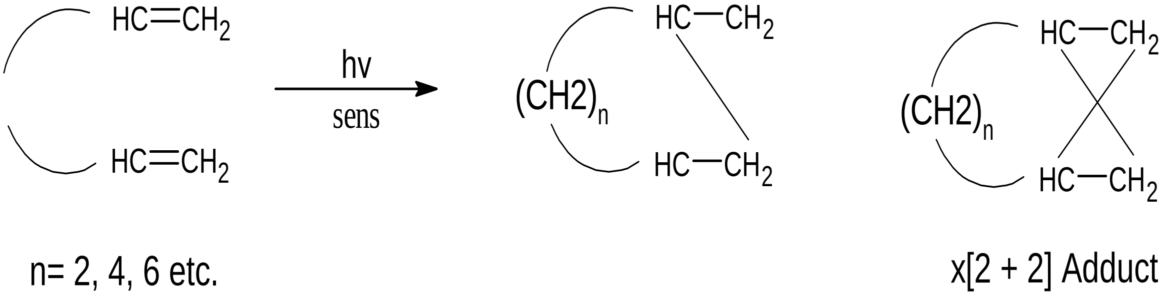


3.7.1 Intramolecular dimarisation

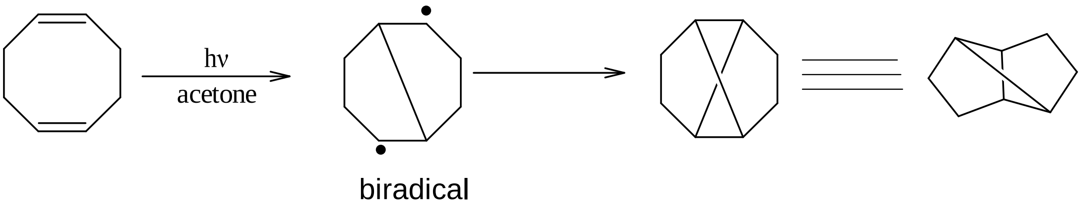
Nonconjugated dienes with isolated double bonds have a photochemistry similar to simple alkenes. Intramolecular [2 + 2] cycloaddition events occur in such alkenes, resulting in bicyclic compounds. The quantity of —CH_2— groups between the two double bonds affect the results of sensitized intermolecular cycloadditions. If the number of intervening groups exceeds a certain threshold When the primary product is odd, such as 1, 4-pentadiene or 1, 6-pentadiene, the major product is produced via a regular [2 + 2]cycloaddition.



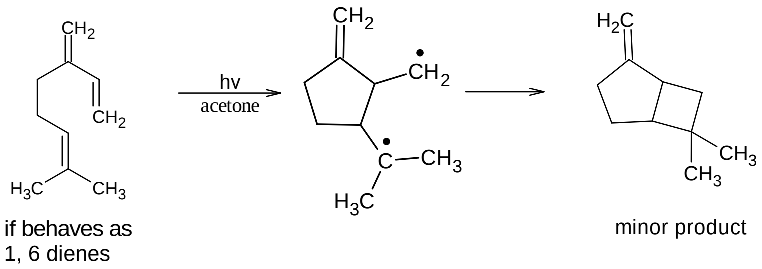
If n is even, such as 1, 5-hexadiene, the primary product is generated by a "cross," i.e., an x [2 + 2] cycloaddition that results in two crossed (sigma) bonds.

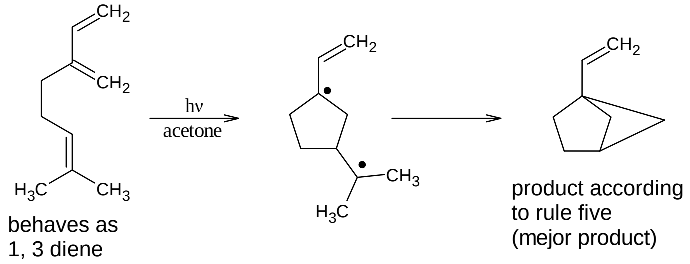


This property is much more obvious in cyclic dienes, such as n = m = 2 (1, 5-cyclooctadiene), where the lone product is the x [2 + 2] cycloadduct.

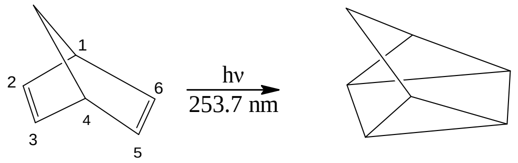


The photoreaction of 1, 5-hexadiene from the T_1 state follows the rule of five, which states that if triplet cyclisation can result in rings of various diameters, the one generated by 1, 5 additions is kinetically favoured. The most stable biradical is created if there are numerous choices for 1, 5 additions leading to different biradicals.

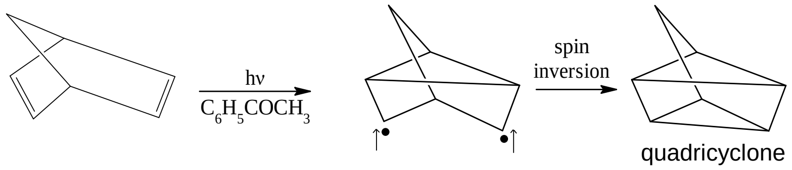




Intermolecular [2+2] cycloadditions can give rise to cage structures, which are theoretically interesting molecules in terms of strain and bond angles. A classic example of such a reaction is norbornadiene (A). In ethanol, the compound's UV spectra show absorptions at 205 nm, 214 nm, and 220 nm, with a shoulder at 230 nm. A non-conjugated diene should not have such a spectrum. The Molecular Model also shows that bonding between C-2 and C-6, as well as C-3 and C-5, is possible without too much strain. Compound (A) undergoes [2+2] cycloaddition by direct irradiation and in the presence of sensitizer for these reasons.



In the presence of sensitizer product formation takes place by triplet state.



3.8 PHOTOCHEMISTRY OF CONJUGATED DIENES

Conjugated dienes can give the following type of photochemical reactions:

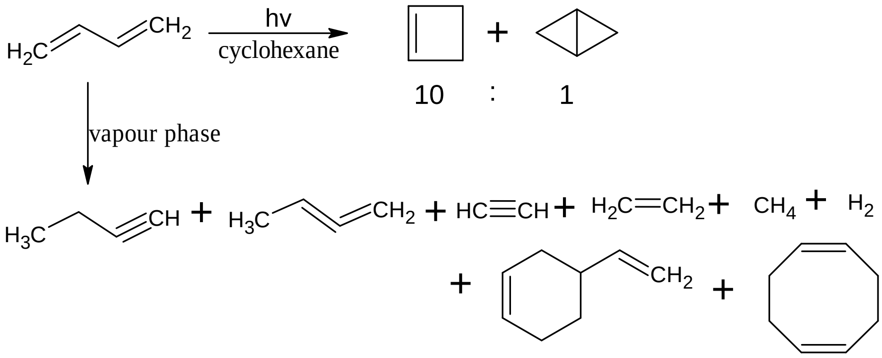
I. Cis-trans isomerisation.

II. Sigmatropic shift.

III. Disrotatory electrocyclic ring closure.

IV. Intermolecular x [2 + 2] cycloaddition.

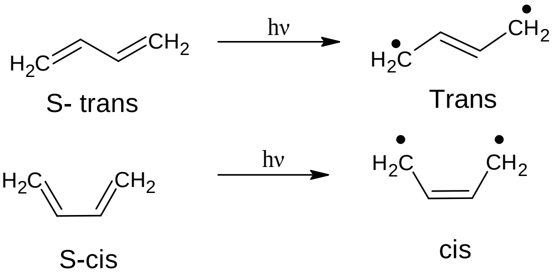
The excited state population and the phase in which the reaction is carried out are both important factors in the above photochemical reactions of conjugated dienes. Intramolecular processes (e.g., disrotatory electrocyclic ring closure and sigmatropic rearrangement) are more common in the singlet excited state, whereas dimerization and addition reactions are more common in the triplet excited state. When a reaction occurs in the gas phase at low pressure, it often results in more fragmentation than when it occurs in solution. Butadiene photolysis in the solution phase produces cyclobutene and bicyclobutane, whereas photolysis in the gas phase produces 1-butyne, methylallene, acetylene, ethylene, methane, hydrogen, and polymeric polymers.



3.8.1 Photochemistry of conjugated dienes in solutions

3.8.1.1 Intramolecular [2 + 2] cycloaddition reaction

In solution, 1, 3-butadiene exists as a quickly equilibrating combination of S-transoid (95%) and S-cisoid (5%) conformers. When butadiene is irradiated, an electron is promoted from HOMO to LUMO ($\psi 2 \rightarrow \psi 3^*$), resulting in stronger bonding between C-2 and C-3 at the expense of C-1 and C-2 and C-3 and C-4. Because of its double bond composition, the lower excited states of S-trans and S-cis butadiene should have even higher energy barriers to rotation around the C2—C3 link. Butadienes' conformational nature is thus preserved in stimulated states.



Although the exact energies of the S1 states are unknown, cisoid S_1 is thought to be lower than transoid S_1. Between S_1 and T_1, there is a significant energy difference. Also, there is no inter-system crossing in this scenario. The energy difference between S_1 and T_1 is responsible for the lack of intersystem crossing. Direct irradiation of 1, 3-butadiene in solution produces only the S_1 state of chemistry.

The energy of the excited states of butadienes are shown in the Fig. 3.4

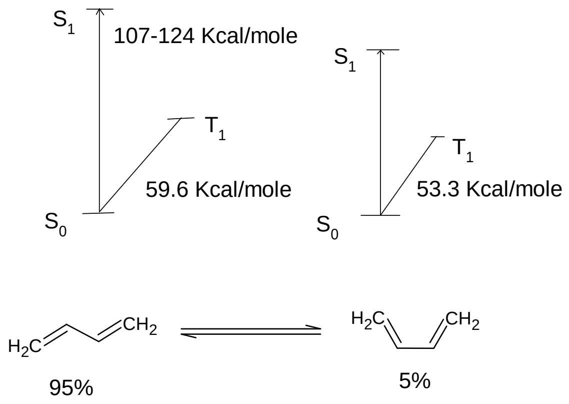
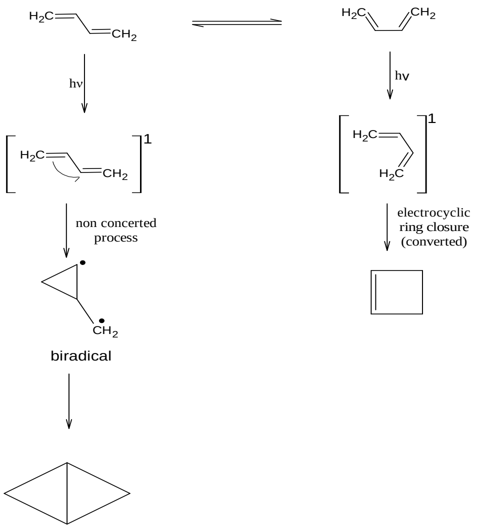
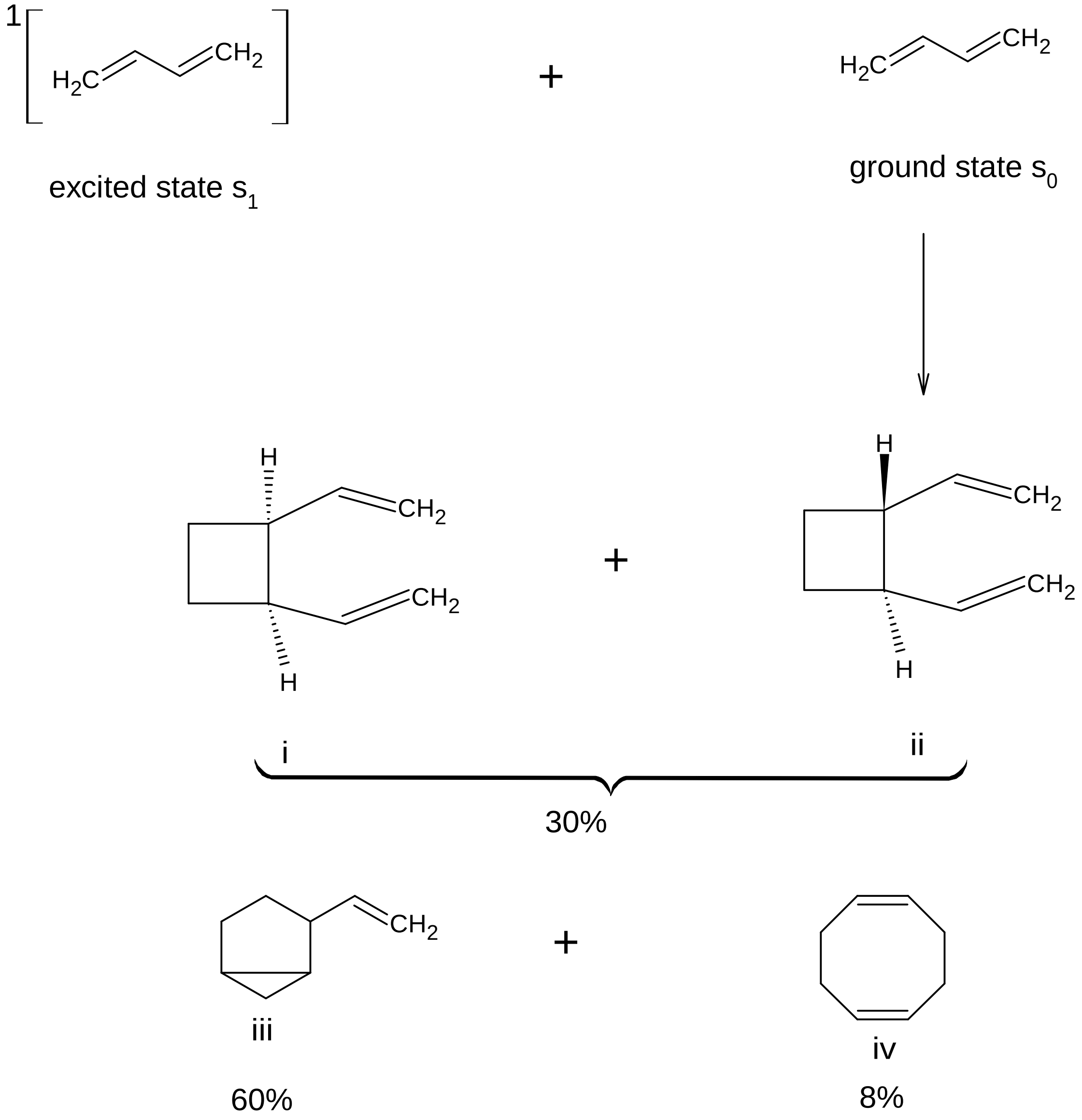


Fig. 3.4 Intramolecular [2 + 2] cycloaddition reaction

When butadiene is irradiated in cyclohexane, it forms cyclobutene from an electrocyclic reaction of the S-cis isomer and bicyclo [1, 1, 0]-butane from an intramolecular x [2+2] cycloaddition of the S-trans isomer in a 6:1 ratio.

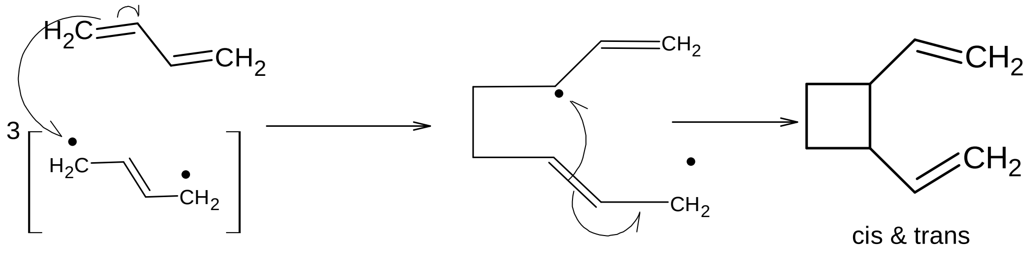


Some dimer formation can be noticed when a concentrated solution of 1, 3-butadiene is irradiated (maximum yield 10 percent). Because it involves the bimolecular reaction of an excited butadiene with a ground state butadiene, we predict dimer production to be concentration dependent. Ring closure reactions, on the other hand, are unimolecular (i.e., the creation of cyclobutene and bicyclobutane). As a result, dimerization can only occur at high concentrations of 1, 3-butadiene. There are four distinct dimers as a result of dimerization:



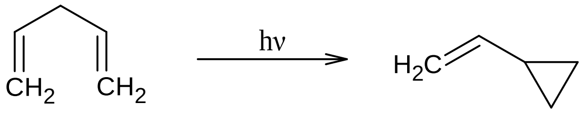
The relative energies of the sensitizer are the source of this significant variation in product composition. Acetophenone is sufficiently energic, with ET = 74 kcal/mole, to transfer energy to either s-cis or s-trans butadiene. Because the s-tarns form dominates by a wide margin and energy transfer happens in nearly every collision, the dimer composition from the acetophenone sensitised experiment must largely represent the s-trans-T1 process. Benzil, on the other hand, is energetic enough to transfer energy to s-cis but not s-trans butadiene (ET = 54 kcal/mole).As a result, the dimer composition from the benzil-sensitized experiment must largely represent the s-cis-T1 process. There would be no dimer formation if a sensitiser with a triplet energy of less than 54 kcal/mole was utilized.

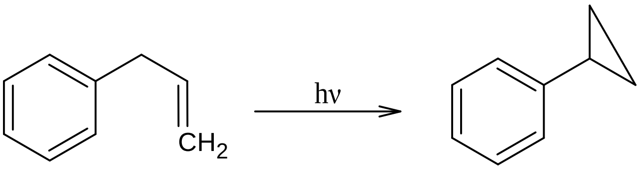
When acetophenone is used as a sensitiser, the reactive species is s-trans-T1, which reacts with the s-trans ground state to produce dimer.



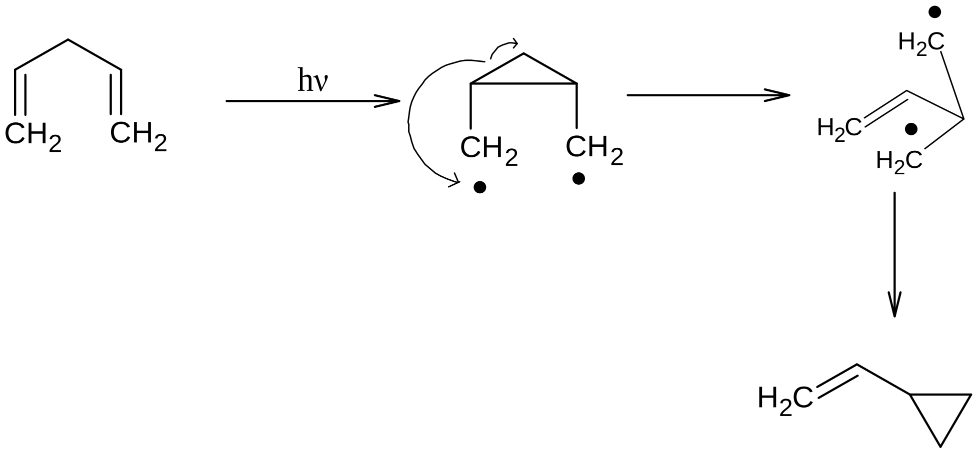
3.9 REARRANGEMENT OF 1,4- AND 1,5-DIENES

Irradiation of 1,4-diene or 3-phenyl alkenes frequently leads to vinyl cyclo propane or phenyl cyclo propanes via a 1,2-shift of the vinyl or phenyl group followed by ring closure, resulting in a photoproduct that is rarely obtained through other routes. The di-methane rearrangement, commonly known as the ***Zimmerman reaction***, is the name given to these reactions.

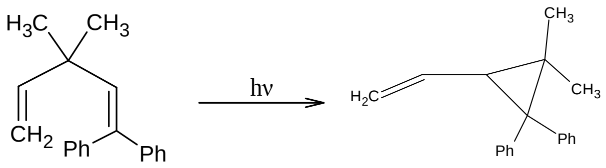


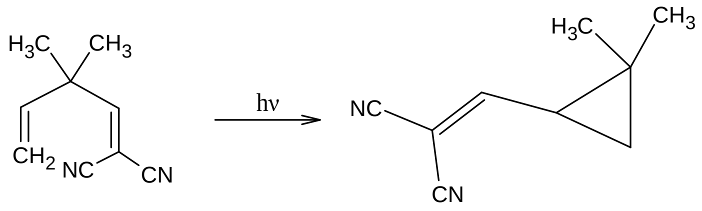


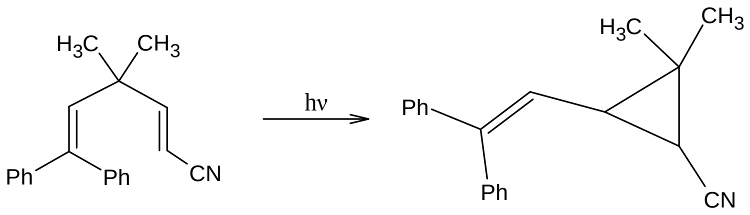
The 1,3- and 1,4-biradical intermediates, as well as the second -bond, may be linked in the suggested stepwise biradical mechanism. The procedure begins with the production of a bond between atoms 2 and 4 of the 1,4-diene unit, followed by the cleavage of the 2,3-bond and the formation of the 3,5-bond.



Due to the poor intersystem crossing efficiency of alkenes, the di-methane reaction usually proceeds through the excited singlet state acquired by direct irradiation, whereas the triplet pathway is only accessible with triplet sensitizers. For example, di-methane rearrangements frequently exhibit high diastereoselectivity and/or regioselectivity.







3.10 SUMMARY

The summary of the present unit is:-

- Photochemical reaction of alkenes take place generally through signlet or triplet π - π* state. Photoisomerization reaction gives less thermally stable geometrical isomer. Photoisomerization in alkenes can be occured through direct radiation, photosensitizer and catalysis process.
- When an organic molecule absorbs radiation, it moves from its ground state to an excited state, causing changes in electrical distribution, structure, and electron spin uncoupling. Although electronically stimulated molecules have a short life span, their strong reactivity allows for frequent photochemical reactions.
- The electrical conductivity of alkenes can be explained using the concepts of and bonding. orbitals, with anit-bonding orbitals that match* and* There are a few options. There are two sorts of transitions in general: With a maximum absorption of around 180nm (10^4 Mol^{-1} dm^3 cm^{-1}), the - π,π* transition (π,π* excited state) is the more intense. The π - σ* transition (π - σ*excited state) is weak. On both sides of the spectrum, there are traces of Rydberg absorption, which leads to a Rydberg state (,3s).

- Simple alkenes absorb UV light at a wavelength of around 180nm, but conjugated systems like dienes and polyenes, as well as aryl-substituted alkenes, absorb at a wavelength of around >200nm, with a 35-nm rise for each subsequent double bond. As a result, for simple alkenes, direct irradiation with vacuum UV sources is required.
- A medium-pressure mercury lamp with a quartz filter can be utilised for strongly substituted alkenes with wavelengths larger than 200 nm.
- The singlet and triplet state reactions are more distinguishable in alkenes photochemistry. Because the singlet (π, π*) and equivalent triplet states for alkenes have a substantial energy difference, intersystem crossing is difficult.In order to populate the triplet state, a triplet sensitizer is required. As a result of the substantial energy difference between the singlet and triplet states, as well as differing spin properties, many alkenes have different reactions in the singlet (direct irradiation) and triplet (sensitizer irradiation) states.
- Geometrical isomerization around the carbon-carbon double bond, concerted reactions like electrocyclic, shifts (typically hydrogen) along the -system, di-methane reactions, and photoaddition reactions are the reactions of alkenes and dienes. The singlet and triplet state reactions are more distinguishable in alkenes photochemistry.
- Direct irradiation of the simplest Alkenes (whose max is below 200 nm) is difficult to achieve, but UV absorptions are pushed above 200 nm. The energy of a π → π* excited species is a function of the angle twist around the carbon-carbon (sigma) bond. Trans-to-cis-isomerisation is thought to be effected by distortion of the trans- excited state initially produced.
- The ratio of both geometrical isomers in the photostationary state depends upon the ratio of the quantum yields of both isomer and the molar absorption coefficients of the corresponding isomers Photochemcial geometrical isomerization is impotent in biological system like vision. Photocyclisation reactions occur through the concerted pericyclic reaction via a disrotatory or conrotatory mode. Electrocyclic process is a key reaction in the synthesis of vitamin D. The di-π-methane rearrangement occurs through biradical mechanism.

3.11 SOME RELATED QUESTIONS :(SAQS TYPE QUESTION)

Question-2

A Multiple Choice:

1 In dimerisation of alkenes the substitution of ethene causes a which kind of shift on the absorption band

a) Hypsochromic shift b) Bathovhromic shift

b) Hyperchromic shift d) Hypochromic shift

2 The dimerisation reaction is

a) Stereospecific b) Stereoselective

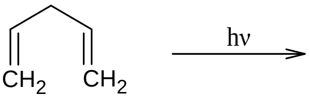
b) Regioselective d) None

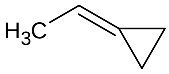
3 When batadiene is treated in the presence of sensitiser, the product formation takes place by

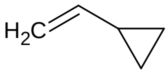
a) Triplet state. b) Singlet stste.

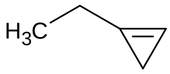
b) Both a & b d) None.

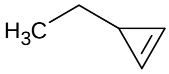
4 product of the reaction



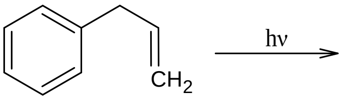
(a) 

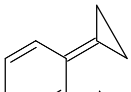
(b) 

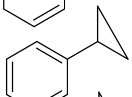
(c) 

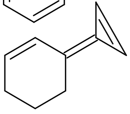
(d) 

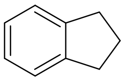
5 Product will be-



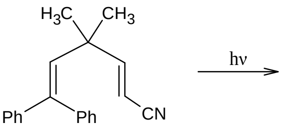
(a) 

(b) 

(c) 

(d) 

6. Product will be-



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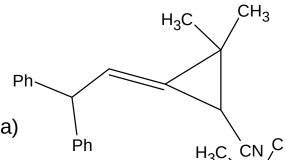

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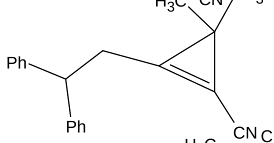

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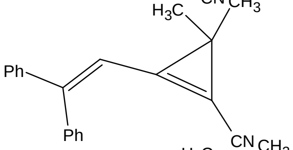

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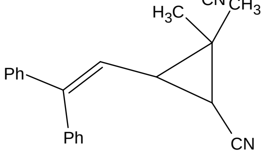


B Fill in the blanks.

(i) di-π-methane rearrangement, also known as the ………………reaction.

(ii) The di-π-methane rearrangement occurs through …………….. mechanism.

(iii) Electrocyclic process is a key reaction in the synthesis of vitamin ……………...

C True / false

a. Photocyclisation reactions occur through the concerted pericyclic reaction via a disrotatory or conrotatory mode. (True / false)

b. Photochemical reaction of alkenes take place generally through signlet or triplet π - π* state. (True / false)

c. Photoisomerization reaction gives more thermally stable geometrical isomer. (True / false)

d. Photoisomerization in alkenes can be occured through direct radiation, photosensitizer and catalysis process. (True / false)

Answers Key:

Question-1

A. 1b 2a 3c 4c 5b 6c 7d 8a 9b 10a

B. a. Stilbenes. b. 90 nm c. 140 – 190 nm.

C. a True b False c False

D. i d ii b iii a iv c

Question-2

A. 1 b 2 a 3 a 4 b 5 b 6 d

B I. zimmerman. Ii. biradical. Iii. Vitamin D

C. a True b true c False d True

3.12 GLOSSARY

Photocycloaddition: A light-initiated reactions in which the termini of two multiple bond systems become joined through σ bonds. The most common example of this type of reactions is the formation of a cyclobutane ring from two ethylene moieties.

Rydberg Transition: Any transition or absorption process in which electron is promoted to an orbital with a larger principal quantum number n than that of the initial orbital is known as Rydberg transition. In ethylene the 2 pπ-3 S transition is a Rydberg transition.

3.13 REFERENCE

1. Coyle, J. D.,(1986), Introduction To Organic Photochemistry, John Wiley & Sons Ltd,
2. Klan, P., Wirz,J., (2009) Photochemistry of organic compounds from concepts to practice, John Wiley & Sons Ltd,
3. Roberts, J. D., Caserio, M. C., (1964),Basic Principles of Organic Chemistry, Benjamin, New York, p. 233;
4. Brown,W. H., Foote,C. S.,(1998), Organic Chemistry, Saunders College Publishing, Fort Worth, p. 25.
5. Cooper, D. Gerrat, L., Raimondi, J. M.,(1987), Adv. Chem. Phys. 69, 319;
6. Shaik,S., Shurki, A.,(1999), Valence Bond Diagrams and Chemical Reactivity, Angew. Chem. Int. Ed. 38, 586-625
7. Hendrickson, J. B., Cram, D. J., Hammond, (1970), G. S., Organic Chemistry, McGraw Hill, New York, p. 156.

8. Michl,J., Bonacic-Koutecky,V., (1990),Electronic Aspects of Organic Photochemistry, Wiley, New York,
9. Hiberty, P. C., Leforestier,C. J.,(1978), Expansion of molecular orbital wave functions into valence bond wave functions. A simplified procedure, J. Am. Chem. Soc., 100, 2012
10. Hiberty, P. C.,(1990),Valence Bond Theory and Chemical Structure (Eds.: D. J. Klein, N. Trinjastic), Elsevier, Amsterdam p. 221.

3.14 SUGGESTED READING

1. P. de Mayo, ed, Rearrangements in Ground and Excited States, vol. 3, Academic Press, New York, 1980.
2. J.M. Coxon and B. Halton, Organic Photochemistry, Cambridge University Press, London, 1974.
3. W. Harspool and D. Armester, Organic Photochemistry, A Comprehensive Treatment, Eillis Horwood/Prentice Hall, 1972.
4. J. Kagan, Organic Photochemistry, Principles and Applications, Academic Press, 1993.
5. Gilbert and J. Baggott, Essentials of Molecular Photochemistry, CRC Press, Boca Raton, Florida, 1991.
6. D.O. Crown and R.L. Drisko, Elements of Organic Photochemistry, Plenum, New York, 1976.
7. J. Kopecky, Organic Photochemistry: A Visual Approach, VCH, Weinhim, Germany, 1992.

3.15 TERMINAL QUESTION

Q.1 Write the mechanism of Di-π-methane reaction?

Q.2 Why geometrical reaction gives cis isomer in large amount?

Q.3 What is role photoisomerization in Vision?

Q.4 Explain rearrangement of 1,5-dienes with mechanism?

Q.5 Give three example of 1,6-triene cyclisation reaction?

Q.6 Discuss photochemistry of 1, 3-butadiene.

UNIT 4: PHOTOCHEMISTRY OF CARBONYL COMPOUND

CONTENTS:

4.1 INTRODUCTION

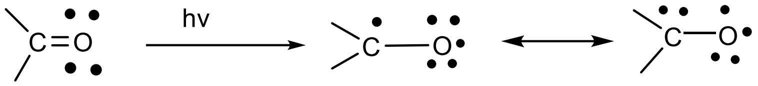
Carbonyl molecules, notably ketones, undergo a number of fascinating and adaptable reactions when exposed to light. Ketones often have four bands in their UV absorption spectra. The most important band for the photochemistry of carbonyl compounds is always 280 nm. The reaction begins with the n-π* transition. The promotion of an electron will result in a singlet or triplet state. The photochemical process initiated by the carbonyl group can occur in a singlet, triplet, or both states. Photochemically generated single electron-transfer (SET) events are unquestionably growing more important as our knowledge of them grows.. As a consequence, the area has attracted exponents to compile reviews such as those by Hasegawa who has reviewed the application of photochemically induced SET reactions to organic molecules, and Mattay and co-workers preparative and mechanistic standpoints.

Another area that attracts much attention is that of photochemical reactions within constrained media, and reviews of this directed at reactions within zeolites have been published Carbonyl compounds undergo various photochemical reactions in both gas and liquid phases. The electronic excited states of saturated ketones are n → π* states, whereas of conjugated ketones are π → π* states chemical processes involve both these excited states in singlet and triplet states. Saturated ketones have activation energies of roughly 80–85 and 75–80 kcal/mol for singlet and triplet states, respectively, whereas unsaturated ketones have activation energies of 45–75 kcal/mol. Most photoreactions in excited carbonyl compounds involve radical intermediates because both the carbon and oxygen atoms of the carbonyl group have radical properties.

The reduction of carbonyl compounds by hydrogen abstraction, fragmentation, including the Norrish types I and II cleavages, cycloaddition to alkenes (the Paterno- Büchi reaction), and rearrangement (the lumiketone and oxa-di-methane rearrangements) reactions are all important photoreactions of carbonyl compounds. All of these reactions are thoroughly explained, with several instances and methods provided.

We looked at type II cleavage and photoreduction in this chapter, two photochemical reactions that occur often in simple carbonyl compounds.

Type II cleavage appears to occur often in both excited singlet and triplet states, but photoreduction appears to occur exclusively in carbonyl triplet states. In each phase, discrete biradical intermediates were identified to be involved. Two other reactions seen in the photochemistry of carbonyls that will be described in this chapter are type I cleavage and oxetane formation.



4.2 OBJECTIVE

The objective of this unit, you will able to-

- Norrish type 1 process or α-Cleavage
- Norrish type II process or β.Cleavage
- Intramolecular hydrogen abstraction (γ-hydrogen abstraction)
- Intramolecular reaction in β,γ unsaturated Carbonyl Compound:
- Intramolecular reaction of α-β- Unsaturated carbonyl compound
- Intramolecular photoreaction of cyclo hexadienones
- Photoreduction of carbonyl compounds
- Photocycloaddition reaction (paterno-Buchi reaction)
- At the end of this unit Summary, Reference, Review questions/Comprehensive questions

Carbonyl compounds give four types of reactions, these are:-

1. Norrish type I process or α-cleavage.
2. Norrish type II process or β cleavage
3. Intramolecular and Intermolecular hydrogen abstraction by carbonyl Oxygen
4. Photocyclo addition reaction and oxetane formation

4.3 NORRISH TYPE-I OR α-CLEAVAGE

In the gas phase, photo induced decarbonylation occurs on saturated carbonyl molecules. R.G.W. Norrish was the first to notice this process, which is known as the Norrish Type I or -

cleavage process. In the gas phase, the Norrish Type I process is very common. This type of solution phase reaction is rare. The Norrish type I reaction is the photochemical cleavage or homolysis of aldehydes and ketones into two free redical intermediates (α-scission). The carbonyl group accepts a photon and is excited to a photochemical singlet state. Through intersystem crossing the triplet state can be obtained. On cleavage of the α-carbon bond from either state, two radical fragments are obtained.

The size and nature of these fragments depends upon the stability of the generated radicals. The bond dissociation energy of carbon-carbon bond adjacent to a carbonyl is comparatively small and consequently photo chemical excitation of ketones usually results in the homolytic fission of the α-cleavage or Norrish type 1 reaction. It occurs more readily in vapour phase. Cleavage of a carbon-carbon bond a to the carbonyl group to give two radicals is known as type I cleavage (also known as the Norrish type I process). a-Cleavage is the process that occurs in all type I cleavage reactions.

4.3.1Primary Processes

Norrish Type I process is characterized by initial cleavage of the carbonyl carbon and alpha carbon bond to give an acyl and an alkyl radical. This process is known as primary photochemical process.

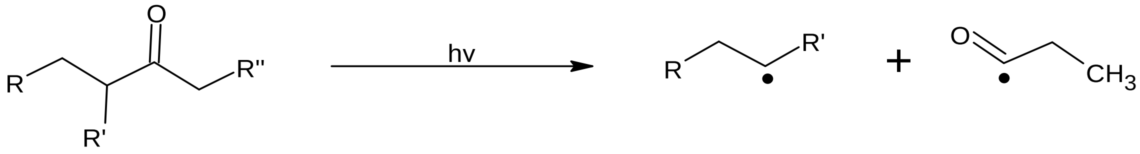


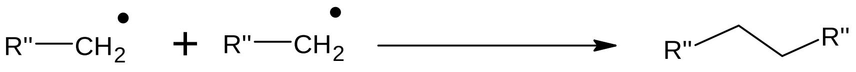
Fig. 4.1 primary process

The initially produced acyl radical is stabilized by one of the secondary processes shown in the Scheme 2. Similarly the alkyl radical can be stabilized by recombination or disproportionation.

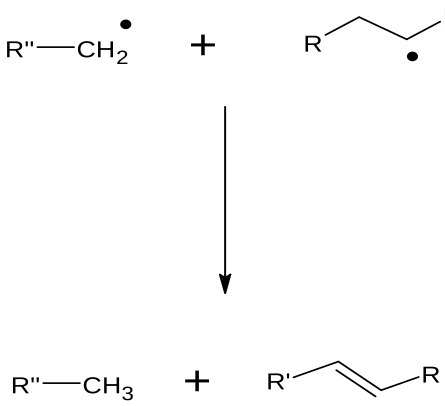
4.3.2 Secondary Processes

4.3.2.1 Decarbonylation of acyl radical

Carbon monoxide and an alkyl radical are produced by decarbonylation of an acyl radical. This alkyl radical can recombine to create an alkane or can undergo intermolecular hydrogen abstraction to form an alkane and an alkene.

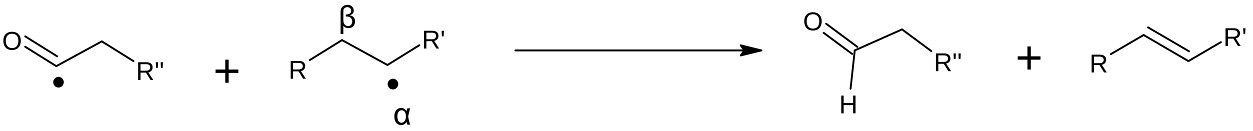


(Recombination)



4.3.2.2 Intermolecular hydrogen abstraction

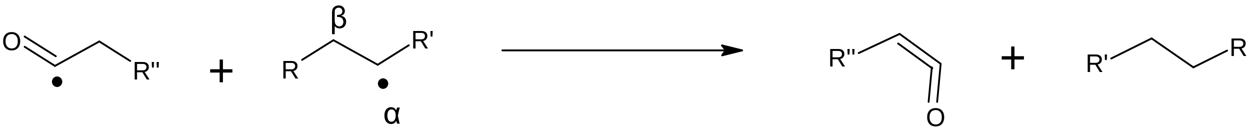
The acyl radical takes intermolecular hydrogen from the alkyl radical to produce an aldehyde and an alkene.



This process can only be possible if alkyl radical has atleast one β-hydrogen.

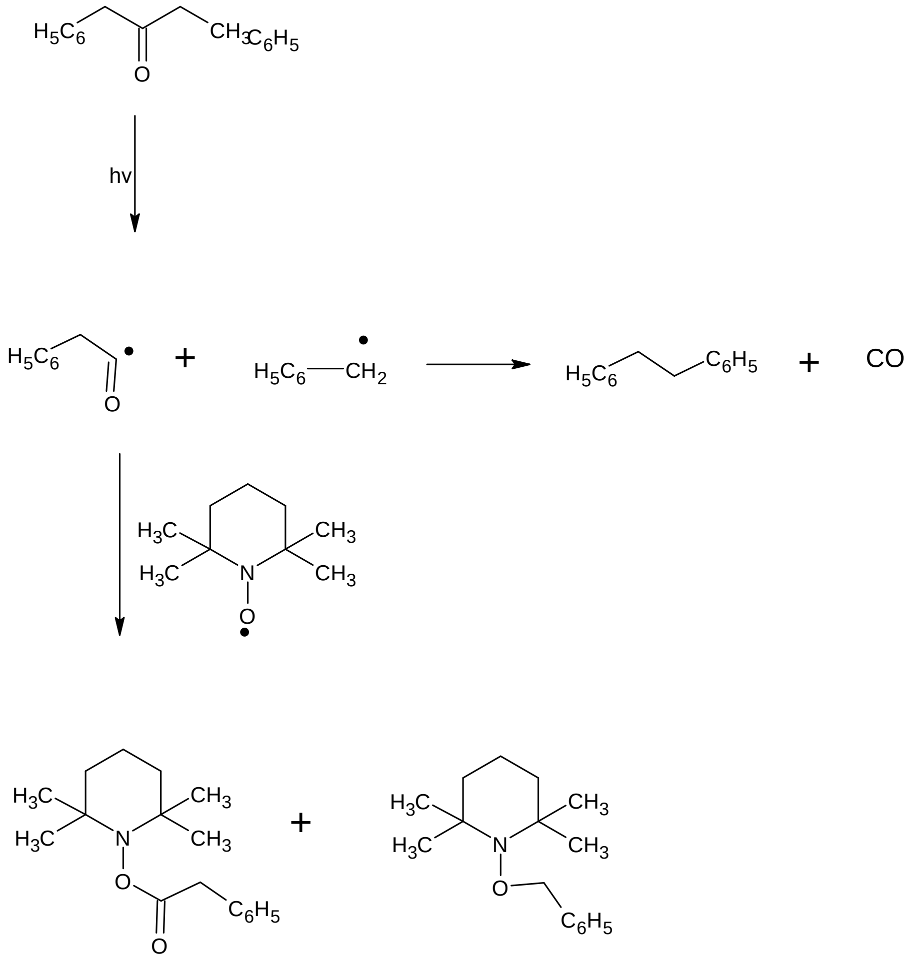
4.3.2.3 Intermolecular hydrogen abstraction

Intermolecular hydrogen abstraction by the alkyl radical from the acyl radical's -carbon to generate a ketene and an alkane



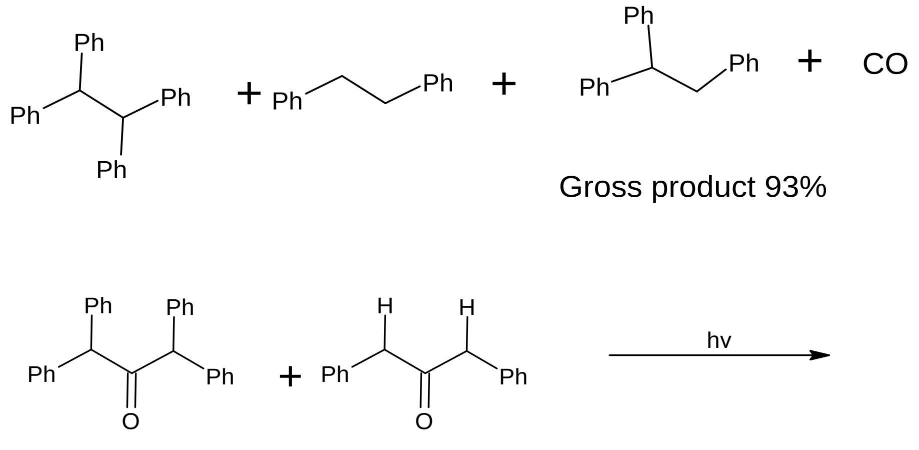
Decarbonylation is the major reaction of saturated acyclic ketones. As a result, the Norrish Type I process is a two-step radical mechanism. The primary process is the first, and the secondary process is the second. The formation of acyl and alkyl radicals can be shown by trapping them with proper trapping chemicals. The radical fragments formed by the fission of

1, 3-diphenylacetone were trapped as an ester and an ether using 2, 2, 4, 4-tetramethylpiperidine-1-oxyl.

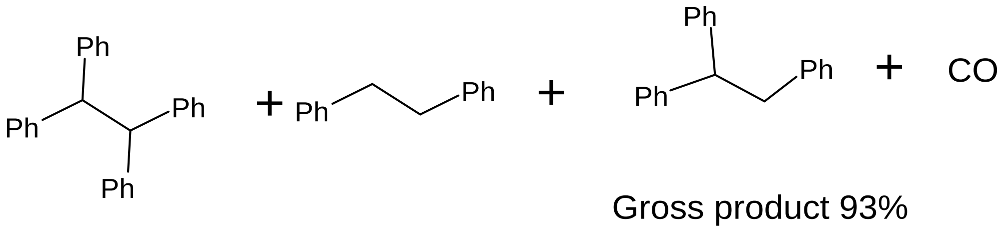


The creation of ether and ester confirms that acyl and alkyl radicals should be formed.

Photolysis of a mixture of ketones (A) and (B) yields molecules from a mixed radical combination, demonstrating the generation of radical intermediates.

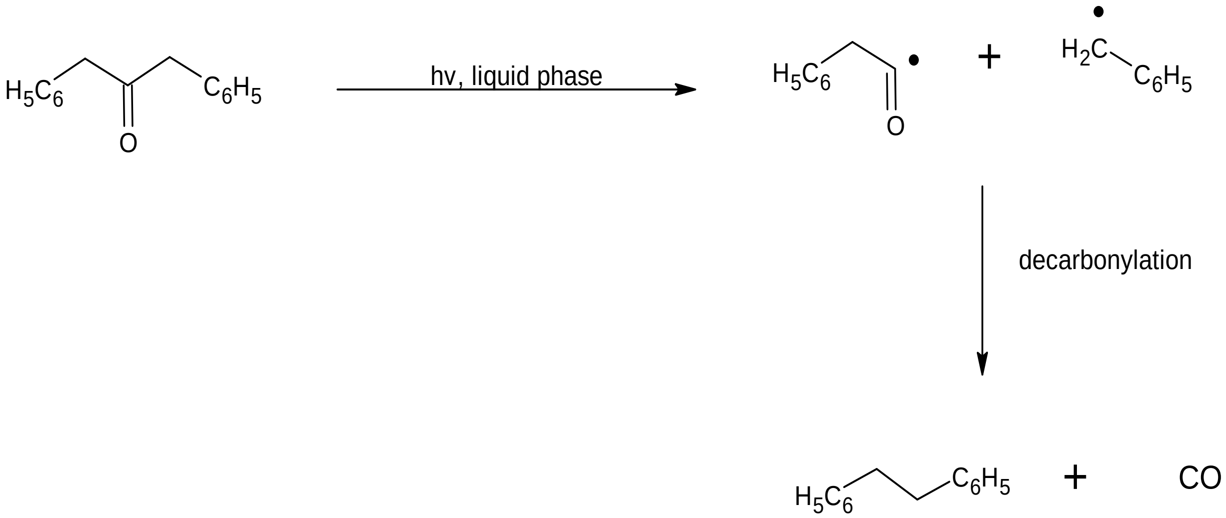


a b



The two-step radical mechanism was likewise validated by this cross-over experiment. The excited singlet and triplet states of the n-π* transition produce the Norrish Type I process. From both the excited singlet and triplet states, photolysis of di tert' butyl ketone yields a large yield of carbon monoxide (90%). This demonstrates that the Norrish Type I processes can occur in both excited and unexcited states. The singlet state has a lifetime of 4.5–5.6 x 10^{-9} seconds, but the excited triplet state has a lifetime of 0.11 x 10^{-9} seconds. Because the reaction takes place in both singlet and triplet excited states, the Type I process must be 100 times faster in the triplet excited state than in the singlet excited state. Studies with triplet quenchers, such as 1, 3-cyclopentadiene, have also shown that Norrish Type I processes occurs from both triplet and singlet excited state.

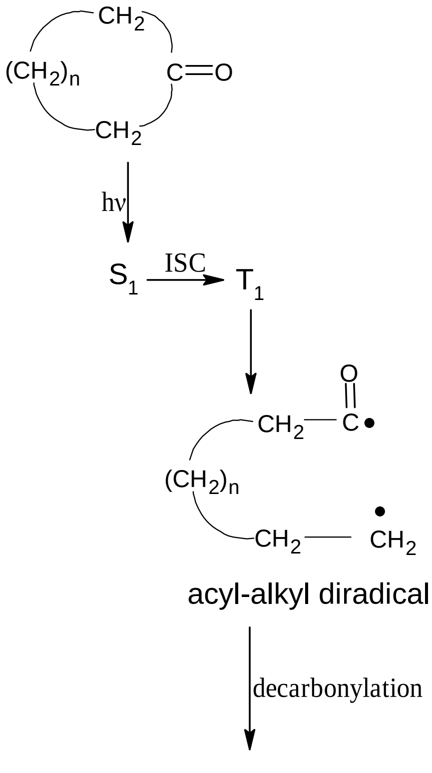
Photolysis in the vapour phase favors the Norrish Type I process, while photolysis in inert liquids favors the Norrish Type II process. Solvent cages are formed in inert solvents. Recombination of the first produced radical pair is aided by the formation of a solvent cage. In inert solvents, this results in a low quantum yield of products. In the liquid phase, the Norrish Type I procedure is only effective if a stable radical is generated. Allylic, benzylic, tert alkyl and acyl radicals are examples of stable radicals.

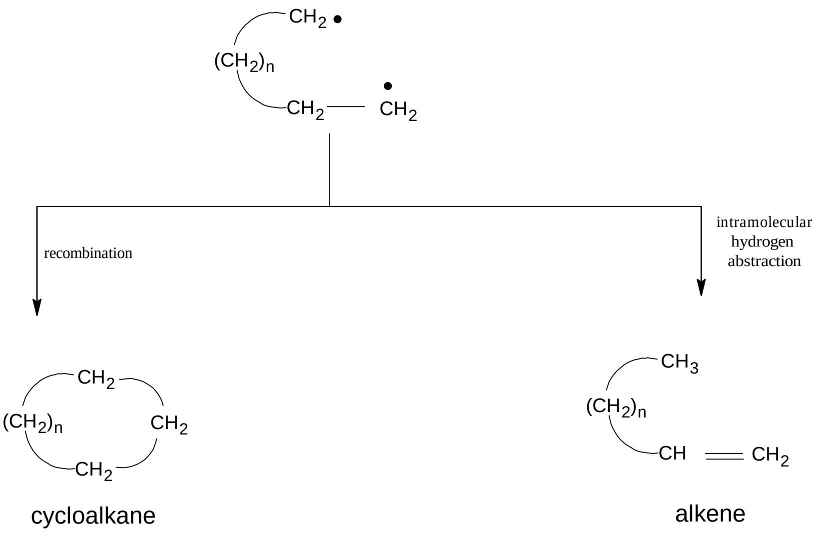


4.3.3 Norrish type I reaction of saturated cyclic ketones

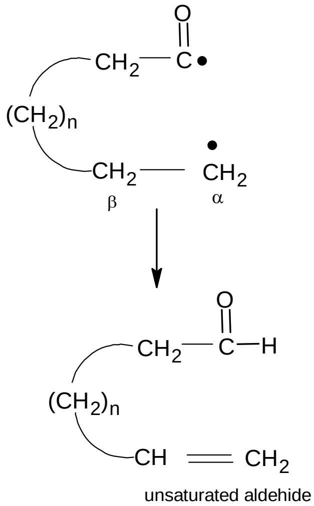
In comparison to acyclic ketones, cyclic ketones are more likely to undergo α-cleavage, resulting in acyl-alkyl biradicals. Acyclic ketones are cleaved by Norrish Type I cleavage in both the singlet and triplet excited states. The triplet state is used only in the reaction of cyclic ketones. However, it's possible that inter system crossing in cyclic ketones is so fast that no reaction from the singlet state is detected. The excited singlet state is 100 times more reactive than the triplet state.The excited triplet state for Norrish Type I processes, according to available knowledge, is the n→ π* triplet state. This was originally observed with cyclopentanone irradiation in both gas and solution phases.

The final product is 4-pentenal in both cases. The wavelengths of 313 nm and 254 nm are used to form 4-pentenal. 1, 3-cyclopentadiene can prevent the production of the aldehyde. The development of the triplet state is confirmed by this quenching experiment. The initial breaking of a carbonyl carbon-alpha carbon bond occurs in the Norrish Type I process. Secondary processes [(a) to (c)] are similar to those seen with acyclic ketones.(a) Carbon monoxide and a dialkyl radical are produced by decarbonylation of an acyl-alkyl diradical. The dialkyl radical can either recombine to produce a cycloalkane or undergo intramolecular hydrogen abstraction to produce an alkene.

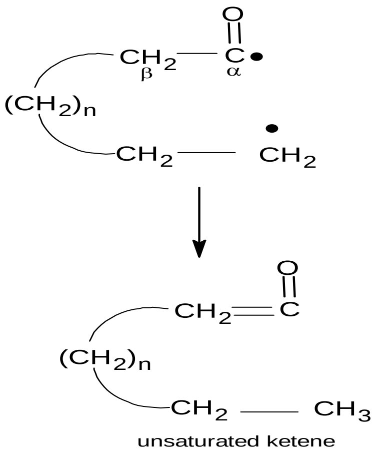




(b) Intramolecular hydrogen abstraction by the acyl radical from the β-carbon of the alkyl radical to give an unsaturated aldehyde.

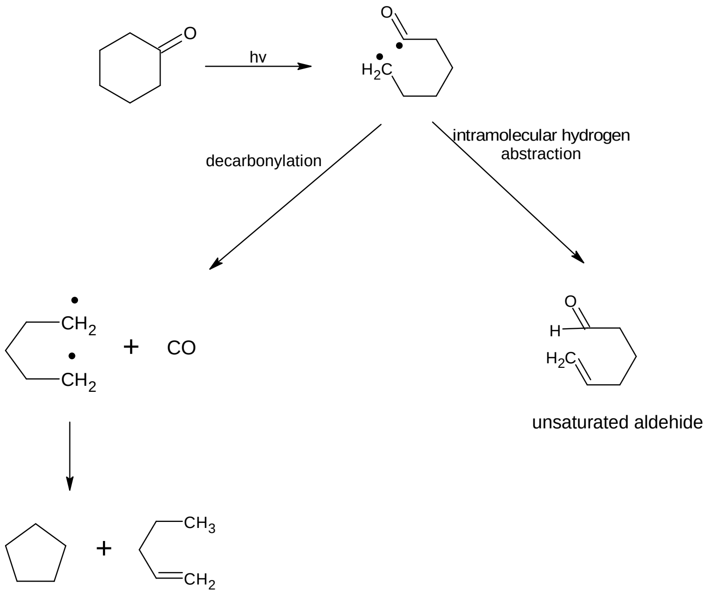


(c) Intramolecular β-hydrogen abstraction from the acyl radical by the alkyl radical, resulting in the formation of ketene.

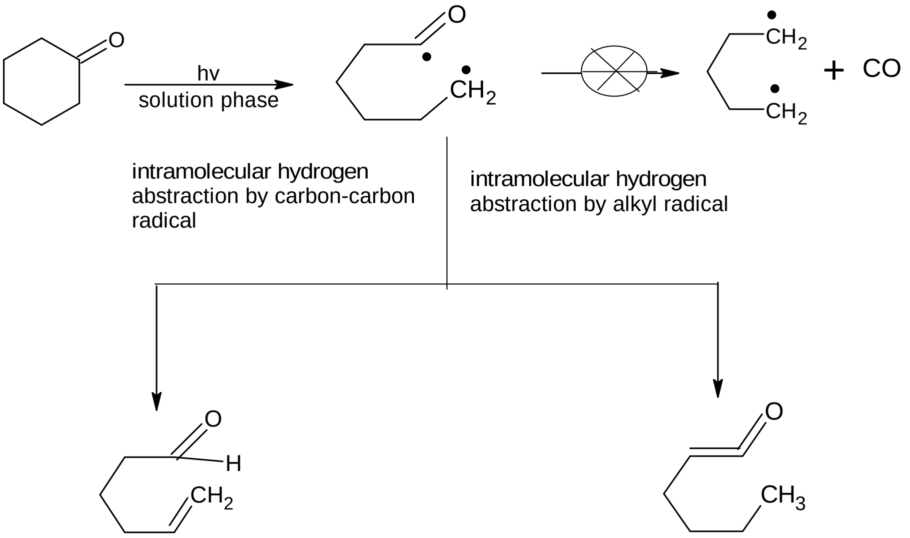


The biradical of cyclic ketones can go through one of two hydrogen transfer processes via a cyclic transition state, in which a hydrogen atom is moved from an atom near to the other radical centre to one radical centre.

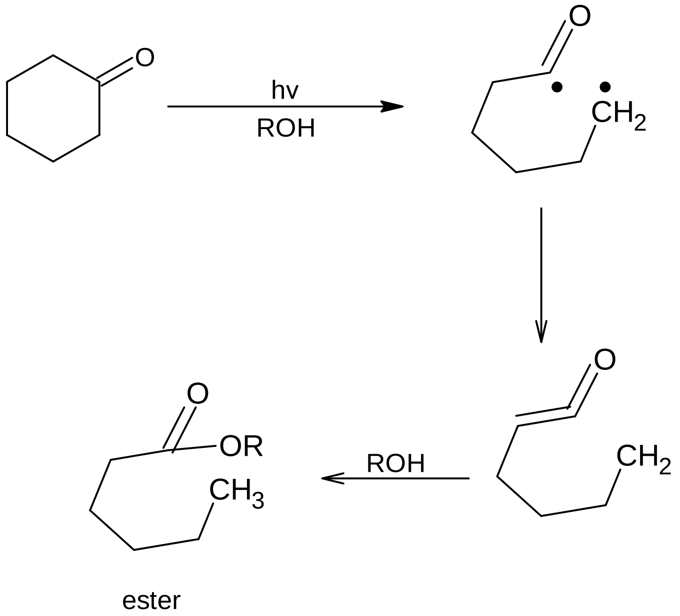
In the gas phase, photolysis of cyclic ketones results in decarbonylation and intramolecular hydrogen abstraction. The synthesis of unsaturated aldehide is mostly achieved by intramolecular hydrogen abstraction.



Decarbonylation doesn't always normally stabilise biradical pairs in solution. Biradical is predominantly stabilised in this scenario by intramolecular hydrogen atom transfer. The creation of an unsaturated aldehyde, a ketene, or both results from this intramolecular hydrogen atom transfer.

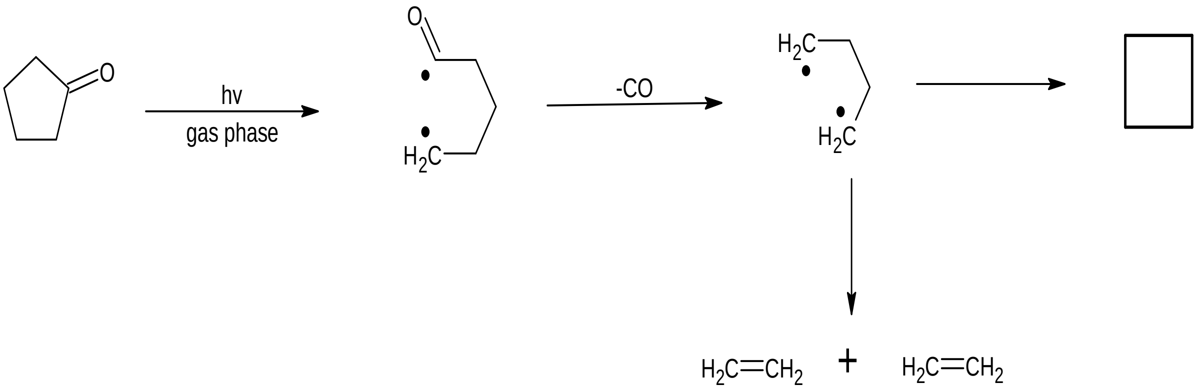


The major species produced by photolysis in the presence of a polar protic solvent is ketene. The carboxylic acid (with water) or its derivative (ester with alcohol) is the only result of solvent addition to this ketene.

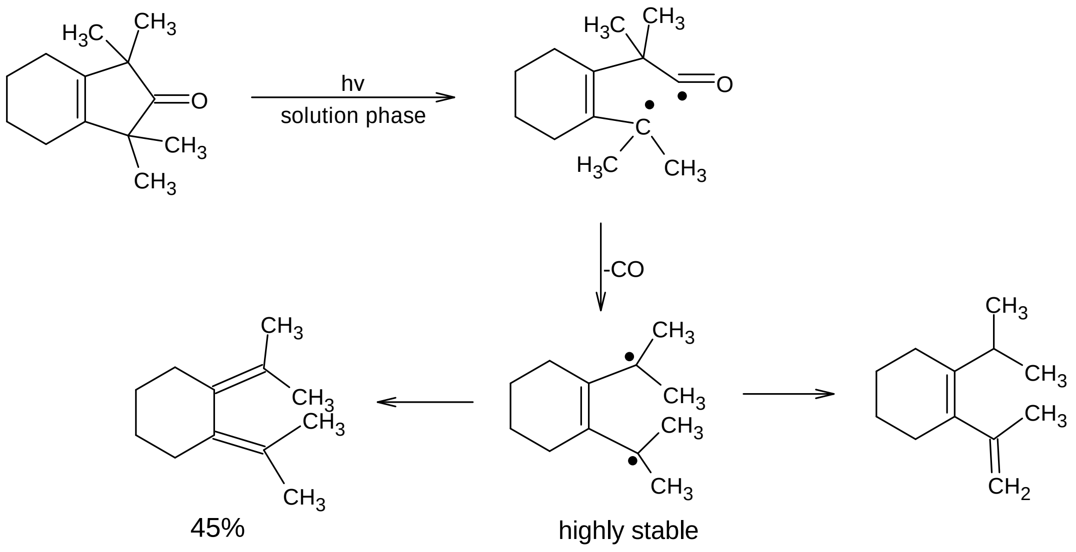


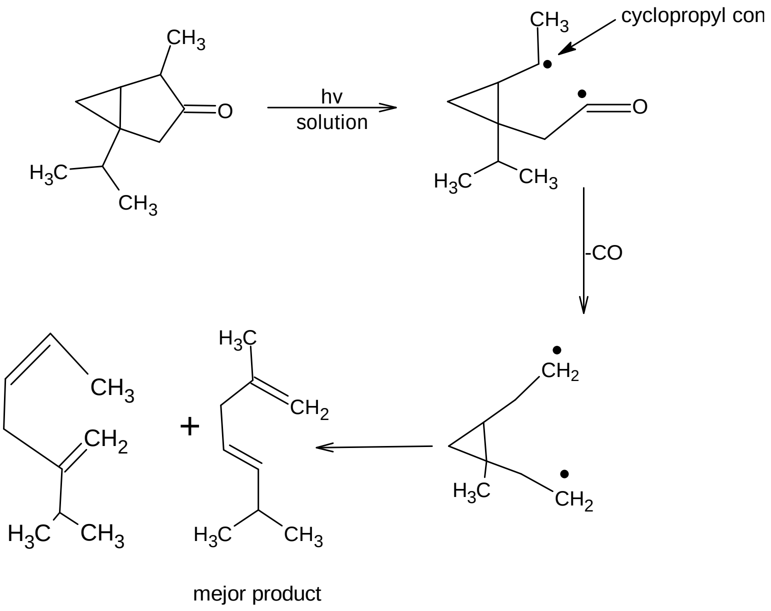
4.3.4 Norrish type-I in Cyclopentanone

Cyclopentanone decarbonylates in the gas phase when irradiated at 147 nm. In this scenario, however, a two-step mechanism is involved, resulting in a biradical that decarbonylates to another biradical that either fragments into ethylene or forms a bond with cyclobutane. In compared to cyclobutane creation, fission to ethylene is substantially more efficient.



Only when the radical centres generated are stabilised by alkyl substitution, double bond, or cyclopropyl ring is the loss of carbon monoxide from a cyclopentanone a prominent path in solution.

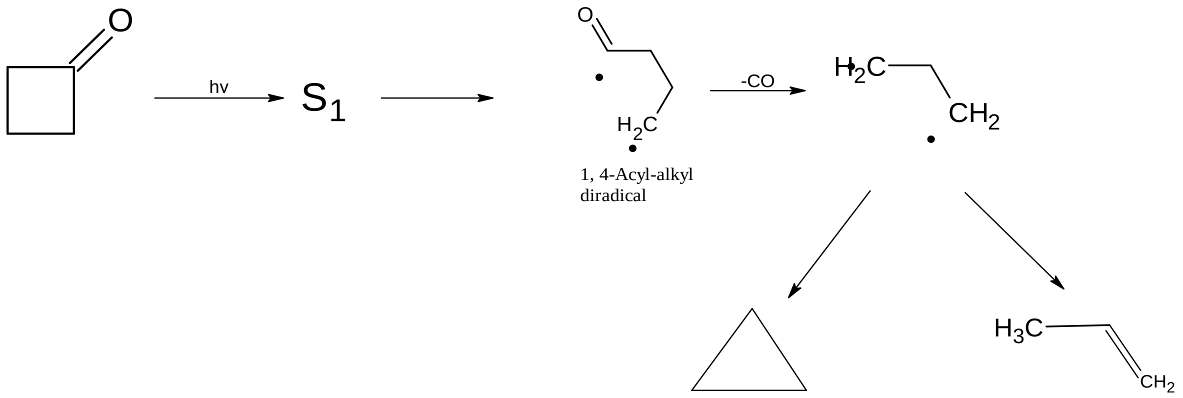




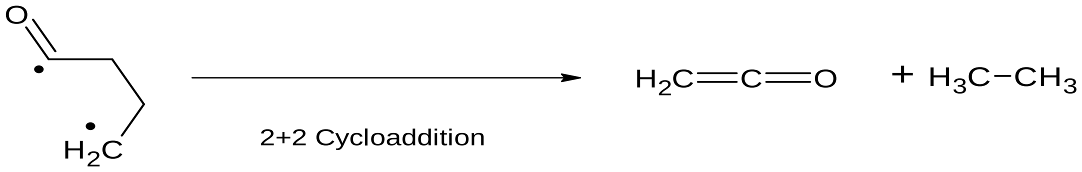
4.3.5 α-cleavage by Cyclobutanone

Cyclobutanone has a cleavage reaction as well. Due to the angle strain, the cyclobutanone - cleavage reaction is ten times more efficient than the cyclopentanone. The efficiency of - cleavage is improved by angle and steric strains. The photochemistry of cyclobutanone-cleavage is distinct from that of other cyclic ketones. Cleavage occurs from S1 (n→π*), unlike other ketones, and results in the creation of a 1, 4-acyl-alkyl diradical. The diradical can be stabilised through one of three possible pathways:

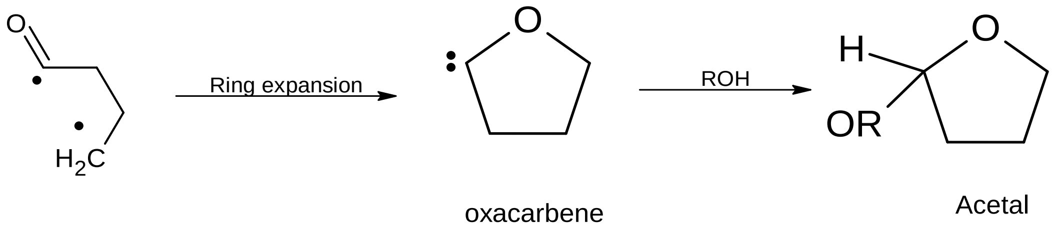
(i) Carbon monoxide is lost, and 1, 3-diradical is formed, which proceeds either recombination to cyclopropane or hydrogen abstraction to generate propene.



(ii) By a subsequent β-cleavage and formation of ethylene and ketene.

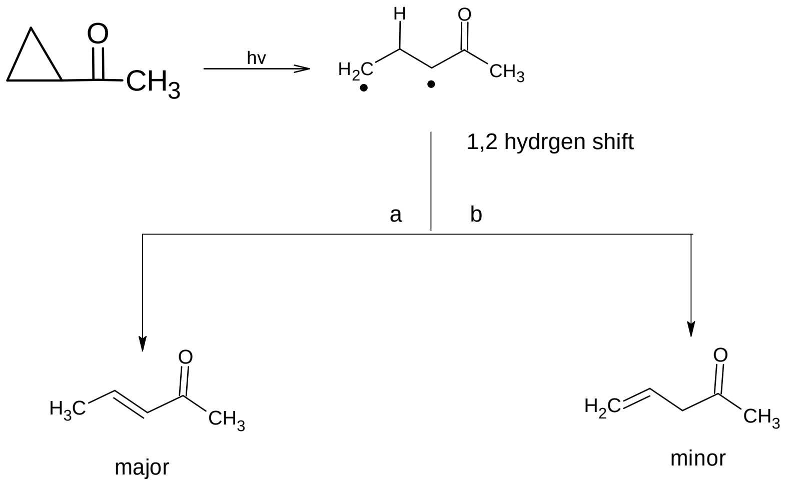


(iii) The 1, 4-acyl-alkyl biradical can expand its ring by rebonding to oxygen, resulting in oxacarbene. Polar protic nucleophile solvents can trap this carbene. A ring expansion is the overall reaction.

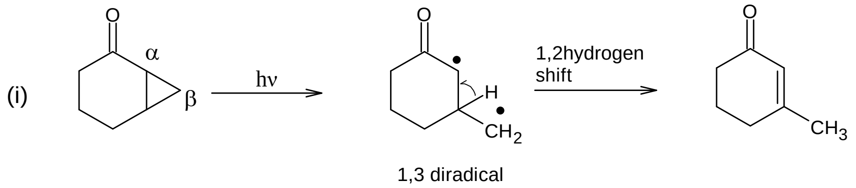


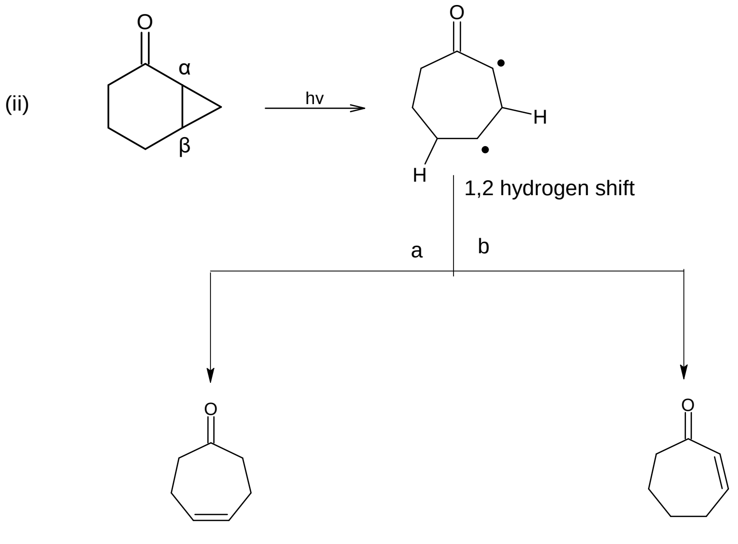
4.4 β –CLEAVAGE OR NORRISH TYPE II REACTION

Some compounds have relatively weak C_{α}-C_{β} bonds that can be cleaved as a result of the carbonyl group's electronic excitation. The UV spectrum shows evidence for coupling between the carbonyl and cyclopropyl groups, which provides a mechanism for energy transfer from the carbonyl group to the broken bond. *Norrish type II reaction is possible If bond between α and β - carbon is weak. If reaction occurs in open chain compounds, the abstraction of hydrogen atom take place from γ - carbon atom and if system is cyclic the abstraction of hydrogen is from δ-Carbon* .The creation of a biradical intermediate has been proven to be part of the reaction process. The cyclopropane ring is cleaved by photolysis of acetylcyclopropane, which is followed by a hydrogen shift.

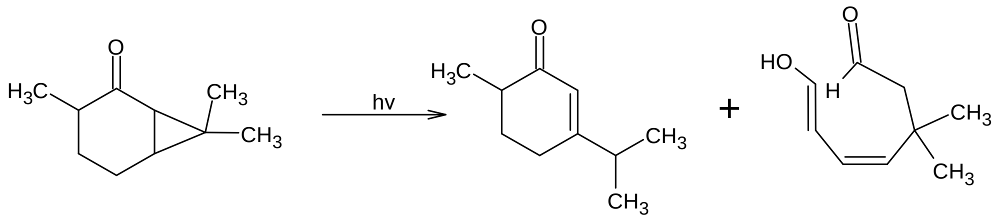


In a similar way, bicyclo [4, 1, 0] heptane-2-ones undergo cleavage of one of the cyclopropyl C—C bonds.





In some cases the α-cleavage and β-cleavage are often in competition as shown below:

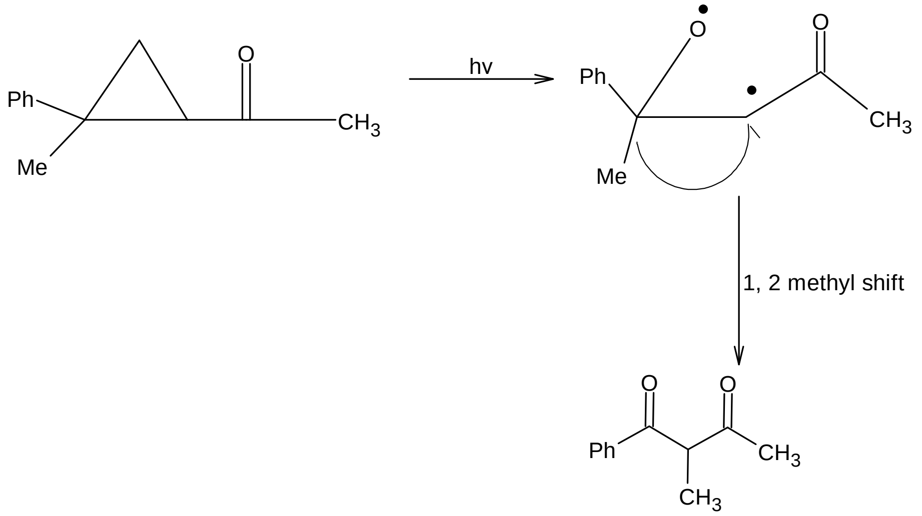


1 2

Product (1) is formed as a result of the -cleavage, while product (2) is formed as a result of the cleavage.

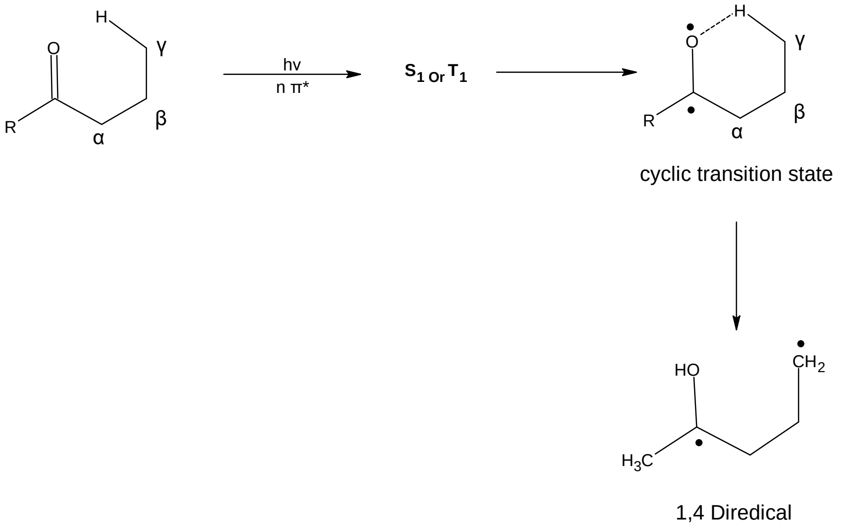
In addition,, -Epoxy ketones have a weak Cα—C$_β$ bond that can be cleaved in the excited state. On photolysis, epoxy ketone undergoes -cleavage and alkyl migration. The fission of the C—O bond is the consequence of this reaction, which starts with a singlet n to π* state. The involvement of a biradical species produced by C—O bond fission best explains the migratory abilities seen inside such compounds. Here are a few examples:

(i)

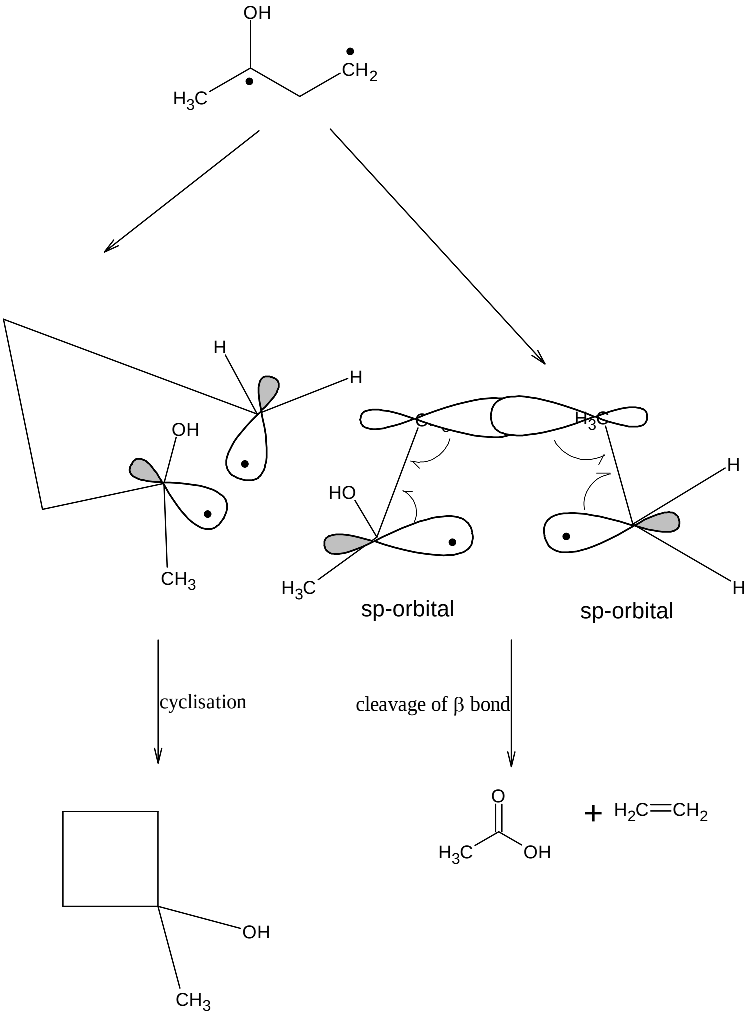


4.5 INTRAMOLECULAR HYDROGEN ABSTRACTION (γ-HYDROGEN ABSTRACTION)

The synthesis of ketyl like 1, 4-diradical occurs when 1, 3 stimulated carbonyl compounds with an accessible hydrogen atom in the -position undergo a distinctive 1, 5-hydrogen atom transfer by an intramolecular cyclic mechanism.



Depending on the structure of the initially synthesized 1, 4-diradical, has two different stabilisation pathways are possible:

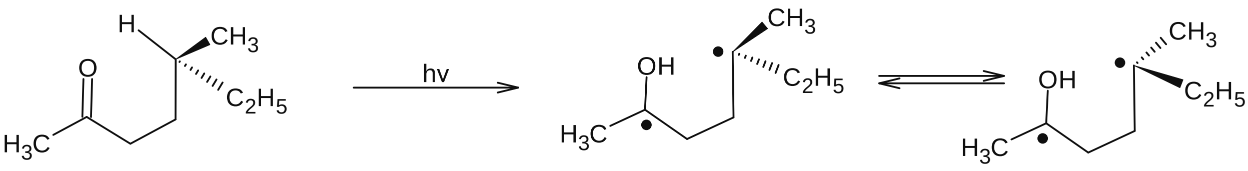


(i) If only the sp-orbitals of the radical centres can overlap, a cyclobutanol is the product.

(ii) When the radical centres' sp-orbitals are parallel to the β -bond, they help in the creation of two double bonds (one in the enol and one in the alkene) as a result of the β-bonds' cleavage.

The second process of this reaction is known as Norrish Type II process which leads the formation of alkene and alkenol. Aside from the fact that the reaction happens in both the singlet and triplet phases of the n,* transition, the quantum yields from the singlet state are often lower than those from the triplet state. Because aromatic ketones can undergo quick intersystem crossing, the reaction happens solely with the triplet state in the case of aryl-alkyl ketones. The efficiency of the reaction is also influenced by the solvents. In the presence of polar solvents, the singlet state processes are unaffected. Polar solvents, such as alcohol, on the other hand, speed up the reaction while it is in the triplet form.

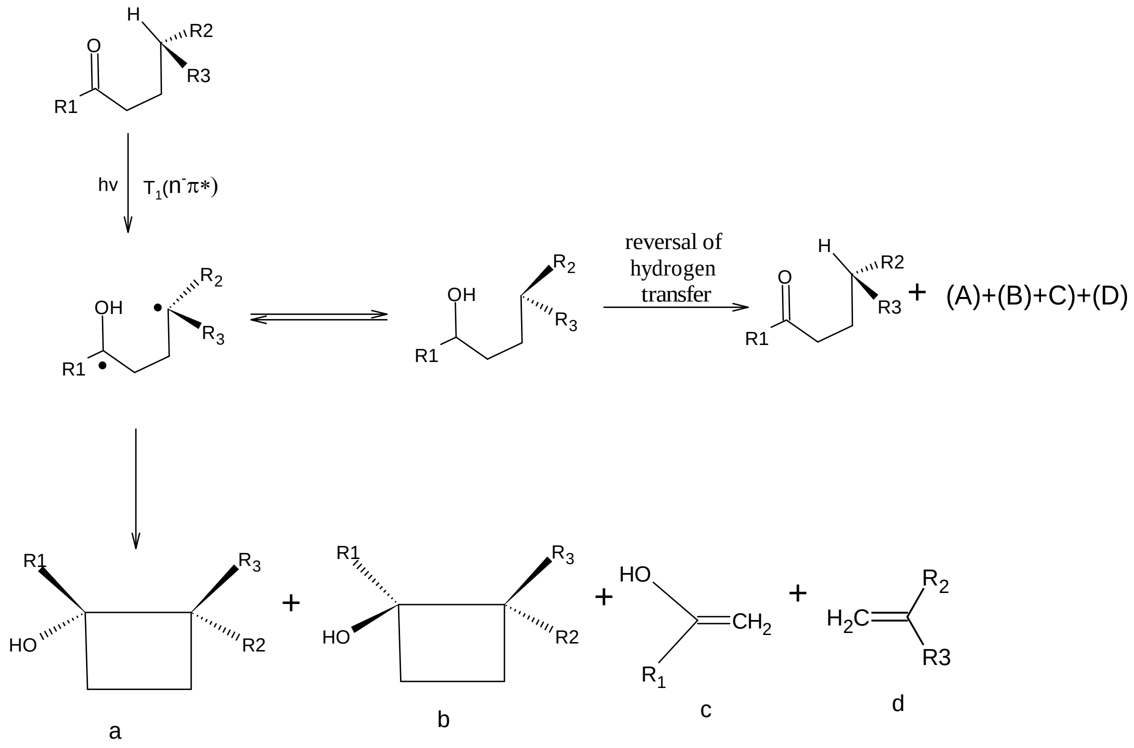
Because radiation less deactivation from the S_1 and T_1 states and reversal of the hydrogen transfer can compete with reactions leading to products, the reaction's quantum yield is low. The optical active ketone (1) with a chiral -carbon is used to test the reversal process. Racemization occurs in ketone (1). The reaction intermediate is 1, 4-diradical, according to the racemisation process. This also validated the hydrogen atoms backward transport.



(i)

The addition of 1, 3-cyclopentadiene can stop back transfer of hydrogen atoms, or photo racemisation. The creation of the triplet state was confirmed by this quenching experiment.

Participation of a 1, 4-diradical intermediate in the Norrish Type II reaction has been confirmed by trapping experiments and spectroscopic techniques. Chemically, the formation of 1, 4-diradical has also been demonstrated. Photo racemisation of a ketone with a γ-chiral carbon atomand loss of the chirality in the product was observed.



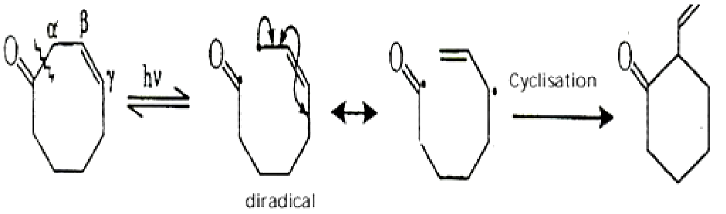
4.6 INTRAMOLECULAR REACTION IN β,γ UNSATURATED CARBONYL COMPUND:

This reaction also consist of α-cleavage. The overall reaction follows by two steps:

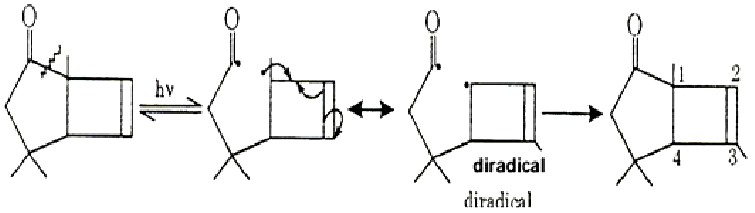
case I - 1,3-acyl shifts is involved, which form an isomeric β, γ- Unsaturated ketones.

Case II- Ring closure process takes place.

(1)



(2)



4.7 SOME RELATED QUESTION :(SAQS TYPE QUESTION)

Question 1

A. Multiple choices

1. The photochemical reaction of carbonyl group is initiated by-

a. n-π^*transition b. π-π^* transition

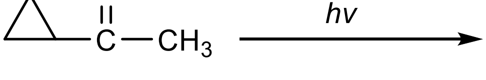
c. σ- σ^* transition d. n- σ^* transition

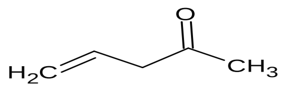
2. Norrish type I reaction commonly occur in phase-

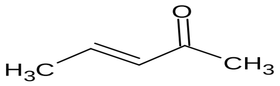
a. Solution phase b. Gas phase

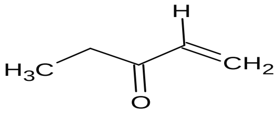
c. None above d. Both (a) & (b)

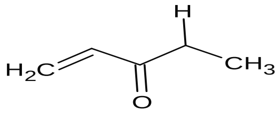
3. Major product of following reaction will be-



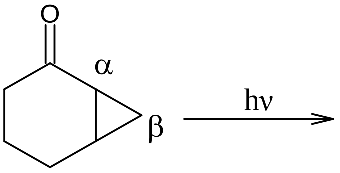
a) 

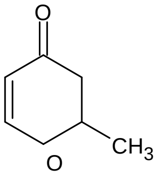
b) 

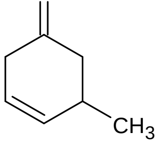
c) 

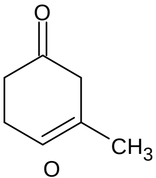
d) 

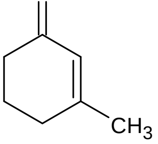
4. Product will be-



(a) 

(b) 

(c) 

(d) 

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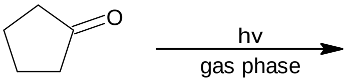
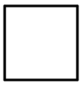


(a)



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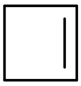

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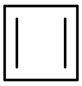

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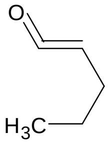


B. Fill in the blanks:

a) Norrish type I reaction is accompanied by…….. Cleavage.

b) …………..of acyl radical occurs in the secondary phase of the Norrish type I process.

c) . the most important band is at ……..nm for the photochemistry of carbonyl compounds.

C. Match the following

a) 1, 5 hydrogen transfer	i. Gas phase
b) β- cleavage	ii. primary process
c) Formation of acyl alkyl radical abstraction	iii. intramolecular hydrogen
d) Decarbonylation	iv. Norrish type II

D. True / false

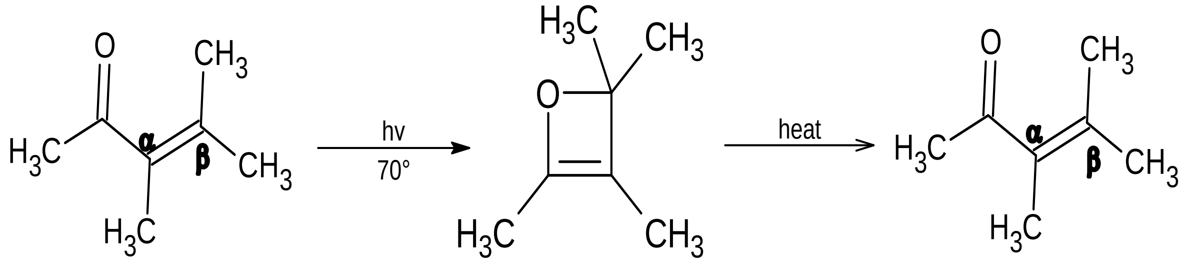
a. Norrish type I cleavage of acyclic ketones takes place only by singlate state. (True/False)

b. Decarbonylation of acyl alkyl doradical to give carbon monooxide and dialkyl radical. (True/False)

c. Weak C_c-$C_\beta$bonds are reason of Norrish type II reaction. (True/false)

4.8 *INTRAMOLECULAR REACTION OF α-β- UNSATURATED CARBONYL COMPOUNDS*

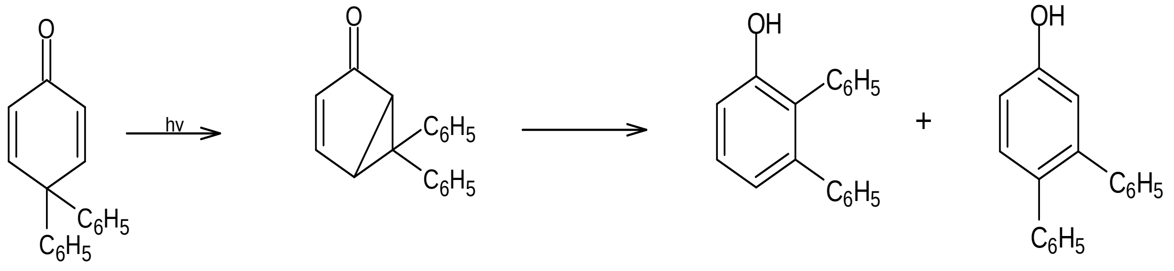
At 70° C, an intramolecular reaction of α-β - unsaturated carbonyl molecule produces oxetene. This product can be turned into reactant by heating it.



α-β- Unsaturated ketone **oxeteneα-β- Unsaturated ketone**

4.9 INTRAMOLECULAR PHOTOREATION OF CYCLO HEXADIENONE:

The photochemical rearrangement of compounds containing the cyclohexadienone chromophore is an example of this type of reaction. Irradiation converts 4,4 diphenylcyclo-hexadinenone (I) to a ketone (II) and two phenols (III) and (IV).

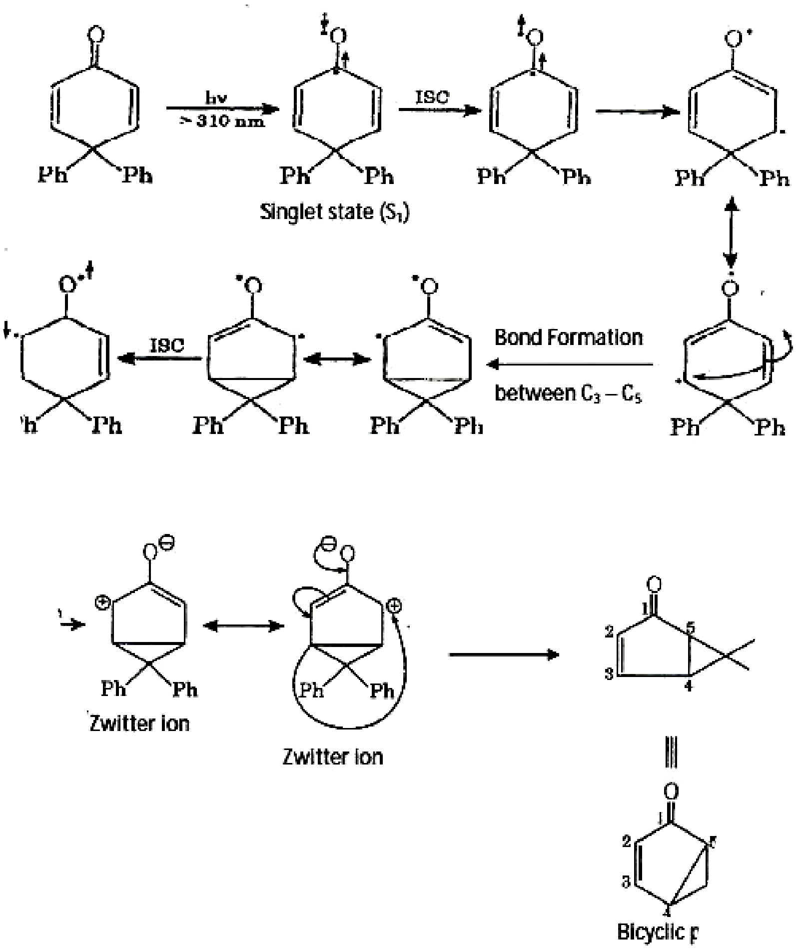


(I) (II) (III) (IV)

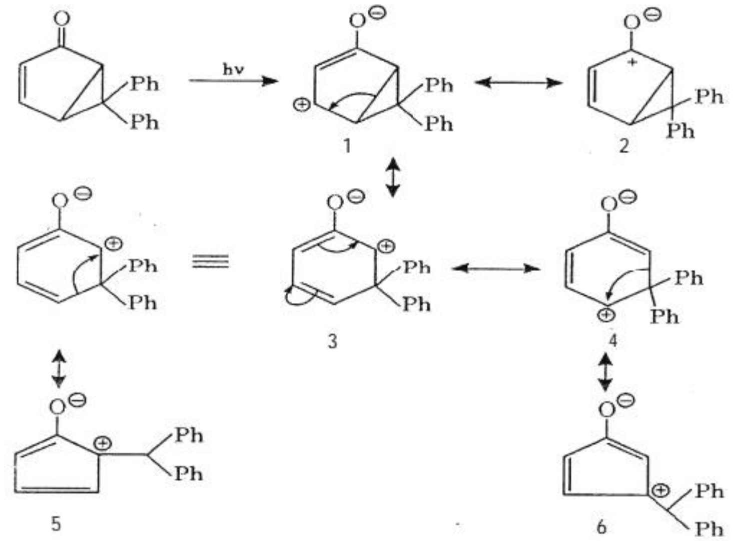
Cyclohexadienone displays absorption at about 300 nm (n-π*) and at 240 nm (π-π*).

Zimmerman explains the mechanism. The dionones' reactive excited state is the n-π* triplet state. Between C3 and C5, a new bond is created. The reaction is followed by ISC, or intersystem crossing, which occurs after the creation of the bond. An intermediate zwitter ion is generated before the final bicyclic product is formed. This intermediary aids in the management of acyclic products.

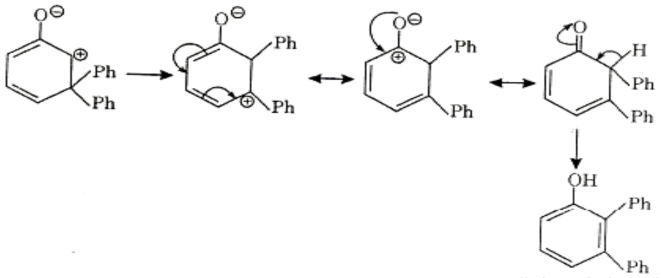
Mechanism:



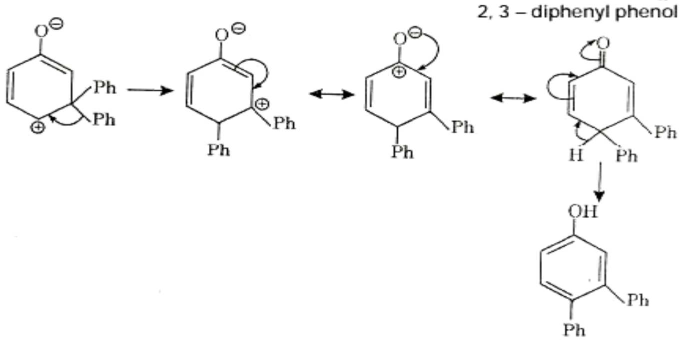
Because it is still a bicyclic product, it can be rearranged again consists of one or more enone systems capable of undergoing n-л*excitement.



The electron rich system in the n-π* state causes the π*-n electron devaluation state in cyclohexaclienones. However, the observed rearrangements are typical with electron deficient centre movement. Product (3) and (4), out of the foregoing (1) to (6) compounds, can undergo phenyl migration and create 2, 3 and 3,4-diphenyl phenol, respectively.

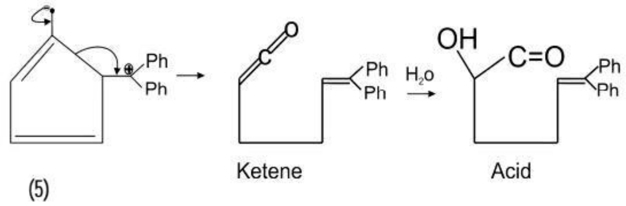


2, 3 – diphenyl phenol



3,4 – diphenyl phenol

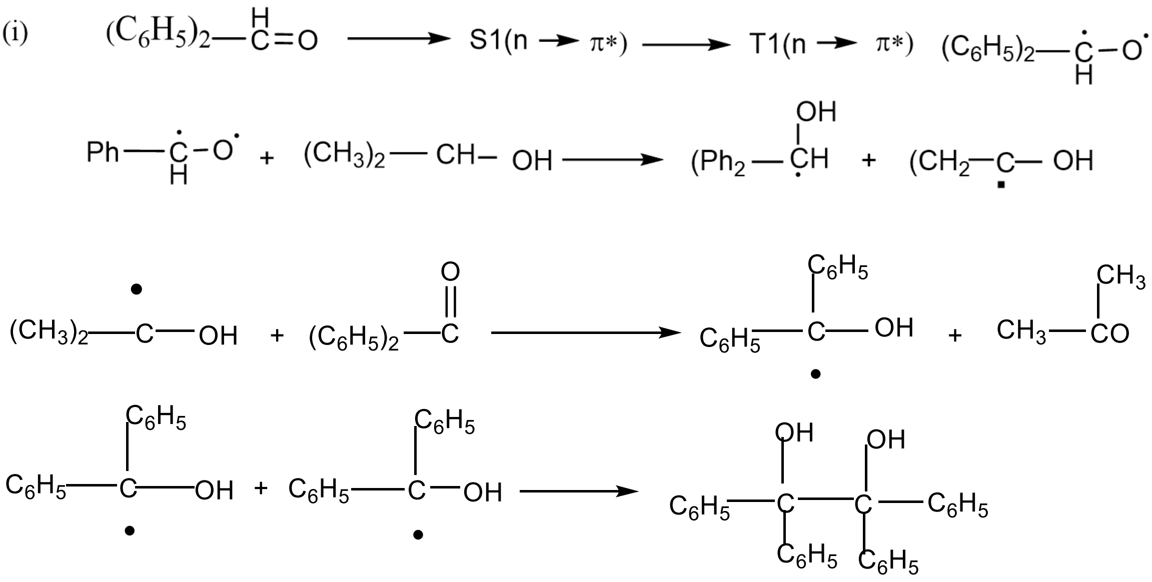
If medium is aqueous, than the structure no (5) can rearrange and gives a ketones and then form an acid.



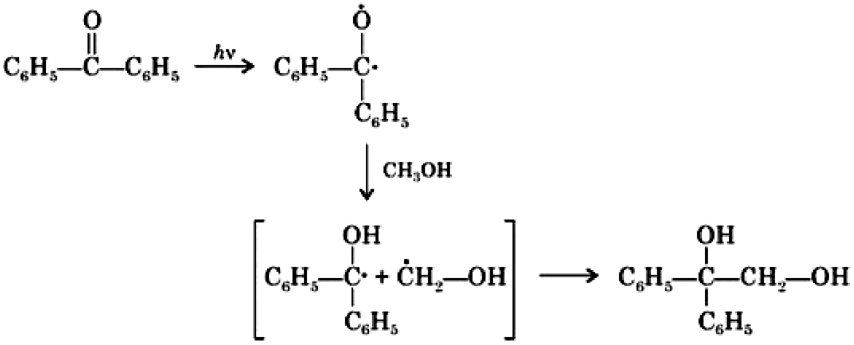
4.10 PHOTOREDUCTION

One of the most well-known photo reactions is the reduction of carbonyl compounds by light. The mechanism begins with the transfer of a hydrogen atom from a donor molecule, such as a solvent, an additional reagent, or a ground state molecule of reactant, to the oxygen atom of the carbonyl excited state. In the presence of a variety of hydrogen atom donors, ketone undergoes photo reduction. Secondary alcohol, toluene, and cumene are all hydrogen atom donors.

(i)

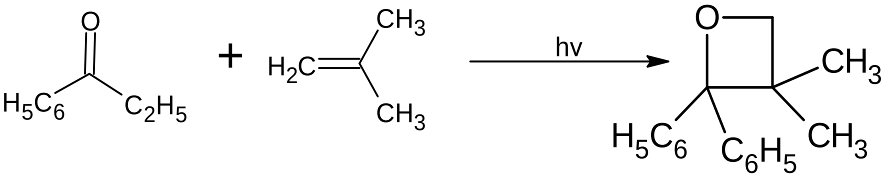


(ii)



4.11 PHOTO CYCLOADDITION REACTION (PATERNO-BUCHI REACTION)

The creation of oxetanes from the addition of carbonyl compounds to alkenes was one of the earliest photocycloaddition processes to be explored. The Paterno-Buchi reaction is the name for this reaction. When benzophenone is combined with isobutene, a large amount of oxetane is produced.



90% yield

The Paterno-Buchi reaction can be classified into two types, depending on the nature of the alkenes.

4.11.1 Addition to electron alkenes

The chemical process changes depending on the type of carbonyl molecule and alkenes involved, according to mechanistic studies. When simple aliphatic or aromatic ketones are added to electron-rich alkenes, the n* triplet state of the carbonyl compound attacks the ground state alkene in a non-concerted fashion, resulting in all possible oxitane isomers. Because the reactive excited state is a triplet state, the reaction is non-concerted.Initially, The reaction's adduct is a triplet 1, 4-diradical, which must undergo spin inversion before the product can be formed. If the intermediate 1, 4-diradical undergoes bond rotation quicker than ring closure, stereospecificity is lost.

Although the reaction is not stereospecific, there is a preference for one orientation of addition, which can be rationalised in terms of initial attack on the alkene by the oxygen atom of the excited carbonyl group to give a biradical intermediate. The existence of biradicals has been confirmed by microsecond spectroscopy. The more energetically stable of the two possible biradicals is formed more readily. Thus reaction is regioselective reaction. The consideration of biradical stability is certainly applicable to the prediction of the major product of the cycloaddition.

Two important rules for the successful synthesis of oxitanes have been put forward. These rules are as follows:

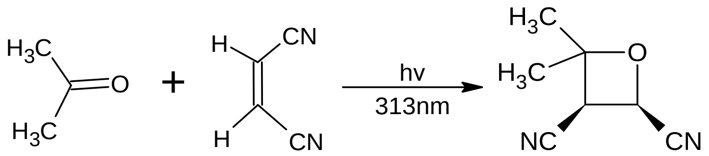
Only carbonyl compounds with a low-lying n → π* state will form oxitanes.

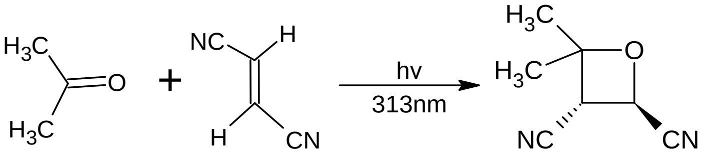
The energy of the carbonyl excited state must be less than that of the alkene to prevent energy transfer from the carbonyl excited state to the alkene.

As far as the addition of aromatic carbonyl compounds is concerned only the triplet state is reactive (because inter system crossing is very efficient in case of aromatic ketones) and consequently a triplet biradical intermediate is produced. The reactions of alkyl ketones can be complicated by the less efficient inter system crossing thus permitting reaction of both the singlet and the triplet state. Both singlet and triplet state show equal reactivity for the reaction. The singlet state reaction obtained at high concentration of the alkene. On the otherhand triplet state reaction obtained at low concentration of the alkene

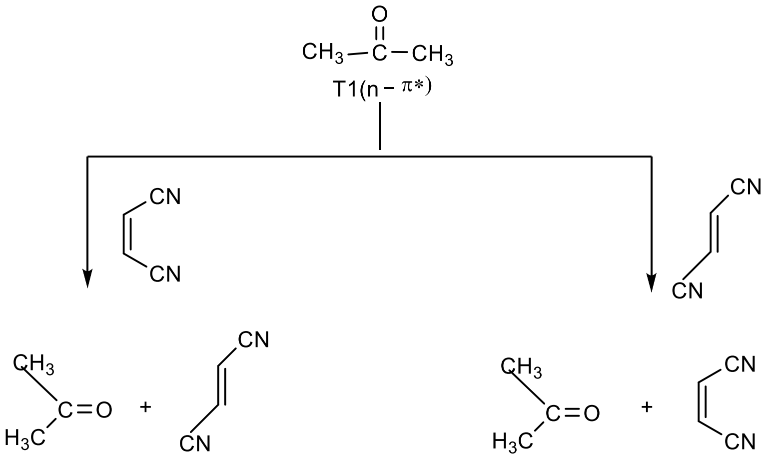
4.11.2 Addition to electron deficient alkenes

Photocycloaddition of aliphatic ketones to electron-deficient alkenes, particularly dicyano-ethene, involves addition of singlet state (n → π*) excited ketone to ground state alkene. The reaction is stereospecific, and the alkene's stereochemistry is preserved in the oxitane product.



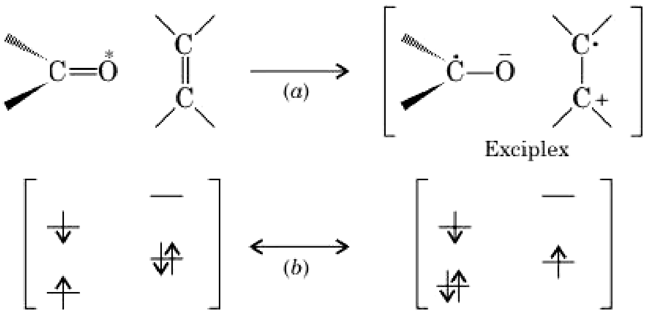


The photocycloaddition of electron-deficient alkenes to ketones proceeds according to a set of rules. While only the S_1(n-π*) state produces oxitanes, the T_1(n-π*) state stereospecifically sensitises the cis-trans isomerisation of electron-deficient alkenes but does not produce them.

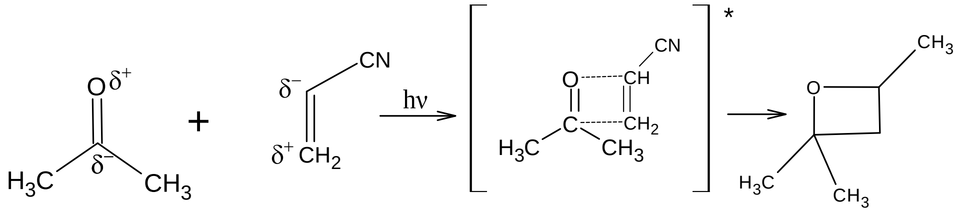


With electron-deficient alkenes, stereospecificity of oxitane production can be described as follows:

In the case of electron-deficient alkenes, oxitane production is thought to occur through the formation of exciplex. Between the singlet excited state of ketone and the ground state of alkene, exciplex production occurs. Charge and energy transfer between the constituent molecules help to keep exciplex stable.

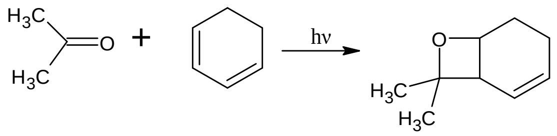


The stereospecific formation of products in the exciplex (i.e., excited state cyclic complex) is accounted for if both new bonds are generated simultaneously in the complex, or if the second is formed after the first at a rate faster than the rate of bond rotation. Again, there is a preference for one addition orientation, but this is the opposite of what would be expected based on the most stable biradical intermediate. The preference indicates the exciplex's preferred orientation, which is regulated by charge densities, as shown.



It is also possible to add carbonyl compounds to conjugated dienes. Dienes often have a lower ET than carbonyl compounds. However, the formation of oxetanes competes successfully with excitation energy transfer because dienes quench the T_1 (n → π^*) state. Thus formation of oxetanes occurs from the S_1 (n → π^*) state of the carbonyl compounds. Therefore, dienes give stereospecific reactions with dienes. Examples are as follows:

i)



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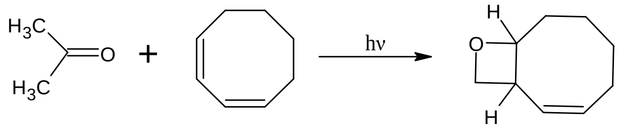

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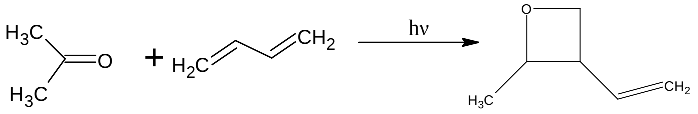
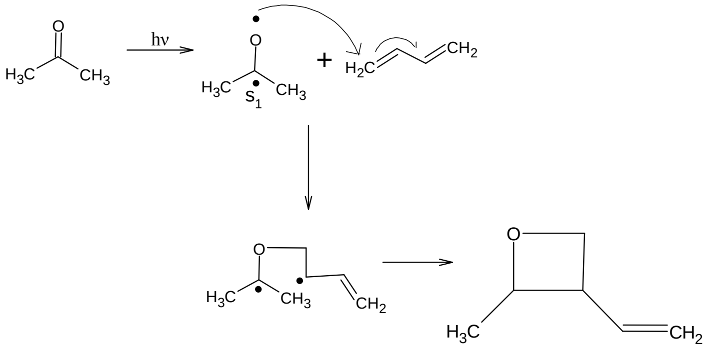
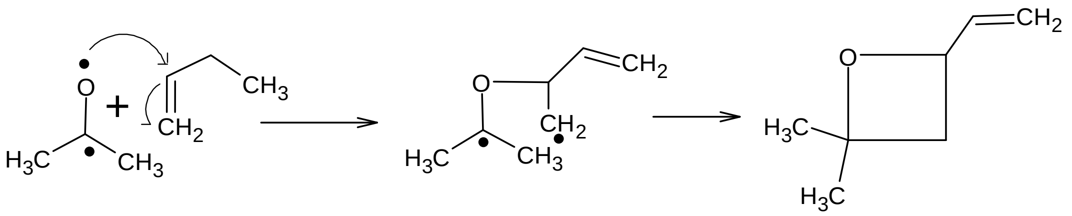
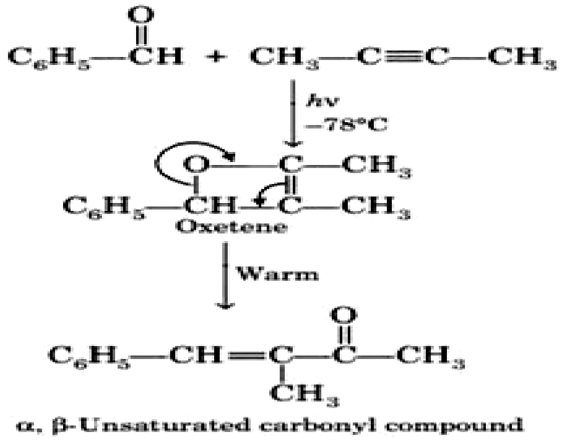


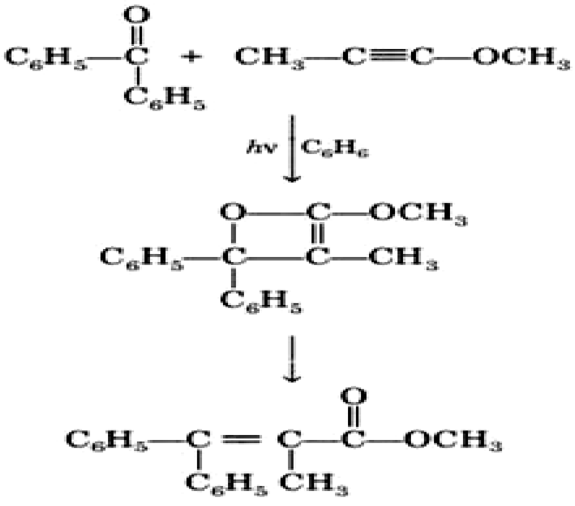
The third reaction takes place as follows:





Photochemical cycloaddition of carbonyl compounds to alkynes produces oxetenes, which are rarely isolated but isomerise to,-unsaturated carbonyl compounds in a subsequent heat process.





4.12 SUMMARY

Summary of this unit is-

- Carbonyl groups are known to absorb light in the 230-330 nm range. Each main reaction in ketone photochemistry starts with the n-π* triplet state, and the end product can be generated following the secondary process.

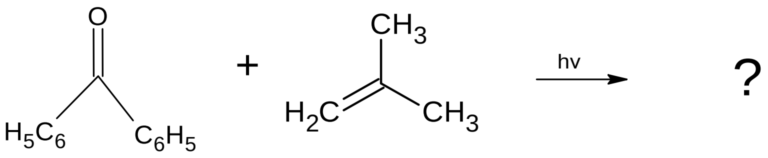
- We concluded that carbonyl compound photochemical reactions can be found in four basic photochemical processes. Cleavage or Norrish type – I Process for substrates with two bonds. The week bond will be the first to fail.
- An abstraction of intramolecular hydrogen bonds occurs when a bond to the carbonyl group must be cleaved during a photochemical reaction.
- The hydrogen atom will abstract from the oxygen of the carbonyl group if the reaction is intermolecular.
- The cycloaddition and cyclodimerisation reactions occur when carbonyl oxygen is added to a carbon-carbon double bond

4.13 SOME RELATED QUESTION: (SAQS TYPE QUESTION)

Question 2

A. Multiple choice

1. Major product of following reaction-



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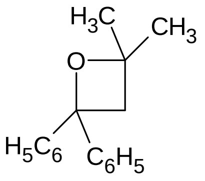

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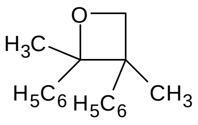

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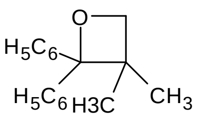

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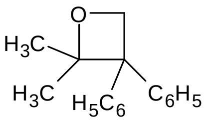
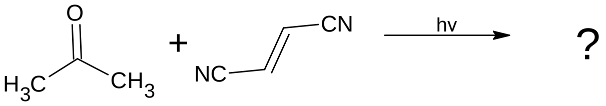


2. Major product of following reaction



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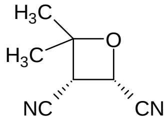

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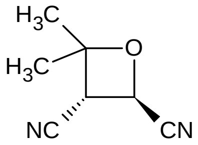

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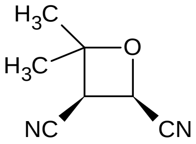

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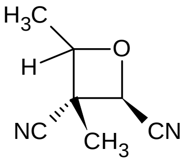
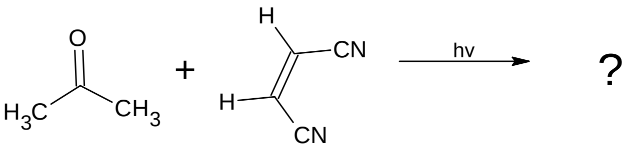


3. Major product-



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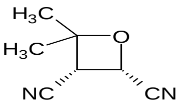

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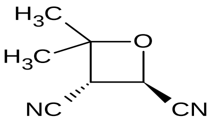

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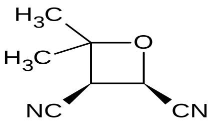

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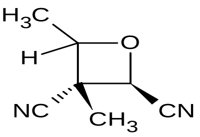
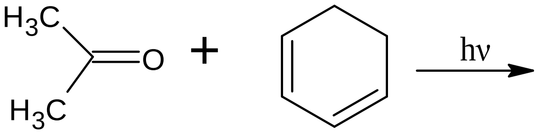


4. Product will be-



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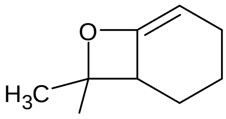

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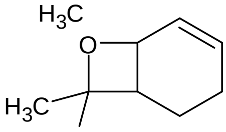
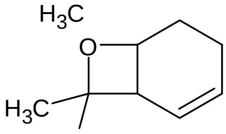


(c)



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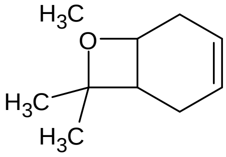
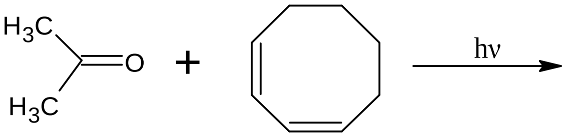
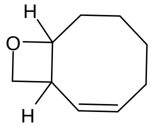


5. Product of the following reaction



(a)



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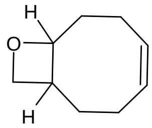

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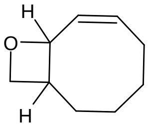

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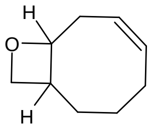

B. Fill in the blanks

a) A complex that is formed by the association of ground state of a molecule and the excited state of different molecule is called…………….

b) A complex that is formed by the association of ground state of a molecule and the excited state of same molecule is called…………….

C.True / False

a. Oxetane formation occurs in paterno-Büchi reaction. True/False

b. Photo reduction is a bimolecular reaction. True/False

Answers:

Question 1

A. 1. (a) 2. (b) 3. (b) 4. (d) 5. (a)

B. a. α- Cleavage, b. decarbonylation, c. 280nm

C. a. Intramolecular hydrogen abstraction, b. Norrish type II, c. primary process,

D. gas phase

E. a. false, b. true, c. true

Question 2:

A. 1.c 2.b 3.c 4.c 5.a

B. a. Exciplex, b. Excimer

C. a. True b. True

4.14 REFERENCE

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1. Carey, A., Sundberg,R. J., (2007) *Advanced organic chemistry structure and mechanism*, fifth edition, francies, Springer

2. Mukherji, S.M., Singh, S.P., (1996)*Reaction mechanism in organic chemistry*, Macmillan India Limited,

3. Gilbert, A., Baggott, J., (1991),*Essential of molecular photochemistry,* CRC Press, Boca Raton, Florida,

4. Coxon, J.M.,Halton, B., (1974), *Organic Photochemistry*, Cambridge University press, Cambridge

5. Singh, J., Singh, J., (2012), *Photochemistry and pericyclic reaction*, New age international publishers.

6. Mayo,P. D.,(1980), *Rearrangements in Ground and Excited States,* , Academic Press, New York,Vol.3, 622.

7. Klessinger, M., Michl, J.,(1995),*Excited States and Photochemistry of Organic Molecules*, VCH, New York.

8. Chen, X.B., Fang, W.H., Fang, D.C., (2003), *An ab Initio Study toward Understanding the Mechanistic Photochemistry of Acetamide,* J. Am. Chem. Soc., 125, 9689.

9. Bacchus-Montabonel,M.C., Vaeck, N., Lasorne, B. Desouter-Lecomte,M., (2003),

Photochemistry, Chem. Phys. Lett., 374, 307

10. Lasorne,B., Bacchus-Montabonel, M.C., Vaeck, N., Desouter-Lecomte, M.,(2004),*Nonadiabatic interactions in wave packet dynamics of the bromoacetyl chloride photodissociation,* J. Chem.Phys., 120, 1271

11. Menzel, J. P., Noble, B. B., Lauer, A., Coote, M. L., Blinco, J. P., Barner-Kowollik, C., (2017), *Wavelength Dependence of Light-Induced Cycloadditions,* Journal of the American Chemical Society, **139** (44), 15812–15820.

12. Protti, S., Fagnoni, M., (2009),*The sunny side of chemistryGreen synthesis by solar light,* Photochemical & Photobiological Sciences. 8 (11): 1499–516.

4.15 GLOSSARY

- Photo-Fries Reaction: The formation of a mixture of o-and p-acylphenols upon photolysis of phenol ester in solution.
- Di-π-Methane Rearrangement: Molecules having the di-π-methane moiety, i.e., having two π-systems bonded to a single sp3 carbon atom undergo a general liquid phase photochemical transformation to vinylcyclopropane, called the di-π-methane rearrangement.
- Oxa-Di-π-methane rearrangement: Di-π-methane rearrangement given by β, γ unsaturated ketone is known as oxa-di-π-methane rearrangement.

4.16 SUGGEST READING

1. S.M. Clegg, B.F. Parsons, S. J. Klippenstein and D.L. Osborn, J. Chem. Phys., 2003, 119, 7222.
2. Y. Chen and S. Ye, Int. J. Quantum Chem., 2004, 97, 725

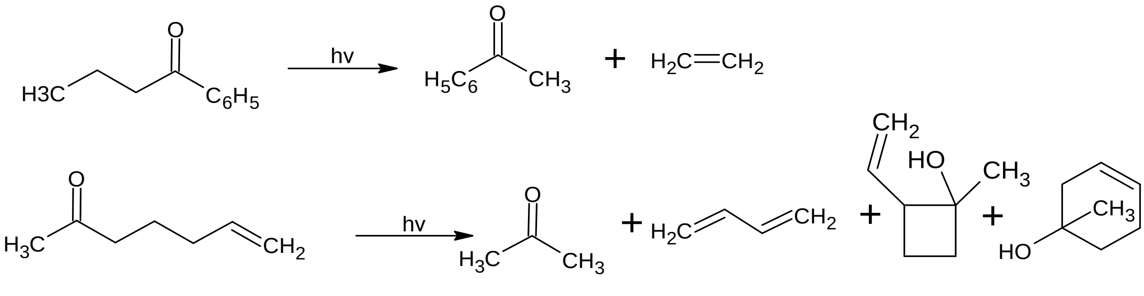
3. . E.D. Skakovskii, M.M. Ogorodnikova, L. Yu. Tychinskaya, V.L. Murashko, N.G. Kozlov and S.V. Rykov, J. Appl. Spectroscop., 2004, 71, 22.

4. D. Ng, Z. Yang and M.A. Garcia-Garibay, Org. Lett., 2004, 6, 645.

5. B. Sket, B. Kosmrlj, M. Harej and D. Dolenc, Tetrahedron Lett., 2003, 44, 4247.H.-M. Tai, M.-H. Huang and C.-C. Yang, J. Chin. Chem. Soc. (Taipei, Taiwan), 2003, 50, 441; (b) H.-M. Tai, M.-H. Huang and C.-C. Yang, Chem. Abstr., 2003, 139, 307897.

4.17 TERMINAL QUSTIONS

1. Carbonyl compound give mainly four types of photochemical reaction. Give name of the reaction with one example each?
2. What is paterno-Buchi reaction? Discuss its mechanism along with the stereochemical consequences?
3. What type of excitation are possible in a compound containing carbonal group on irradiation with UV light?
4. Give mechanism of the Norrish Type I process. How many types of carbonyl compounds give this reaction? Give one example for each compound.
5. Give mechanism of Norrish Type II reaction. Explain why cyclopropyl ketones are the most common class of compound for β-cleavage reactions?
6. Suggest mechanism for the following photoreactions



7. What will the product of the reaction when carvone camphor is irradiated with UV light in the presence of MeOH?

UNIT 5: PHOTOCHEMISTRY OF AROMATIC COMPOUNDS

CONTENTS:

5.1 INTRODUCTION

Aromatic hydrocarbons are a type of organic chemical present in the environment that is extremely reactive and produces enormous amounts of emissions. Aromatic species are thought to generate around 10% of total global anthropogenic nonmethane organic carbon (NMOC) emissions, with automotive exhaust from gasoline-powered vehicles accounting for the majority of this, as well as solvent use. Because such activities occur on a worldwide scale, the discovery that biomass burning is a large source of aromatics has gotten a lot of attention in recent years. Aromatic emissions from soils and plants have also been recognized as natural, small sources. Aromatic emissions will thus have an impact on tropospheric processes at the local, regional, and global levels. When emissions of volatile organic compounds (VOCs) and nitrogen oxides (NOx) are mixed under climatic conditions that promote smog formation, dangerous quantities of ground-level ozone and particle matter (PM) can be formed. In metropolitan environments, aromatic hydrocarbons contribute significantly to the generation of ozone and other photooxidants.

The percentage contribution of aromatic hydrocarbons to ozone formation has been estimated to be between 30 and 40%. With such a significant contribution, aromatic hydrocarbons would be the most important hydrocarbon class in photochemical ozone production. However, it is important to remember that the oxidation mechanisms of aromatic hydrocarbons are still unknown, and therefore such figures must be verified. Aside from their high photochemical reactivity in the atmosphere, which has a significant impact on the formation of tropospheric ozone and the oxidizing capacity of the atmosphere, it is now well established that aromatic compounds' photochemistry results in the formation of secondary organic aerosols (SOAs), which are known to be harmful to human health, reduce visibility, and contribute to climate change. In fact, studies have revealed that the aromatic percentage of gasoline can account for the whole gasoline vapors atmospheric organic aerosol production potential. The development of SOAs becomes more pronounced as aromatic emissions become concentrated in urban areas, where many people live and work. In terms of health impacts, benzene, a common aromatic environmental pollutant, is hematotoxic, clastogenic, and leukemogenic in humans, and causes bone marrow damage and cancer in animals. The cause of benzene's carcinogenesis is yet unknown; however the US Environmental Protection Agency has categorized it as a Group-A human carcinogen.

Photooxidation of other aromatic hydrocarbons results in the generation of mutagenic chemicals, according to laboratory investigations. Aromatic hydrocarbons are a type of organic chemical that can be found in the atmosphere. Aromatic species are thought to generate around 10% of total global anthropogenic nonmethane organic carbon (NMOC) emissions, with automotive exhaust from gasoline-powered vehicles accounting for the majority of this, as well as solvent use. Because such activities occur on a worldwide scale, the discovery that biomass burning is a large source of aromatics has gotten a lot of attention in recent years. Aromatic emissions from soils and plants have also been recognized as natural, small sources. Aromatic emissions will thus have an impact on tropospheric processes at the local, regional, and global levels.

For a long time, benzene and its derivatives have been investigated in depth. Experiments eventually discovered that benzene is also capable for photochemical reactions. The electronic transition in benzene is known to occur between 230 and 270nm, which corresponds to an energy value of roughly 448.0kJmol-1, and since this value surpasses the resonance energy of benzene (36kcals or 151.2kJ mol-1).When benzene is exposed to electromagnetic radiation of the above wavelength, it appears that a photochemical reaction occurs, with the creation of compounds that are not aromatic in nature. In fact, aromatic compounds undergo transformations of numerous benzene derivatives, yielding unexpected results that contradict aromatic compounds' thermal stability.

Furthermore, photochemical rearrangements of benzene derivatives afford direct paths to a number of highly strained compounds. In their excited singlet and triplet states, photo-induced aromatic compounds undergo a variety of chemical reactions. In most situations, photochemical reactions include triplet states with relatively lengthy life periods. Isomerization, [2+2]- and [4+2]- cycloadditions, hydrogen abstraction and addition, electrocyclization, dimerization, oxidation, substitution, and rearrangement reactions are the most common photochemical reactions of aromatic compounds. With several instances, the regio- and stereoselectivity of cycloaddition reactions of aromatic compounds with alkenes, allenes, and dienes is highlighted. The oxa- and aza-di-methane rearrangements, as well as the photo-Fries rearrangement, are studied in depth.

The mechanism and stereoselectivity of the photo-induced Diels–Alder reaction are described. When it comes to benzene, its absorption ranges from 180 to 200 nanometers, with one set of bands, 200 to 220, with another set of bands, and 220 to 250, with still another set of bands. All of them belong to the PI-PI-Star excitation band, which corresponds to electronic excitation and progresses from S_0 to S_1, and S_2 states as the wavelength lowers and the energy increases, corresponding to excitation. The principal photochemical processes of Benzene and its derivatives can be divided into the following categories. One can expect intermediate states, which are Zwitter ionic in nature, from the first excited Singlet state, which is a PI-PI-Star state. Once created, the Zwitter ionic intermediate is transferred to the end product. There is strong evidence for the participation of the Zwitter ionic intermediate, which was discovered through a trapping experiment. The initial excited Singlet state, which is a PI-PI-Star excited state, can also travel to the product by a funnel mechanism, which is a concerted mechanism, without the need for any intermediates. Finally, the Triplet excited state, PI-PI-Star state, can go through an intermediate step, a Diradical state, which leads to the production of the product. In the following slides, we'll see examples of each of these cases.

5.2 OBJECTIVES

After learn this unit you able to-

- Photochemistry is the chemistry of electronic excited states of organic molecules these states are generated by irradiating the molecules by Uv or Visible light.
- This unit comprises the detailed study of the singlet and triplet state of organic molecule these have different physical properties and chemical reactivity the product obtained at the end of photochemical reactions unexpected and entirely different from those obtained in thermal reactions, typical photochemical reactions include isonmerisation around carbon-carbon double bonds, molecular rearrangements, fragmentations, inter and intera molecular hydrogen abstractions, cycloadditions and dimerisations.
- After that you will be able to benzene and its various excited states.
- Photochemical addition reactions of aromatic compounds.
- You also will be able to known photochemical substitution reaction of aromatic compounds.
- And end of the unit you will be learn about thephotochemistry of diazo compounds.

5.3 BENZENE AND ITS VARIOUS EXCITED STATES

Consider the benzene exited states for a better understanding.The state T_2 is formed when liquid benzene is bombarded with electromagnetic radiation having a wavelength less than 205 x 10^{-9} metre. The 265 singlet state T_1 is then transformed to a new vibrationally excited state. Bicyclo hexenyl biradical is produced in this condition.

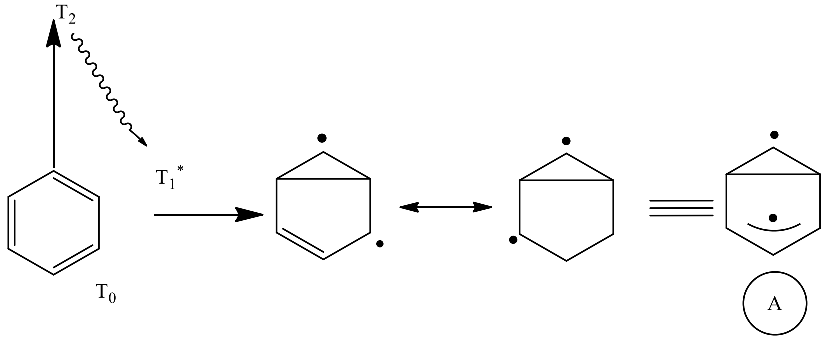


Fig. 5.1 Benzene and its various excited states.

When substituted benzenes are irradiated, various extremely stretched compounds (Dewar benzene, prismane, and so on) have been formed. The strained systems are photochemical isomerisation of substituted benzene reaction intermediates. The nature of these intermediates is influenced by the state of the aromatic starting material as well as the wavelength of light employed in photochemical reactions. Thus

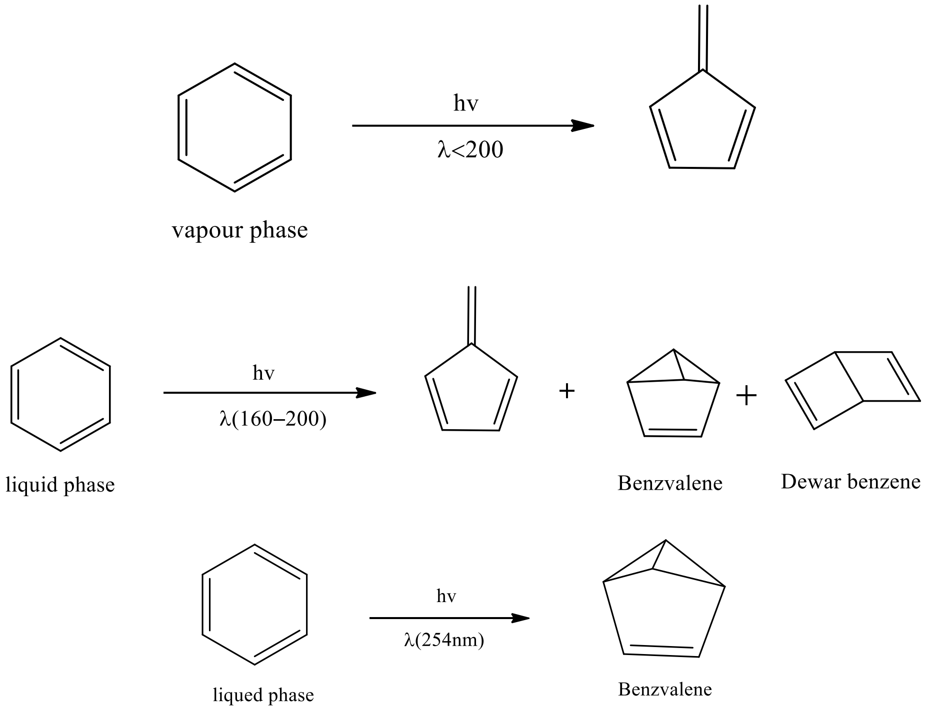


Fig. 5.2 Isomerisation of Benzene

In contrast to the thermal stability of aromatic compounds, the foregoing photochemical rearrangements of the benzene molecule provide paths to several extremely strained molecules.

5.3.1 Isomerisation of Aromatic compounds

Aromatic hydrocarbons with one ring undergo a variety of photochemical rearrangements, causing the formation of different isomers. When o-xylene is irradiated, it produces a combination of 1,2, 1,3 and 1,4 di methyl benzene, for example.

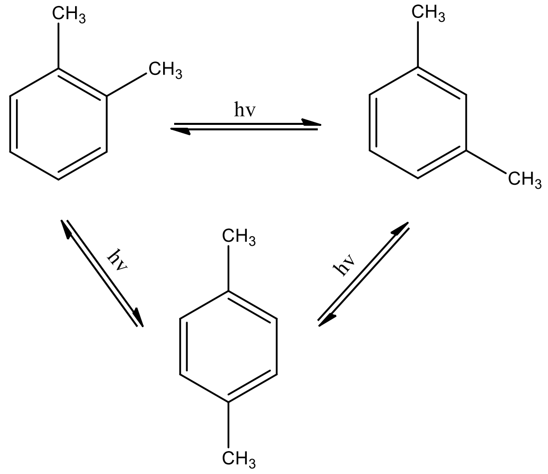
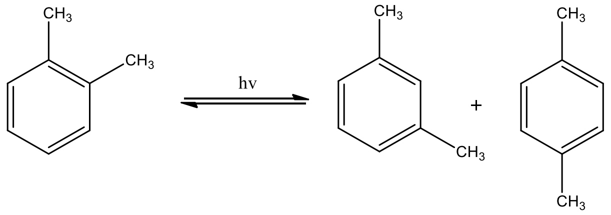
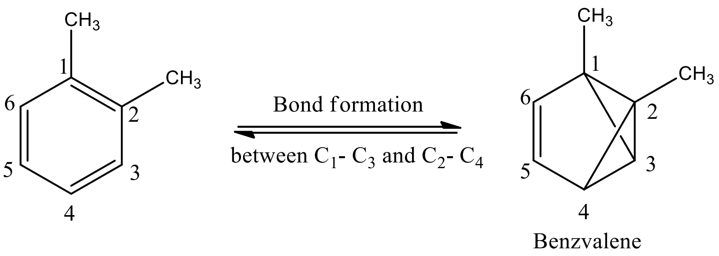


Fig.5.3 Isomerisation of O-Xylene

It can be seen that the 1,2 -xylene group (-CH_3) shift happens in the conversion of O - xylene to m - xylene and the conversion of m - xylene to p - xylene. The shift of the -CH_3 group is required for conversion of o -xylene to p -xylene and vice versa. It has been discovered that 1,2 alkyl shift happens via intermediates such as benzvalene & prismane.



5.3.2 Mechanism of 1,2-shift by benzvalene intermediate



The ring carbons of benzvalene are now reorganised via bond cleavage between C1 - C2 and C3 - C4, followed by bond formation between C1 -C3 and C2 - C4, viz.

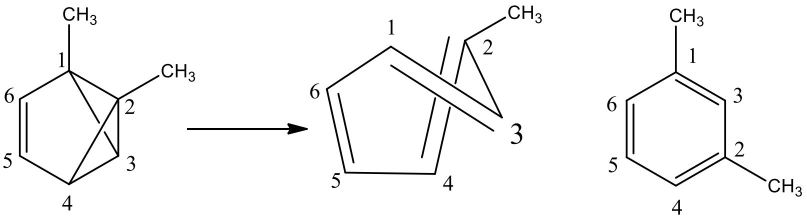
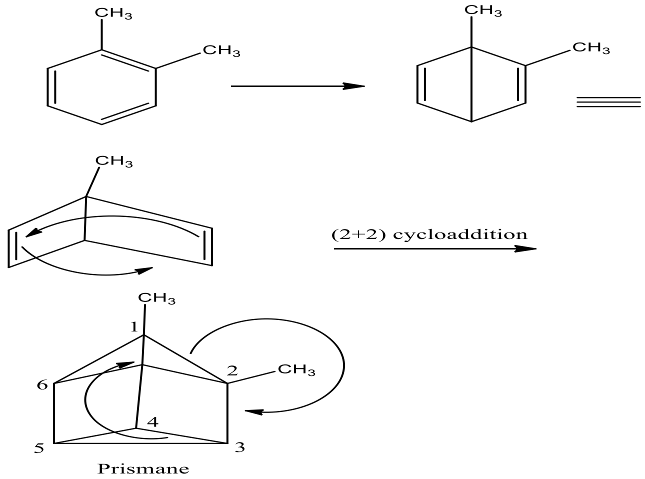


Fig. 5.4 Mechanism of 1,2-shift by benzvalene intermediate

5.3.3 Mechanism of 1,2-alkyl shift through prismane intermediate

This mechanism is shown in the diagram below.



Now, as illustrated below, this prismane undergoes ring rearrangement by breaking the links between C1 - C2 and C3 - C4, followed by the creation of bonds between C2 - C3 and C1 - C4.

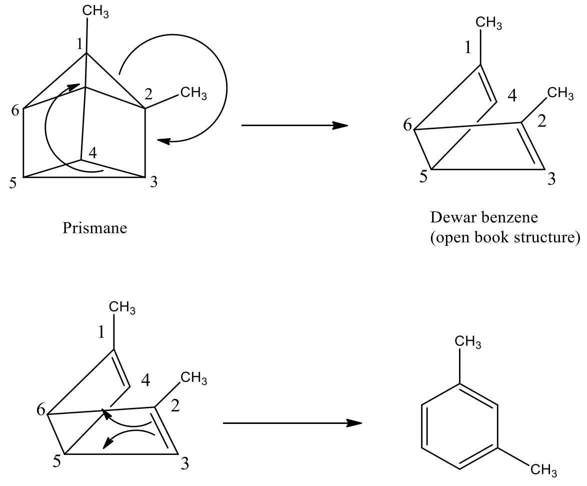
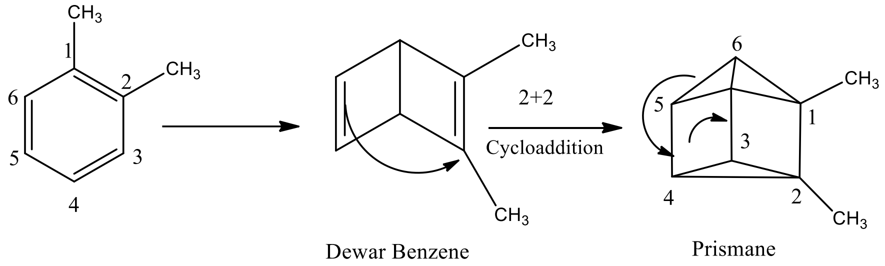


Fig. 5.5 Mechanism of 1,2-alkyl shift through prismane intermediate.

5.3.4 Mechanism Of 1,3 Alkyl Shift Through Prismane

It is known that 1, 3-alkyl shift takes place through the formation of prismane as an intermediate. This is shown below.



As shown below, the substituted prismane undergoes ring reorganisation by breaking bonds between C3-C4 and C5-C6, followed by bond formation between C3-C6 and C4-C3 atoms.

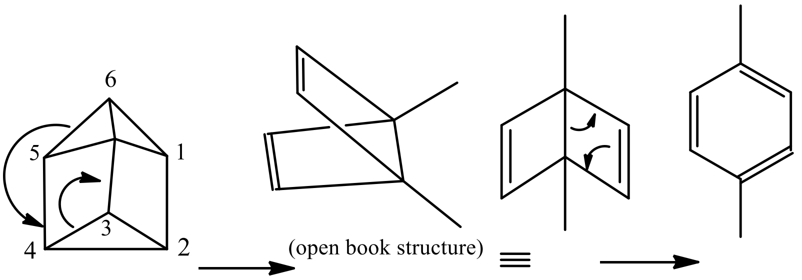
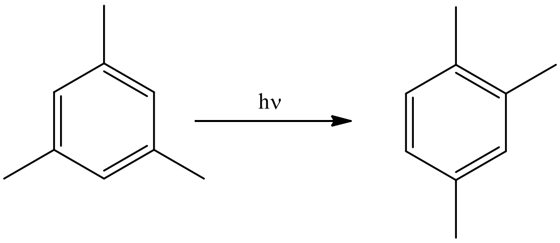


Fig. 5.6 Mechanism of 1,3 alkyl shift through prismane

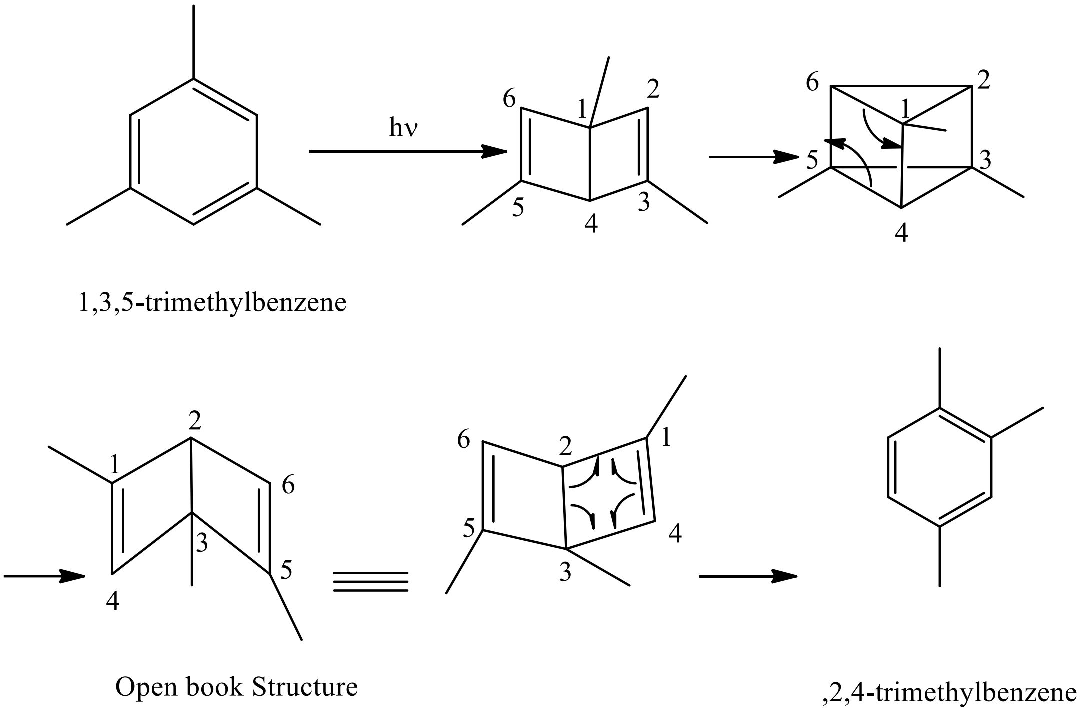
5.3.5 Photochemical isomerisation of trisubstituted benzene

The photochemical isomerisation of 1,3,5-trimethylbenzene to 1,2,4-trimethylbenzene, which occurs via a 1,2-alkyl group shift, is a fascinating photochemical reaction. Tracer method with C_{14} labelling was used to thoroughly investigate the process.

The overall reaction is,



The reaction's mechanism entails the following pathway.



The photochemical conversion of 1, 3,5-tri-t-butyl benzene to 1,2,4-tri-tbutyl benzene is fraught with difficulties. It is depicted in the diagram below.

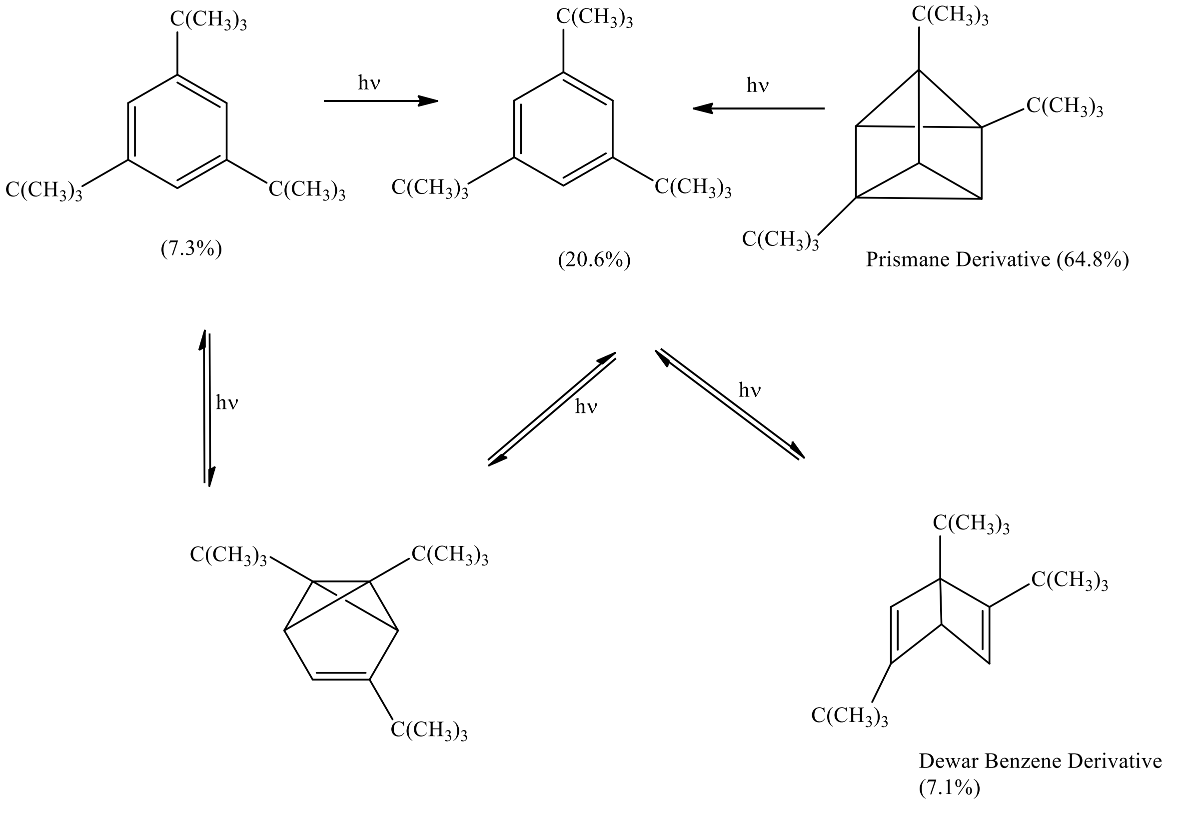
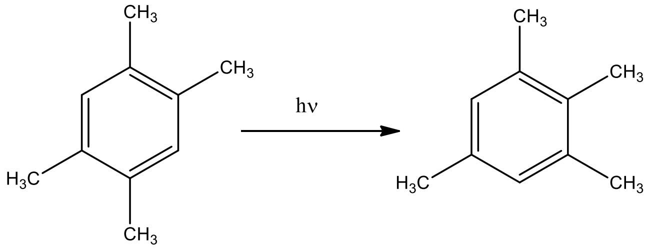


Fig.5.7 Photochemical Isomerisation Of Trisubstituted Benzene

A photostationary state (a form of pseudo equilibrium) is clearly established in this procedure. This equilibrium includes all of the species in the reaction, including the two tri-t-butyl reactants and products, as well as the intermediates in benzene derivatives, prismane derivatives, and dewar benzene derivatives. Below them is listed the percentage of various species.

5.3.6 Photochemical Isomerisation Of Tetra substituted Benzene:

Photochemical isomerization occurs in tetrasusbtituted benzene, namely 1,2,4,5 tetramethylbenzene, which is transformed to 1,2,3,5-tetramethylbenzene. The following is the general reaction:



The following method demonstrates the mechanism of the given photochemical reaction.

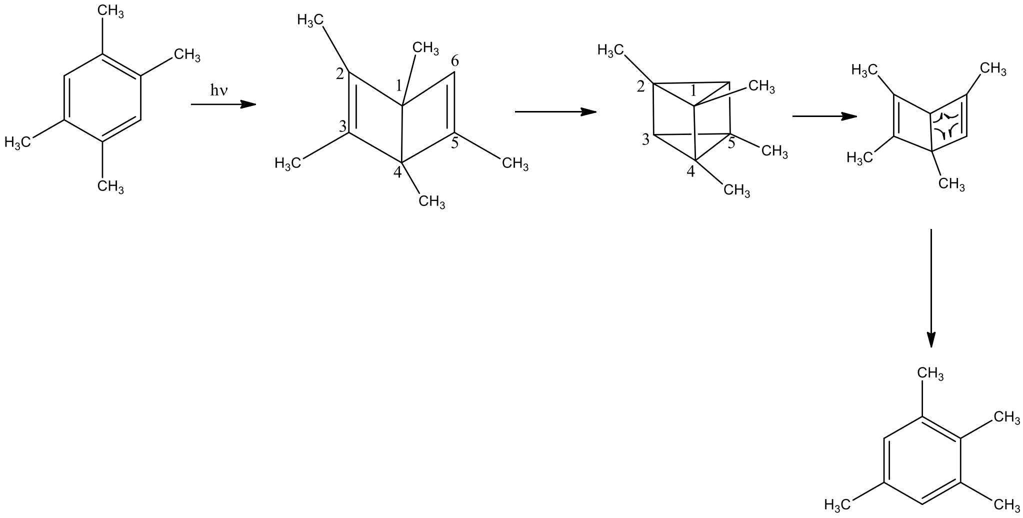


Fig.5.8 Photochemical Isomerisation of Tetra substituted Benzene

Prismanes and Dewar benzene derivatives are clearly involved in this isomerization.

5.4 PHOTOCHEMICAL ADDITION REACTIONS OF AROMATIC COMPOUNDS

In the S_1 state, benzene and its derivatives perform cycloaddition reactions with a variety of π (pi) systems, particularly alkenes, alkynes, and dienes. Because the T_1 state of aromatic compounds is quenched by the transfer of excitation energy to the alkene, cycloaddition processes are not possible. Under certain structural and electronic/scircumstances a reverse model, i.e., S_1 alkene + S_0 arene prevails. Cycloaddition processes have been reported in three different modes: 1, 2 or ortho, 1, 3 or meta, and 1, 4 or para. The 1, 4-addition is the cycloaddition reaction with the lowest efficiency. These reactions might take place on a bimolecular or intramolecular level. Photochemical addition processes are discovered to be reversible in nature. Because a cyclic molecule is generated as a final product, these reactions are known as cycloaddition reactions. when a mixture of olefin is irradiated with light of apporopriate wavelength, large variety of products are obtained The addition takes place at 1,2-1,3 and 1,4 position of benzene ring. For these reactions, four types of mechanisms have been proposed: -

1. The excited state of an aromatic compound reacts with the ground state of an alkene.
2. The excited state of an olefin reacts with the ground state of an aromatic participant.
3. Conversion of an excited aromatic chemical to a biradical intermediate that interacts with an olefin to form the final product.
4. Charge-transfer complexes or electron transfer are used to create reactions between polar species.

To produce reactions between polar species, charge-transfer complexes or electron transfer are utilised.

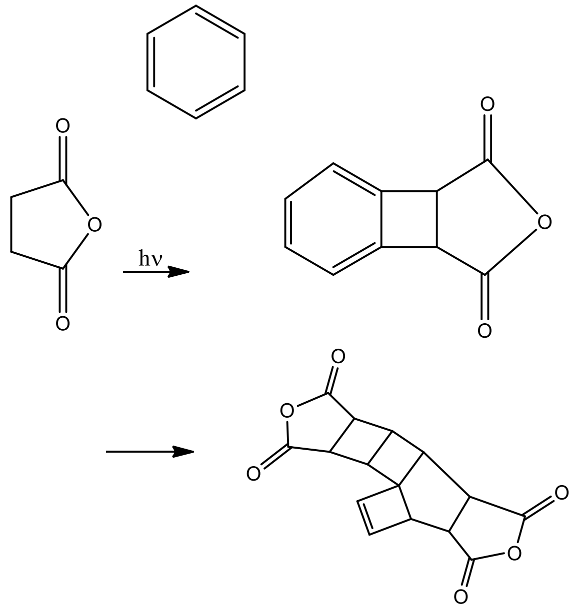


Fig.5.9 Photochemical Addition Reactions Of Aromatic Compounds

With mono and disubstituted benzenes, a similar reaction is observed to proceed via a charge transfer complex involving benzene and the maleic anhydride, but with a delayed kinetics due to steric hindrance by the substituent (S) present on the benzene ring. However, no reaction occurs with substantially substituted benzenes.

5.4.1 [1, 2]-Photochemical Addition Reactions Of Aromatic Compounds

In addition to some 1, 4 products, electron poor alkenes (alkenes with electron withdrawing groups) give a 1, 2-addition reaction with arenes. The secondary product is the para product. Donor-acceptor contact is often beneficial to the creation of the ortho product. The longer the fraction of ortho and para cycloadditions, the more polar the contacts (charge-transfer) in the exciplex.

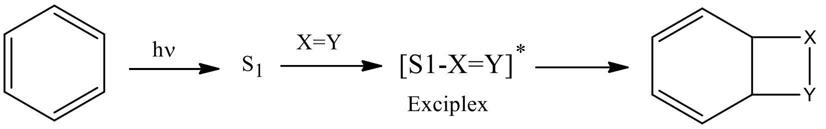


Fig.10 [1, 2]-Photochemical Addition Reactions Of Aromatic Compounds

The reactions of 1, 2-cycloaddition are coordinated reactions. In the liquid phase, photocycloaddition of cis and trans-2-butene to benzene produces the 1, 2-adduct stereospecifically, indicating that the reaction is concerted. This also proved that the product is formed by the creation of exciplex.

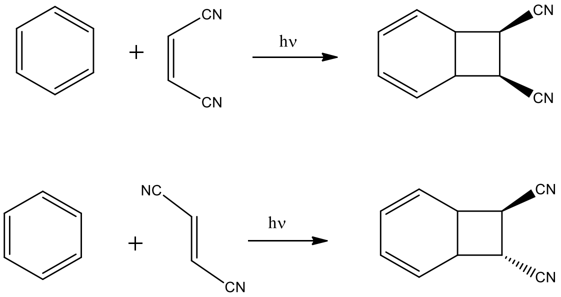
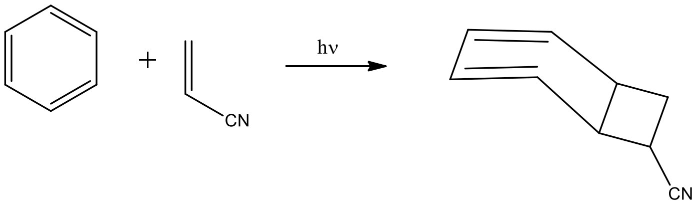
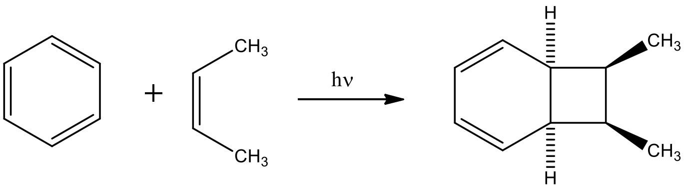


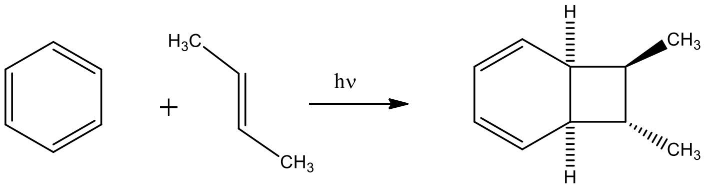
Fig.5.11 Cis Alkene & Trans Alkene Addition

As a result, benzene and its derivatives form charge transfer complexes (exciplexes) with dienophiles and produce ortho-cycloaddition adducts when exposed to irradiation. Exo orientation is common for the adduct.



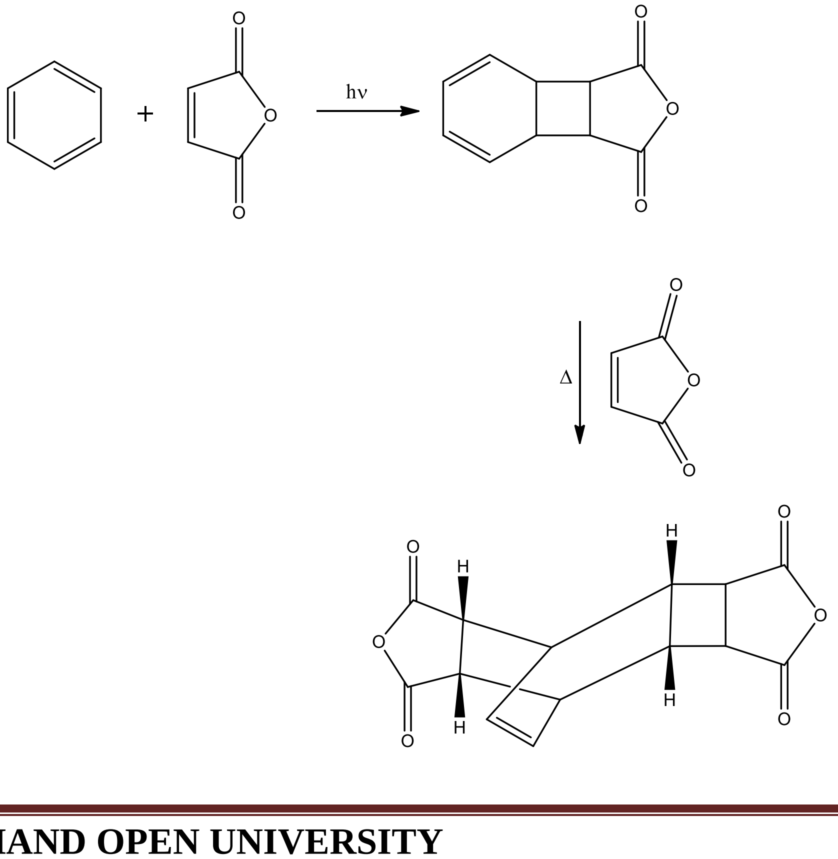
When light is shone on benzene (liquid) and 2-butane (Cis or Trans), 1,2 photoaddition occurs. It's worth noting that the stereochemistry of 2-butene is preserved in this reaction. This demonstrates that the reaction is stereotypical and coordinated.





The photo-excited alkene combines with ground state benzene in the aforementioned reaction, and because the stereochemistry of the alkene is preserved, the process must be concerted. The following photochemical addition is similar.

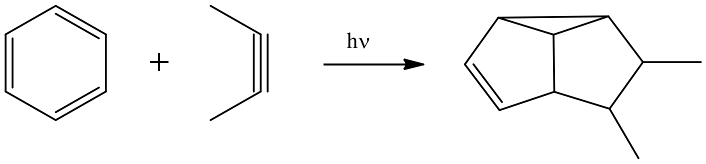
When benzene is irradiated in the presence of maleic anhydride, an exo 1, 2-cycloadduct is formed. The production of the product occurs in the S1 state of a charge transfer complex. A photochemical | 2 + 2 | ortho-cycloaddition reaction is followed by a thermal | 4 + 2 | cycloaddition to produce the exo-1, 2-adduct.



The ortho cycloaddition products are the principal products of irradiating alkynes, especially those having electron-withdrawing groups, with benzene. At room temperature, these adducts are frequently unstable.

5.4.2 [1, 3]-Photochemical Addition Reactions of Aromatic compounds:

The creation of a tricyclic system is caused by the insertion of an olefinic double bond across the meta position of benzene during the 1,3 addition. Viz-



Only when alkyl substituents are present across the double bond in an olefin, such as in 2-butene (as illustrated above), norbornene, cyclobutene, allene, and other olefins, does the aforementioned reaction occur. It can be found in both liquid and gaseous forms. The olefin's stereochemistry is preserved, and the signlet excited state of benzene is implicated. It's worth noting that the reaction proceeds in the opposite direction of the production of the prefulvene biradical, with no involvement of fulvene or benzvalene. Following method is the finest technique to demonstrate the mechanistic route.

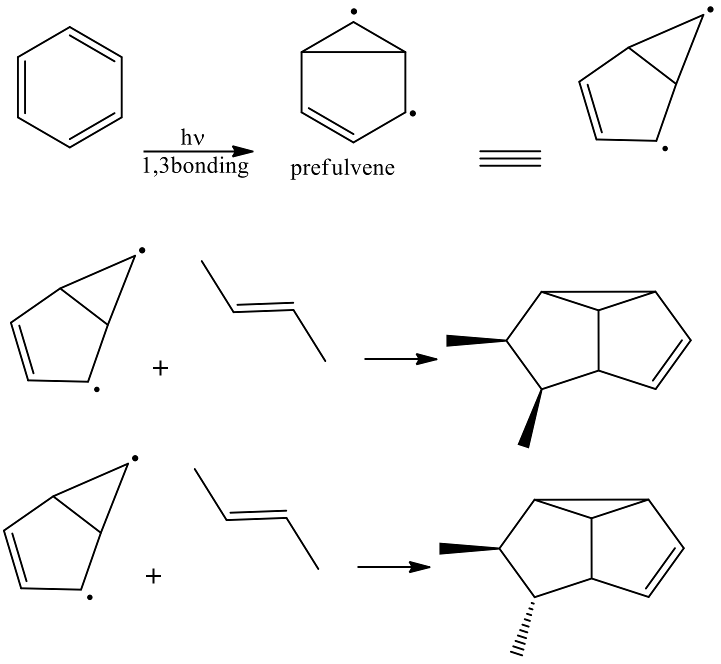


Fig.5.12 [1, 3]-Photochemical Addition Reactions of Aromatic compounds

Benzene also adds to cyclooctene in the following way.

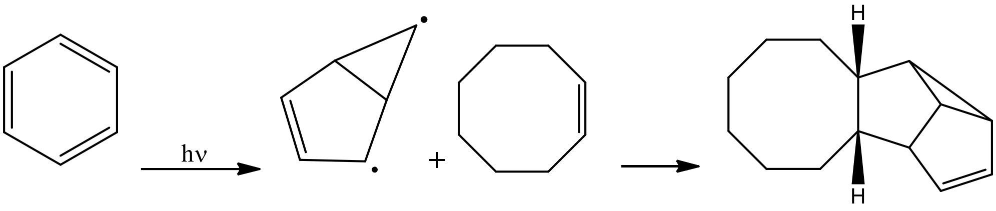


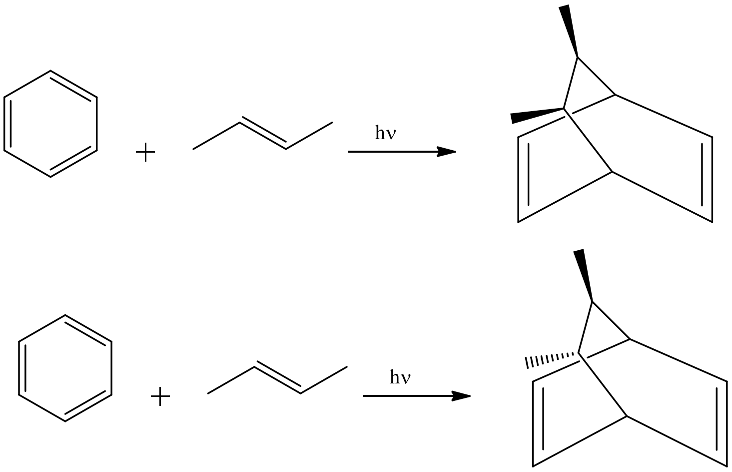
Fig.5.13 Addition of Benzene to cyclooctene

When an olefinic side-chain is present on the benzene ring as a substituent, it is sometimes found that an intramolecular addition occurs. When 6-phenylhex-2ene is irradiated, for example, the following product is formed.

An olefinic double bond has been added across the meta-positions of a benzene ring as a result of this extraordinary mechanism, resulting in a tricyclic system.The reaction appears to be limited to alkyl substituents on double bonds such as 2-butene, norbornene, allene, and cyclobutene. In both the gaseous and liquid phases, it occurs with 254 nm light. It involves singlet excited benzene and is stereospecific. Neither fulvene nor benzvalene are known to be precursors. The creation of prefulvene biradical leads to the formation of the product. The endo product is the most important product in a 1, 3-cycloaddition reaction.

5.4.3 [1, 4]-Photochemical addition reaction of aromatic compounds

The olefin is added at the para position of benzene in these types of photochemical reactions. The reaction takes place in benzene's singlet excited state and is stereospecific, meaning the olefin's stereochemistry is preserved. Because benzene acts as a diene in these reactions, they are similar to Diels-Alder reactions. Viz.



Butadiene undergoes [4+4] cycloaddition when irradiated with benzene, and the reaction is found to be stereospecific in nature. viz-

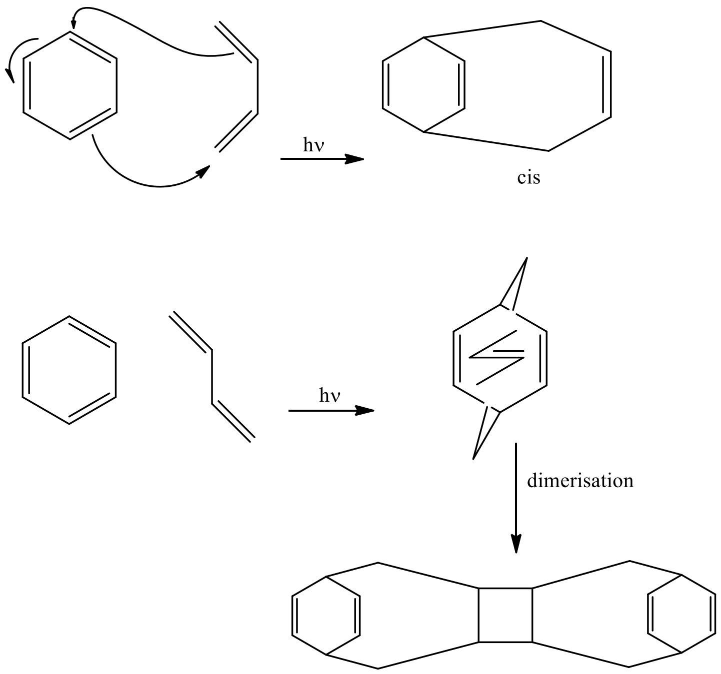


Fig. 5.14 [1, 4]-Photochemical Addition Reaction of Benzene.

Benzene and its simple homologues are not the only olefinic systems that can be photoadditioned. Condensed aromatics like naphthalene, phenanthrene, and anthracene go through a similar process. The cycloaddition of anthracene is [4 + 2], while that of phenanthrene and naphthalene is [2 + 2].

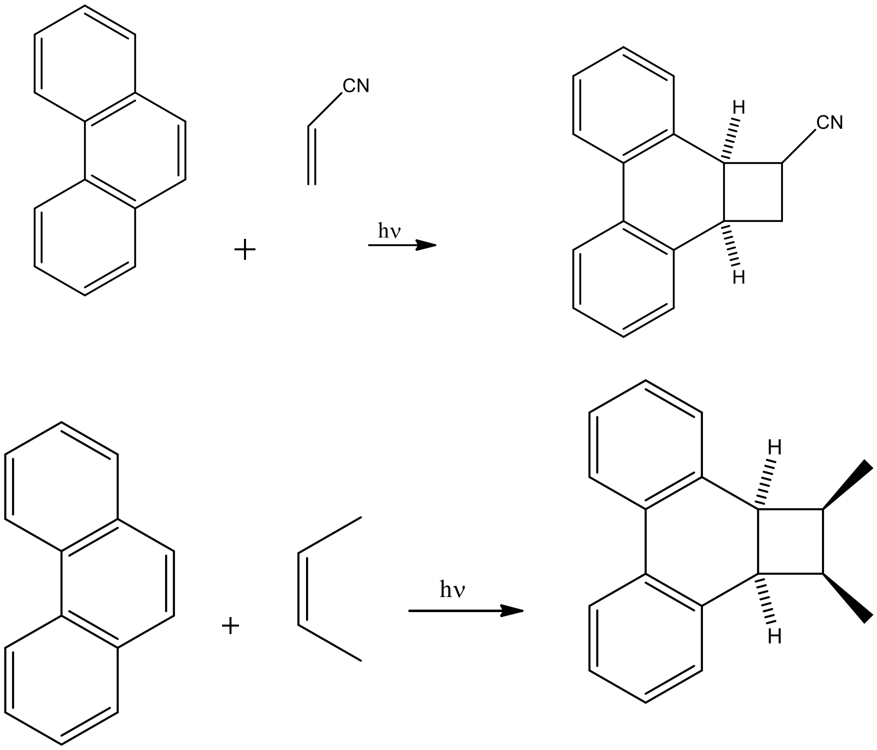


Fig. 5.15 Cycloaddition of Anthracene

5.4.4 Photochemical addition of Oxygen:

Peroxides are formed when condensed ring systems, such as nepthalene and anthracene, are photochemically combined with oxygen. The character of the final product, for example, is determined by the substituents present in the aromatic system.

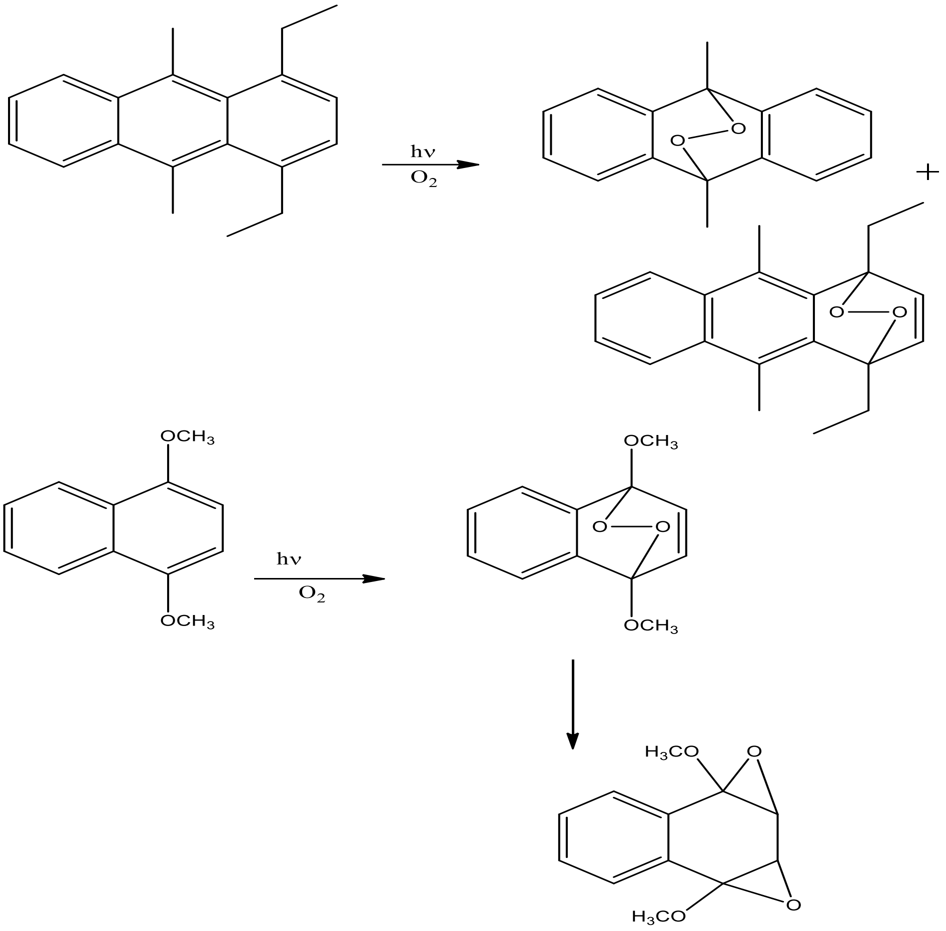


Fig.5.16 Photochemical Addition of Oxygen.

Dynamical studies of this photochemical reaction have revealed that the triplet excited state of aromatic hydrocarbon first excites oxygen molecule via energy transfer, resulting in the production of singlet oxygen. This singlet oxygen now reacts thermally with the aromatic hydrocarbons ground state. As a result, the reaction is a [4+2] cycloaddition. When transannular peroxides are excited in the presence of oxygen, polynuclear aromatic hydrocarbons such as naphthalene and anthracene are formed, and the site of attack is substituent dependant. Mechanistic investigations show that the hydrocarbon's triplet excited state stimulates oxygen into its 1 g state via energy transfer, and the singlet oxygen created thermally contributes to the ground state hydrocarbon. As a result, the reaction is a cycloaddition reaction [4 + 2].

5.4.5 Photochemical dimerisation reactions of aromatic hydrocarbons

Some typical photochemical dimerisation reactions have been seen in the presence of large concentrations of aromatic compounds. Consider the photodimerization of napthalene and anthracene, as well as the reaction of anthracene.

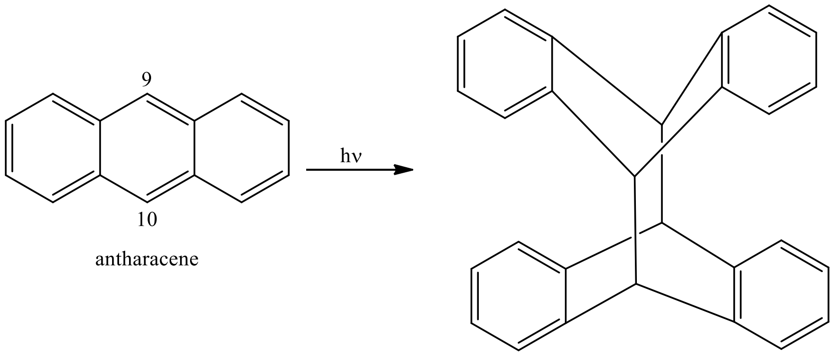


Fig. 5.17 Photochemical dimerisation reactions of aromatic hydrocarbons.

At the 9, 10-positions, two anthracene molecules are added together. A head to tail dimer is formed when a substituent is present at the 9-position of anthracene. The wavelength of the light utilised in the photochemical process has been discovered to affect dimerisation. Shorter wavelength radiation causes photochemical cleavage of the dimer formed, but longer wavelength radiation causes other processes. Shorter wavelength radiation is coupled with high energy; hence it causes photochemical cleavage of the dimer formed.

When 9-nitroanthracene is irradiated with long wavelength light, the result is a dimer; however, when the same procedure is carried out with shorter wavelength light, the result is nitric oxide (NO), anthraquinone, anthraquinone monoxime, and 10,10/ - bianthrone. These products are thought to be made from a 9-anthryl nitrile intermediate. The following is a representation of the reaction.

It's worth noting that the electron distribution in an aromatic compound's excited and ground states is considerably different. The dissociation constants of phenyl in its excited and ground states can be compared to demonstrate this. The pKa values for 2-nepthol and 2-nepthylamine are shown in the table below. The discrepancy between the readings in the S_0 and S_1 states indicates a significant change in electron density in these states.

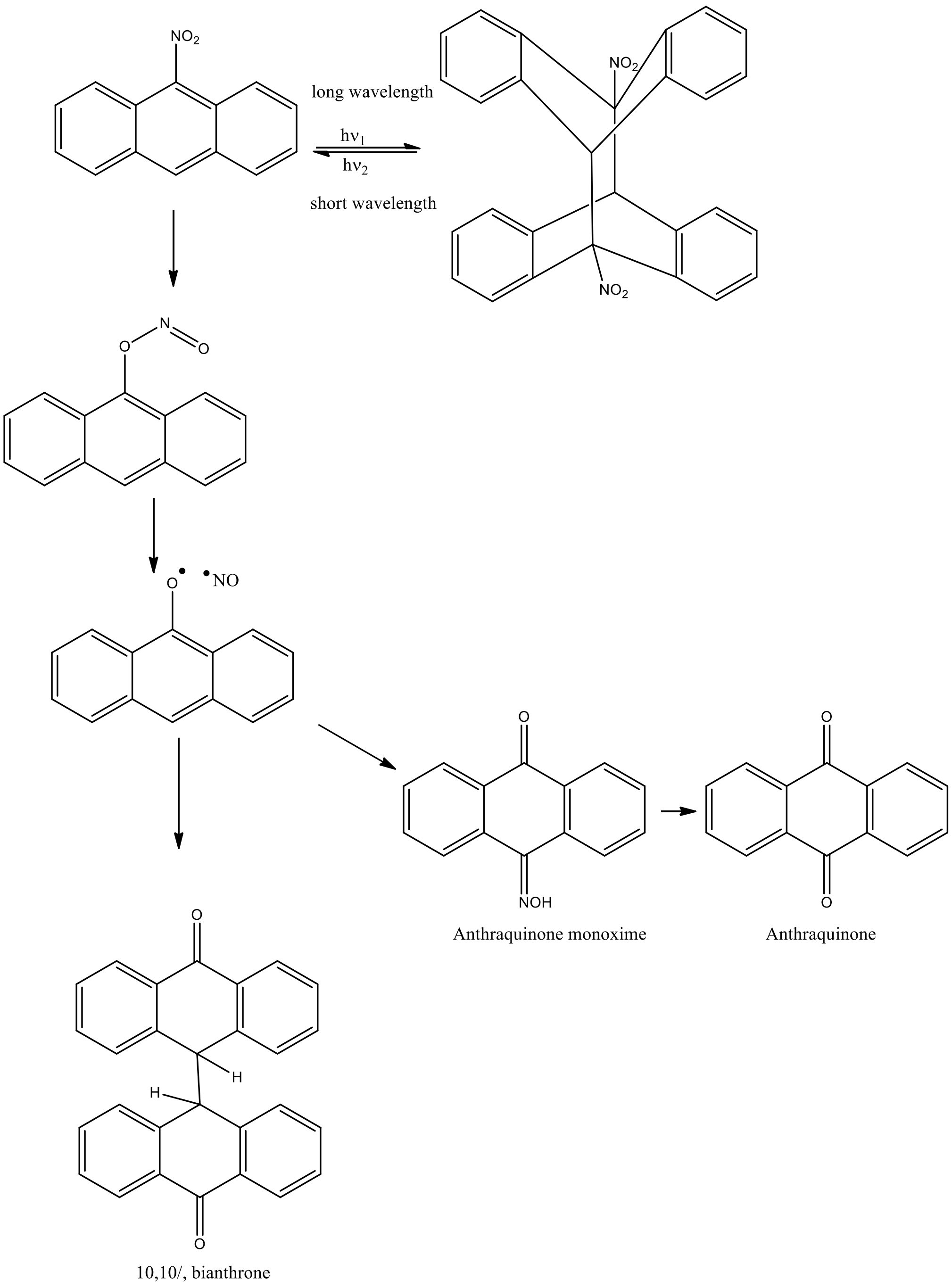


Fig. 5.18 Dimerisation Reactions of Aromatic Hydrocarbons.

5.5 PHOTOCHEMICAL SUBSTITUTION REACTION OF AROMATIC COMPOUNDS

In aromatic compounds, light-induced substitution can occur on a ring carbon atom or on an atom of a substituent. The heterolytic or radical mechanisms can be used to carry out these substitution reactions. Heterolytic substitutions are the most prevalent reactions, and they can be divided into two categories:

Type A: The orientation rules in these reactions are different from those in the ground state.

Type B: In these reactions, the orientation rules are the same as in the ground state, but light absorption speeds up the process. All these reactions seem to be functions of the lowest singlet excited state, and many proceed in high quantum yield. Substitution reactions can be carried out photochemically in the aromatic ring or in the side chain of the ring. The bond in the substrate molcule can be cleaved either homolytically or heterolytically in these processes.

The quantum yield of such a process is discovered to be extremely high, and it involves the lowest singlet state.The distribution of charge in the ground and excited states of the molecule differs significantly, as previously stated. Thus, in photochemical reactions, the position of the nucleophile can be controlled, resulting in substitution reactions, which are explained in depth on the following pages. All these reactions seem to be functions of the lowest singlet excited state, and many proceed in high quantum yield.

5.5.1 Nucleohilic substitution:

The attacking nucleophile is activated at ortho and para position Viz when the -NO2 group is seated on the benzene ring, as is recognised in general chemistry.

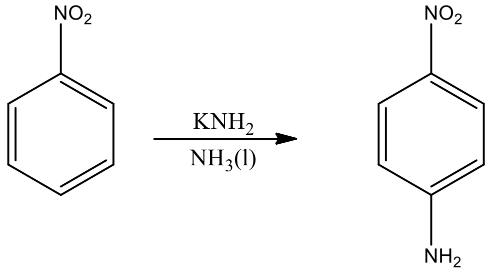


Fig.5.19 Nucleohilic substitution by amine group

However, it has been discovered that the -NO_2 group acts as a Meta directing group during photochemical reactions involving excited states.

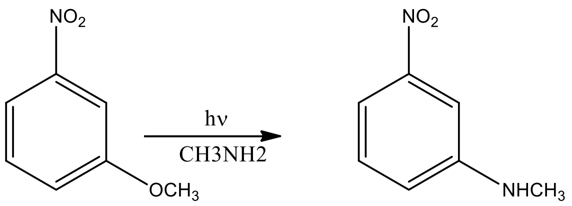


Fig. 5.20 Nucleohilic substitution m-position

When heated with -OH ions, the molecule 3,4-dimethoxynitrobenzene becomes 4-hydroxy-3-methoxynitrobenzene, in which the -OCH_3 group at position 4 is replaced by the -OH group.

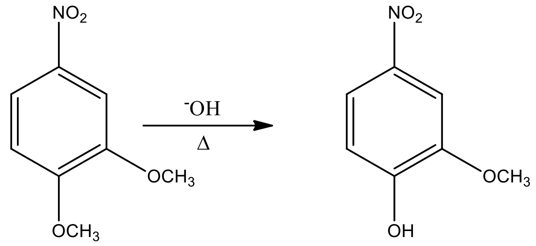


Fig. 5.21 Nucleohilic substitution.

When the same reaction is carried out photochemically, that is, by irradiating with UV light, the -OCH_3 group in the 3-position is replaced by the OH group. ie.,

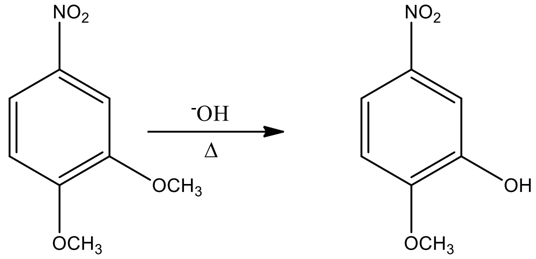


Fig. 5.22 Nucleohilic substitution.

The explanation for this behaviour is that the -NO_2 group makes ortho and para positions of the ring positive under the influence of heat due to its -I and -M action, whereas ortho and meta positive become positive under photochemical conditions compared to para position.

When the cyano group is present on nepthalenes and substituted nepthalenes, similar reactions occur.

5.5.2 Electrophillic substitutions

Photochemical electrophonic substitution of substituted benzene might yield unexpected results. As an example,

Under normal thermal settings, the -CH_3 group is ortho and para directing, but when toluene is irradiated in the presence of CF_3COOD, m-deuterio substituted toluene is produced as a main product viz.

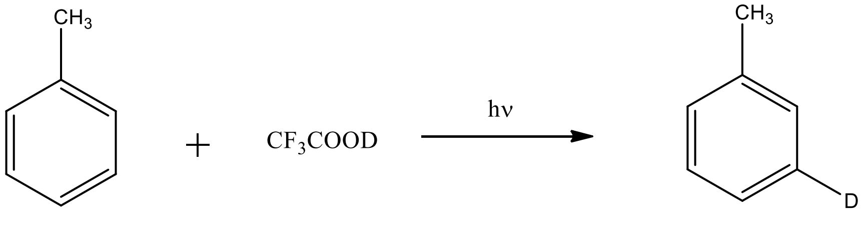


Fig. 5.23 Electrophillic substitutions.

When the identical reactions are performed with anisole and nitrobenzene, an unexpected result is produced, as illustrated below.

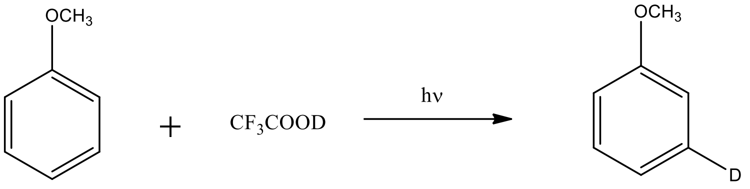


Fig. 5.24 Electrophillic substitutions of methoxy benzene.

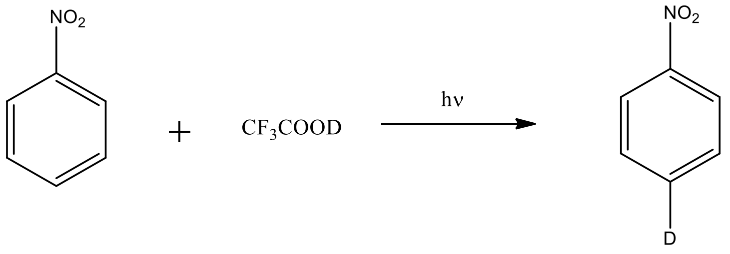


Fig. 5.25 Electrophillic substitutions of nitro benzene.

As a result, it may be stated that in photochemical reactions, the orientation of distinct groups changes. The paraposition is activated by the nitro group, whereas the Meta position is activated by the methoxy group.

The change in the change distribution in the ground and excited state of the ring of the point of attack can be explained by reorganising the orientation rules for electrophillic and nucleophillic susbtitution by considering the change in the change distribution in the ground and excited state ie S0 S1. Because an electron withdrawing substituent lowers the electron density at the m-position, it works as an m-directing group for the nucleophilic substituent that follows.

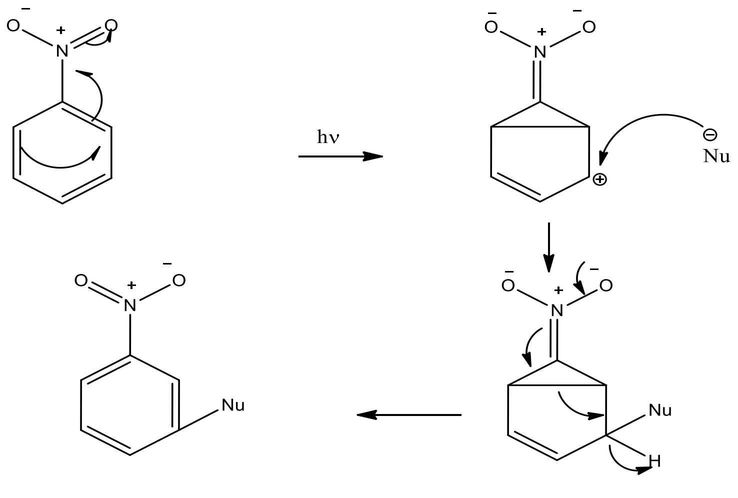


Fig. 5.26 Mechanism of photonucleophilic substitution

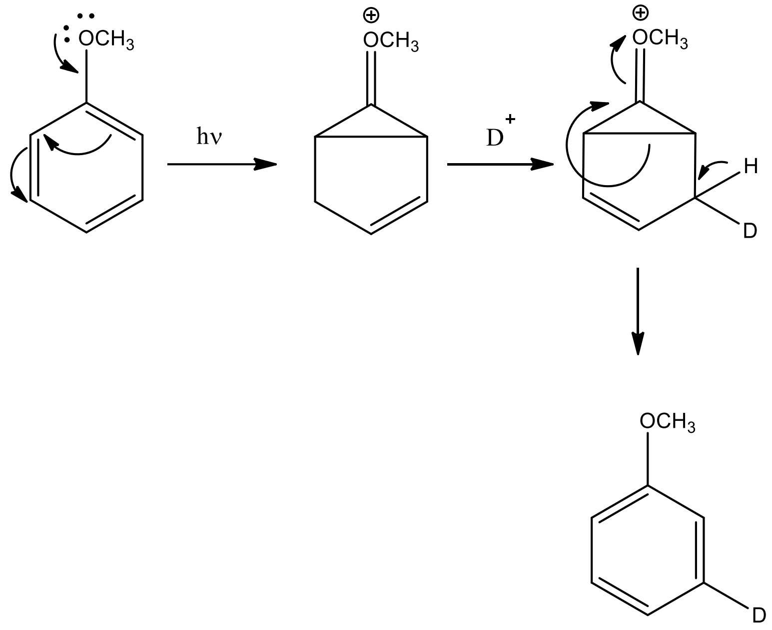


Fig. 5.27 Mechanism of Photoelectric Substitution.

5.5.3 Other type of substitutions:

The orientation rules of the benzene ring's ground state are followed in these types of photochemical substitutions. The exact process of various kinds of photochemical substitution is currently being researched. As an example,

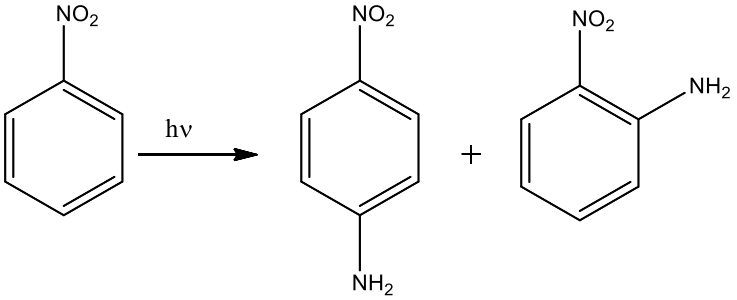


Fig. 5.28 Ortho para substitution

5.5.4 Photochemical radical substitution reactions

When exposed to light, the aromatic molecule undergoes homolytic cleavage in its ground state, leading in the generation of free radicals, which end up giving rise to the end products. It's important to note that in such circumstances; the products are really not necessarily the best.obtained are those characteristic of reactions. When Chlorobenzene is irradiated in liquid phase the benzene radical and the chlorine radical combine to generate transient π– chlorobenzene and an isomer of chlorobenzene in which the chorine forms a π– complex with benzene radical Viz- .

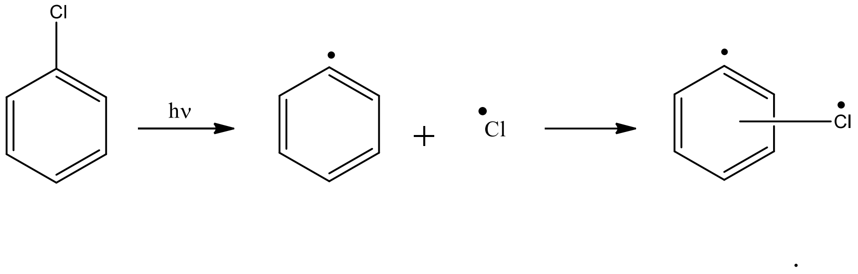


Fig. 5.29 Photochemical radical substitution of Chlorobenzene

Phenyl substituted aromatic compounds have been made using this form of photochemical homolytic cleavage of a bond between an aromatic ring's carbon atom and a halogen.It's worth noting that these compounds have a very high yield.These photochemical processes can also yield significant amounts of polynuclear molecules.

5.6 PHOTOCHEMISTRY OF DIAZO COMPOUNDS

A modest absorption band in the visible region (400–500 nm) is observed in diazoalkanes, which is linked to an n-π* transition. The matching excited states easily fragment to generate molecular nitrogen and a carbene, and this is a common approach for producing divalent carbon species. Direct irradiation produces a singlet state of the diazo compound and hence a singlet carbene at first, but collisional deactivation produces a triplet carbene before further reaction. It could be essential for carbenes with a lower triplet state energy than the singlet state, especially at greater pressures in the vapour phase or in solution. By way of the triplet excited state, the triplet sensitised breakdown of diazoalkanes yields triplet carbene. These mechanisms are used for intramolecular reactions such as the ring contraction of cyclic diazoketones and the synthesis of -lactams from -diazoamides, and they provide a valuable route to carbene.

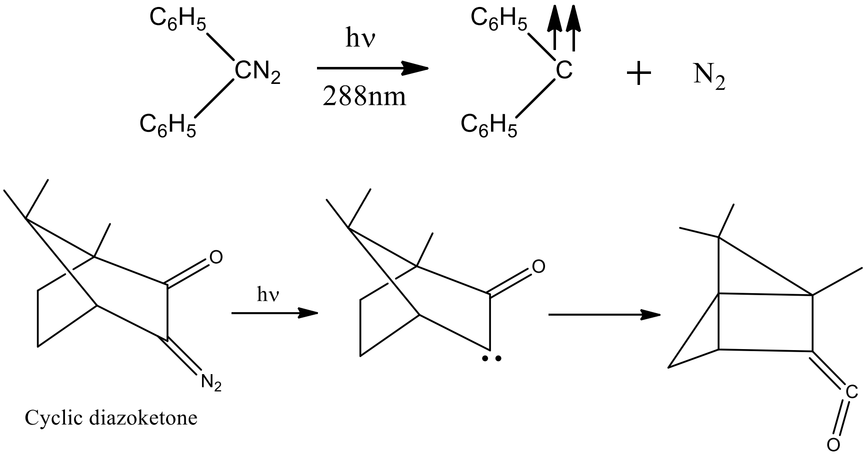


Fig. 5.30 Reaction of Diazo compounds

5.7 SUMMARY

Summary of the present unit is:

- Benzene generates benzvalene, fulvene, and prismane in the excited state, and most photochemical isomerisation events of benzene require a 1-2 shift by the benzvalen intermediate.
- During 1-2,1-3 alkyl shifts, prismane intermediate plays a role in several molecular pathways. The mechanical pathway was investigated utilising the 14C tracer method. Photochemical addition reactions of aromatic system produce unexpected products through the charge transfer process.
- Through the charge transfer mechanism, photochemical addition reactions of aromatic systems yield unexpected compounds.
- In photochemistry, the orientation rule is completely altered throughout the substitution reaction. The photochemical processes of aromatic compounds in which C—C or C—X (X: heteroatom) bonds are generated at a benzene moiety are the subject of this chapter.
- The aromatic substrate, as well as a sensitizer or photocatalyst, absorb UV or visible light. It is possible that photocycloaddition or electrocyclic processes are involved. Rearomatization occurs in this scenario. Photochemical electron transfer can also cause coupling reactions.
- Photosensitized coupling reactions are frequently carried out using photocatalysts such as ruthenium and iridium complexes with visible light irradiation. Typical sensitizers, such as aromatic ketones of colours, can be used in place of these catalysts.

5.8 GLOSSARY

Photocycloaddition: A light-initiated reactions in which the termini of two multiple bond systems become joined through σ bonds. The most common example of this type of reactions is the formation of a cyclobutane ring from two ethylene moieties.

Rydberg Transition: Any transition or absorption process in which electron is promoted to an orbital with a larger principal quantum number n than that of the initial orbital is known as Rydberg transition. In ethylene the 2pπ-3S transition is a Rydberg transition.

5.9 REFERNCES

1. Mayo P. D., (1980), *Rearrangements in Ground and Excited States,* Academic Press, New York, vol. 3.
2. Harspool W., Armester D., (1972), *Organic Photochemistry, A Comprehensive Treatment,* Eillis Horwood/Prentice Hall.
3. Gilbert, Baggott J., (1991), *Essentials of Molecular Photochemistry,* CRC Press, Boca Raton, Florida,
4. Coxon J.M., HaltonB., (1974), *Organic Photochemistry*, Cambridge University Press, London.
5. Kagan J., (1993), *Organic Photochemistry, Principles and Applications*, Academic Press,
6. Kopecky J., (1992), *Organic Photochemistry: A Visual Approach,* VCH, Weinhim, Germany.
7. Crown D.O., Drisko R.L., (1976), *Elements of Organic Photochemistry*, Plenum New York.

5.10 SUGGESTED READING

1. Gurdeep R., *Organic Photochemistry,* Chatwal,Himalya Publication House.

2. rohatgi-MukherjeeK.K., *Fundamental of Photochemstry*, New age international.

3. AmetaR.C.,*Organic Photochemistry,*

5.11 TERMINAL QUESTIONS

1. Discuss in detail various excited state of benzene.
2. Discusses the mechanism of 1-2 Alkyl shift by benzavalene intermediate. (2) by primane intermediate
3. Write an explanatory note on photochemical isomerisation of the tetra substituted benzene.
4. Discuss photochemistry of 1, 3-butadiene.
5. Discuss the chemistry of photoaromatic nucleophilic substitution.
6. Discuss the chemistry of photoelectrophilic aromatic substitution reaction.

7. Explain why NO2 is meta directing for photo induced aromatic nucleophilic substitution reactions.
8. write short notes on
   - 1,2 photochemical addition reaction
   - 1,2 photochemical addition reaction
   - Photochemical addition reaction

UNIT 6: GREEN CHEMISTRY

CONTENTS:

6.1 INTRODUCTION

Green Chemistry also known as "clean Chemistry" or "sustainable Chemistry", has emerged as an important tool for meeting the major challenges of global sustainability. Innovations and applications of Green Chemistry in education have helped companies not only benefit environmentally but at the same time achieve economic and societal goals also. Green chemistry is the design of chemical products and processes that reduce or eliminate the use or generation of hazardous substances. Green chemistry applies across the life cycle of a chemical product, including its design, manufacture, use, and ultimate disposal.

Green Chemistry:

- Prevents pollution at the molecular level.
- Is a philosophy that applies to all areas of chemistry, not a single discipline of chemistry?
- Applies innovative scientific solutions to real-world environmental problems.

- Results in source reduction because it prevents the generation of pollution.
- Reduces the negative impacts of chemical products and processes on human health and the environment.
- Lessens and sometimes eliminates hazard from existing products and processes.
- Designs chemical products and processes to reduce their intrinsic hazards.

- Attempts have been made to design synthesis for manufacturing processes in such a way that the waste products are minimum they have no effect on the environment and their disposal is convenient. For example: Benzene as a solvent is carcinogenic in nature, so it must be avoided. It is best to carry out reactions in the aqueous phase, now synthetic methods should be designed in such a way that the starting materials are consumed to the maximum extent in the final product and no toxic by product.

6.2 OBJECTIVES

Objective of this chapter is to provide students with a concise and succinct detail on the basic fundamentals of Green chemistry. After studying this Unit, students should be able to:

- Basic Principal of Green Chemistry
- Designing a green reagents
- Green catalyst phase transfer catalysis for green synthesis
- Choice of starting materials
- Organic synthesis in solid phase reagents
- Ionic liquid

6.3 *BASIC PRINCIPLES OF GREEN CHEMISTRY*

In 1991 Paul T. Anastas, (organic chemist) and John C. Warner developed the Twelve Principles of Green Chemistry**.** These principles can be grouped into "Reducing Risk" and "Minimizing the Environmental Footprint.

1. Prevention of waste

It is better to prevent waste than to treat or clean up waste after it has been created. This principle is the most obvious and over-arches the other principles.

2. Atom economy:

Synthetic methods should be designed to maximize the incorporation of all materials used in the process into the final product. This principle gets into the actual chemistry of how products are made. As chemists, atoms are assembled to make molecules. The molecules are assembled together to make materials. This principle states that it is best to use all the atoms in a process. And, those atoms that are not used end up as waste. The atom economy is a simple calculation that can be used when teaching stoichiometry and chemical reactions. The calculation is:

$$\text{AE} = \frac{Formula\ weight\ (FW) OF\ Product}{Formula\ of\ all\ of\ the\ reactants}$$

It is a simple measure of the amount of waste in a process.

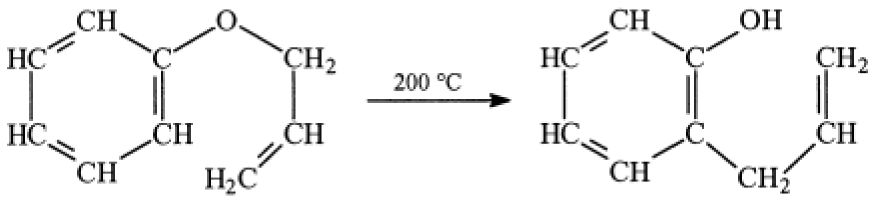
For example:

i) Consider the addition of hydrogen to an olefin.

$$H_3C{-}CH = CH_2 + H_2 \xrightarrow{Ni} H_3C{-}CH_2{-}CH_3$$

Here, all elements of the reactants (propene and hydrogen) are incorporated in the final product (propane). The reaction is a 100% atom economical reaction.

ii) Allyl phenyl ether on heating at 200°C gives o-Allyl phenol.



Allyl phenyl ether

o-Allyl phenol

This is a 100% atom economical reaction, since all the reactants are incorporated into the product.

3. Less Hazardous Chemical Syntheses

Wherever practicable, synthetic methods should be designed to use and generate substances that possess little or no toxicity to human health and the environment. This principle is focused on how we make molecules and materials. The goal is to reduce the hazard of the chemicals that are used to make a product (the reagents). Throughout the history of how we have invented products and developed the process for making them, chemists have traditionally not thought about what reagents they are using and the hazards that are associated with them. Chemists have traditionally used whatever means necessary. Today we are finding that less hazardous reagents and chemicals can be used in a process to make products and, many times they are made in a more efficient manner.

4. Designing Safer Chemicals

This principle focuses that, everyone wants safe products, means chemical products should be designed to affect their desired function while minimizing their toxicity. This principle is aimed at designing products are safe, non-toxic and efficacious. A good example of this is pesticides; which are products that are designed to be toxic. Many researchers are focused on created pesticides that are highly specific to the pest organism, but non-toxic to the surrounding wildlife and ecosystems.

5. Safer Solvents and Auxiliaries

The use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used. Many chemical reactions are done in a solvent. And, traditionally organic solvents have been used that pose hazards and many are highly toxic. They also create volatile organic compounds (VOC’s) which add to pollution and can be highly hazardous to humans. This principle focuses on creating products in such a way so that they use less hazardous solvents (such as water). We use solvents regularly in our daily lives (cleaning products, nail polish, cosmetics, etc.) and in the chemistry laboratory. The solvents traditionally used have potential toxicity and are certainly not pleasant to smell. A water-based alternative polish would avoid the exposure that goes along with the nail products and reduce the hazards associated with traditional products.

6. Design for Energy Efficiency

This principle focuses on energy requirements of chemical processes should be recognized for their environmental and economic impacts and should be minimized. If possible, synthetic methods should be conducted at ambient temperature and pressure. Today there is a focus on renewable energy and energy conservation. We use energy for transportation purposes and to provide electricity to our homes and businesses. Traditional methods for generating energy have been found to contribute to global environmental problems such as Global Warming and the energy used can also be a significant cost.

7. Use of Renewable Feedstock's

According to this principle to a raw material or feedstock should be renewable rather than depleting whenever technically and economically practicable, and also seeks to shift our dependence on petroleum and to make products from renewable materials that can be gathered or harvested locally. Biodiesel is one example of this where researchers are trying to find alternative fuels that can be used for transportation. Another example is alternative, bio-based plastics. PLA (polylactic acid) is one plastic that is being made from renewable feed stocks such as corn and potato waste.

8. Reduce Derivatives

This principle is perhaps the most abstract principle for a non-chemist. The methods that chemists use to make products are sometimes highly sophisticated. And, many involve the manipulation of molecules in order to shape the molecules into what we want them to look like. This principle aims to simplify that process and to look at natural systems in order to design products in a simplified manner , and Unnecessary derivatization (use of blocking groups, protection/ deprotection, temporary modification of physical/chemical processes) should be minimized or avoided if possible, because such steps require additional reagents and can generate waste.

9. Catalysis

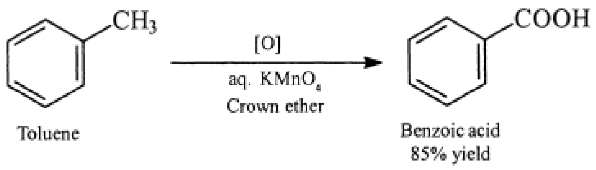
Catalytic reagents (as selective as possible) are superior to stoichiometric reagents. In a chemical process catalysts are used in order to reduce energy requirements and to make reactions happen more efficiently (and many times quicker). Another benefit of using a catalyst is that generally small amounts are required to have an effect. And, if the catalyst is truly a “green” catalyst it will have little to no toxicity and it will be able to be used over and-over again in the process. Enzymes are wonderful examples of catalysts that have been proven to perform amazing chemistry – our bodies are wonderful examples! Green chemists are investigating using enzymes to perform chemistry in the laboratory in order to obtain the desired product. Many times enzymes will have reduced toxicity, increased specificity and efficiency. Therefore, use of catalyst should be preferred whenever possible. Some of the advantages are:

(i) Better yields**:** Hydrogenation or reduction of ole fins in presence of nickel catalyst,

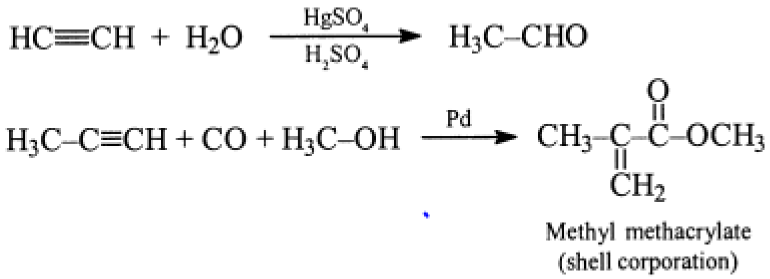
$$C_6H_5CH_2Cl + \text{aqueous } KCN \xrightarrow[\text{Catalyst}]{\text{Phase transfer}} C_6H_5CH_2CN$$

Benzyl chloride

90% yield
Benzyl cyanide



(ii) The reaction becomes feasible**:** In those cases where no reaction is normally possible,



$$HC\equiv CH + H_2O \xrightarrow[H_2SO_4]{HgSO_4} H_3C{-}CHO$$

$$H_3C{-}C\equiv CH + CO + H_3C{-}OH \xrightarrow{Pd} CH_3{-}\underset{\underset{CH_2}{\|}}{C}{-}\overset{\overset{O}{\|}}{C}{-}OCH_3$$

Methyl methacrylate
(shell corporation)

In addition to the above mentioned beneficial use of catalysts, there is significant advantage in the energy requirement. With advances in the selectivity of catalysts, certain reactions in green synthesis have become very convenient.

10. Design for Degradation

Chemical products should be designed so that at the end of their function they break down into innocuous degradation products and do not persist in the environment. Not only do we want materials and products to come from renewable resources, but we would also like them to not persist in the environment. There is no question that many products we use in our daily lives are far to persistent. Plastics do not degrade in our landfills and pharmaceutical drugs such as antibiotics build up in our water streams. This principle seeks to design products in such a way so that they perform their intended function and then, when appropriate, will degrade into safe, innocuous by-products when they are disposed of.

11. Real-time analysis for Pollution Prevention

This principle focuses on Analytical methodologies need to be further developed to allow for real-time, in-process monitoring and control prior to the formation of hazardous substances there is a way to see inside the reaction and to know exactly when it would be done, then reduce waste in the process and ensure that your product is “done” and is the right product that you intended to make reduce waste in the process and ensure that your product is “done” and is the right product that you intended to make.

12. Inherently Safer Chemistry for Accident Prevention

This principle focuses on safety for the worker and the surrounding community. According to principle Substances and the form of a substance used in a chemical process should be chosen to minimize the potential for chemical accidents, including releases, explosions, and fires. When creating products, it is best to avoid highly reactive chemicals that have potential to result in accidents. When explosions and fires happen in industry, the result is often devastating.

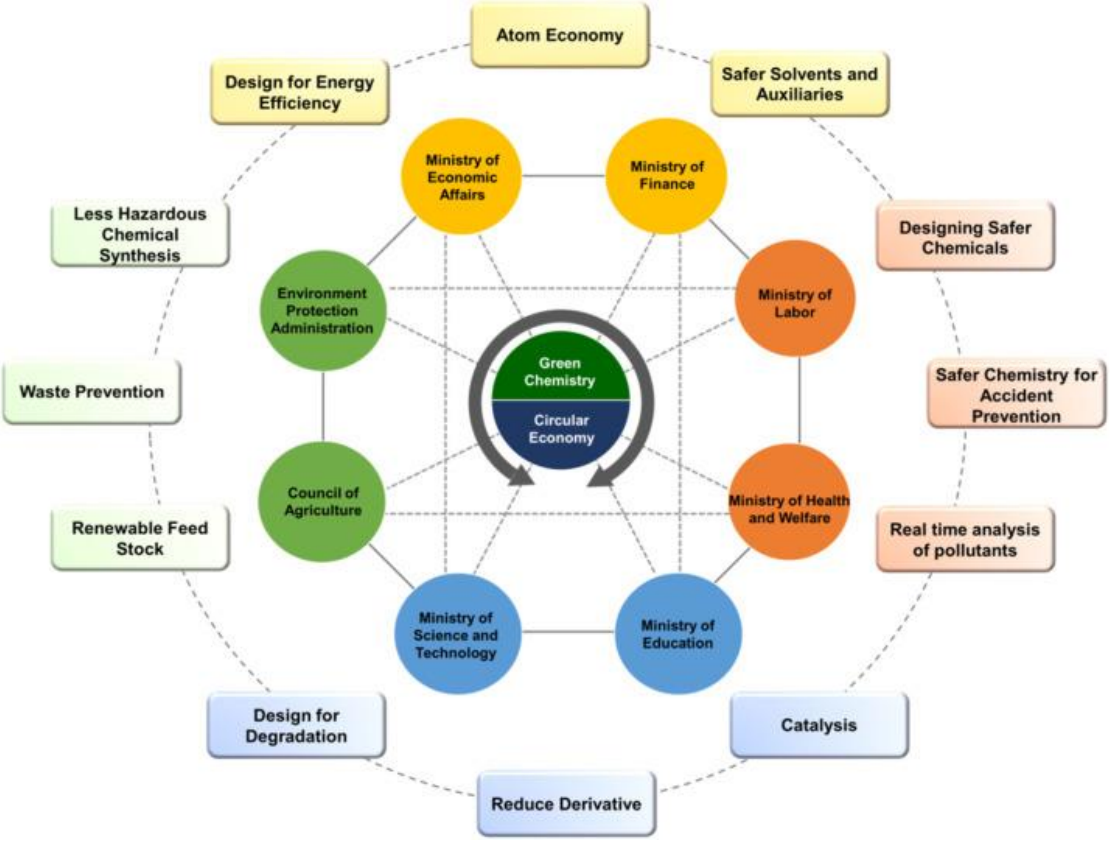


Fig. 6.1 Cycle of Green Chemistry

6.4 DESIGNING A GREEN REAGENT

6.4.1. Definition of green reagents

In a similar spirit to alternative solvents, alternative reagents are relatively environmentally benign reagents that are used to replace more toxic ones. In order to carry out the transfonnation of selected raw material, into the target molecule the criteria of efficiency, availability and effect of the reagent used must be kept in mind. Some of the green reagents are as follows.

Green chemistry aims to replace the hazardous reagents. It is illustrated for the methylation reaction which conventionally uses the hazardous reagents like CH_3-X(methyl halide), DMS (dimethylsulfate), etc. The green alternative is DMC (dimethylcarbonate). Methylation of an active methylene group can be done by using the green reagents.

6.4.2. Dimethyl carbonates (DMC)

A. Method of formation

DMC is prepared industrially by the reaction of methanol with carbon monoxide and oxygen. The process produces a mixture of methanol and DMC, which cannot be separated by simple distillation owing to the formation of an azeotrope.

(i) Phosgenation of methanol was the most popular method of DMC synthesis before the 1980s .

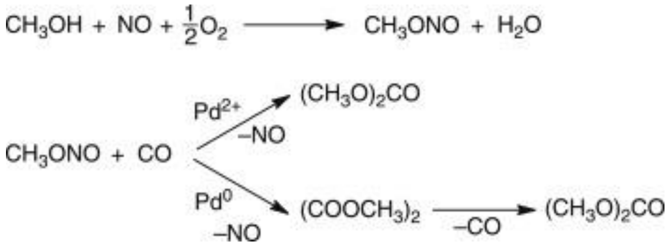
$$2CH_3OH + COCl_2 \longrightarrow (CH_3)_2CO + 2HCl$$

Since the 1980s, researchers, mainly within the chemical industry, have intensively developed non-phosgene routes to DMC synthesis. At present, all of the non-phosgene processes are utilized in the commercial production of DMC.

(ii) It can be formed by the oxidation of CH_3OH through CO in the presence of air.

$$2CH_3OH + CO + \frac{1}{2}O_2 \longrightarrow (CH_3O)_2CO + H_2O$$

(iii) The methyl nitrate process developed by Ube Industry, Japan is a variation of the direct methanol oxidative carbonylation process. Methanol is first oxidized to methyl nitrate (MN) with NO and O_2 under mild conditions (2–3 atm, 40°C) in the absence of a catalyst. The MN is separated from the coproduced water and carbonized by palladium (Pd^{2+}) catalysts in the presence of O_2 to form DMC. The reaction occurs in the gas phase over a heterogeneous catalyst bed. Using palladium metal (Pd^0) catalyst, methyl nitrate is carbonized to dimethyl oxalate (DMO), which can also be converted to DMC

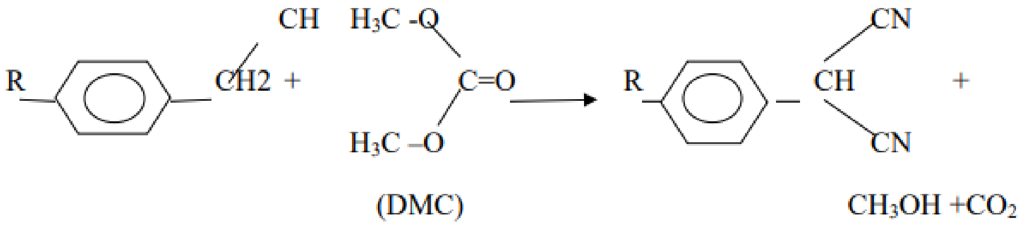


Dimethyl carbonate (DMC)

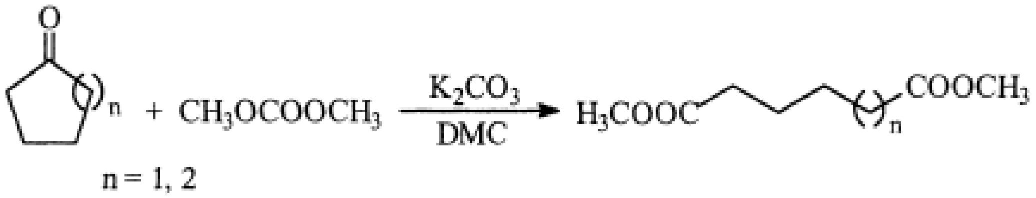
B) Silent features of DMC

Dimethylcarbonate Conventional methylation reactions employ methyl halides , methyl sulfate , Phosgene etc. The toxicity of these compounds and their environmental consequences render these syntheses somewhat undesirable.

Tundo developed a method to methylate active methylene compounds selectively using dimethyl carbonate (DMC) in which no inorganic salts are produced .



Dimethy1carbonate (DMC) can also act as an organic oxidant. Cyclopentanone and cyclohexanone react with DMC and a base to yield adipic and pimelic methyl (or ethyl) esters, respectively.



Cyclopentanone pimelic acid di methyl esters,

Many oxidative processes have negative environmental consequences. By creating long-lived catalytic and recyclable oxidants, metal ion contamination in the environment can be minimized by using molecular oxygen as the primary oxidant. Several ligand systems that are stable towards oxidative decomposition in oxidizing environments are being developed by Collins.

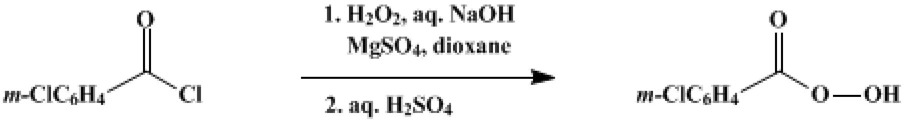
6.4.3 Polymer supported reagents

Besides DMC, there are a group of reagents which though are ordinary reagents, are bound to polymer support. The main advantage of using these reagents is that any excess of the reagent can be recovered by filtration and used again. Also, the isolation of the product is very easy. Some of such reagents are given as follows:

6.4.3.1. Polymer supported peracids

A) Method of formation of meta chloro per benzoic acid (m –CPBA)

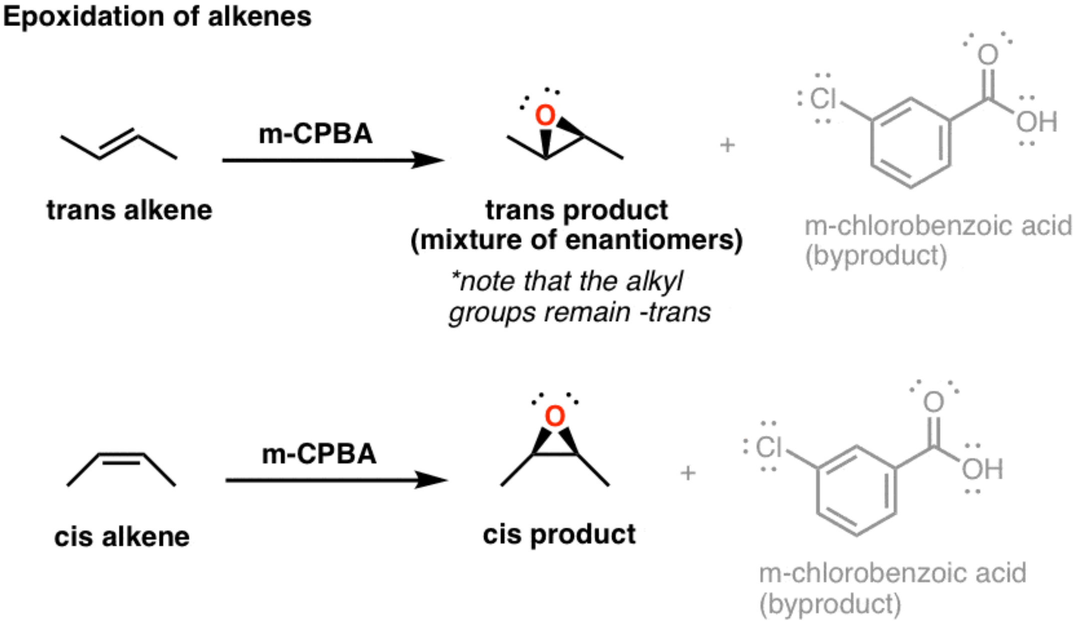
m -CPBA can be prepared by reacting m-Chlorobenzoyl chloride with a basic solution of hydrogen peroxide, followed by acidification. It is sold commercially as a self-stable mixture that is less than 72% m-CPBA, with the balance made up of m-chlorobenzoic acid (10%) and water.



m-Chlorobenzoyl chloride **m-CPBA(72%)**

B) Silent features of m-CPBA

m-CPBA are used for epoxidations of alkenes in good yields. m-CPBA forms epoxides when added to alkenes. One of the key features of this reaction is that the stereochemistry is always retained. That is, a cis alkene will give the cis-epoxide, and a trans alkene will give a trans epoxide. This is a prime example of a stereoselective reaction.



- Another useful reaction of mCPBA – commonly encountered in is the **Baeyer-Villiger reaction.** This is a rare example of a reaction that results in the oxidation of a ketone – remember that chromic acid leaves ketones alone, for instance. mCPBA can also oxidize aldehydes.

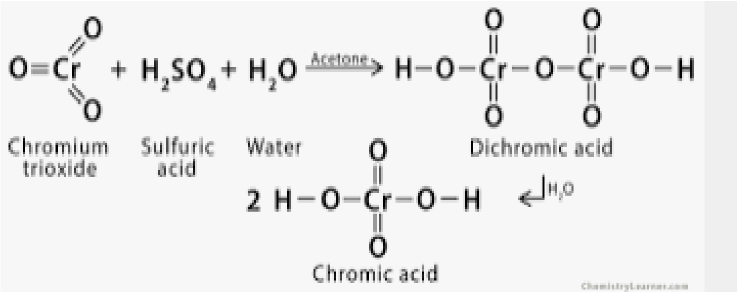
Example 2: The Baeyer-Villiger reaction

The Baeyer-Villiger converts a ketone into an ester

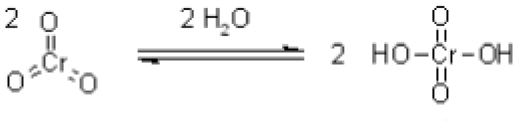
6.4.3.2 Polymer supported chromic acid

A) Method of formation

i) Chromic Acid is a naturally occurring oxide with a formula H_2CrO_4. Chromic Acid is also called Tetraoxochromic acid or Chromic(VI) acid. It is usually a mixture made by adding concentrated sulphuric acid (H_2SO_4) to a dichromate which consists of a variety of compounds and solid chromium trioxide.



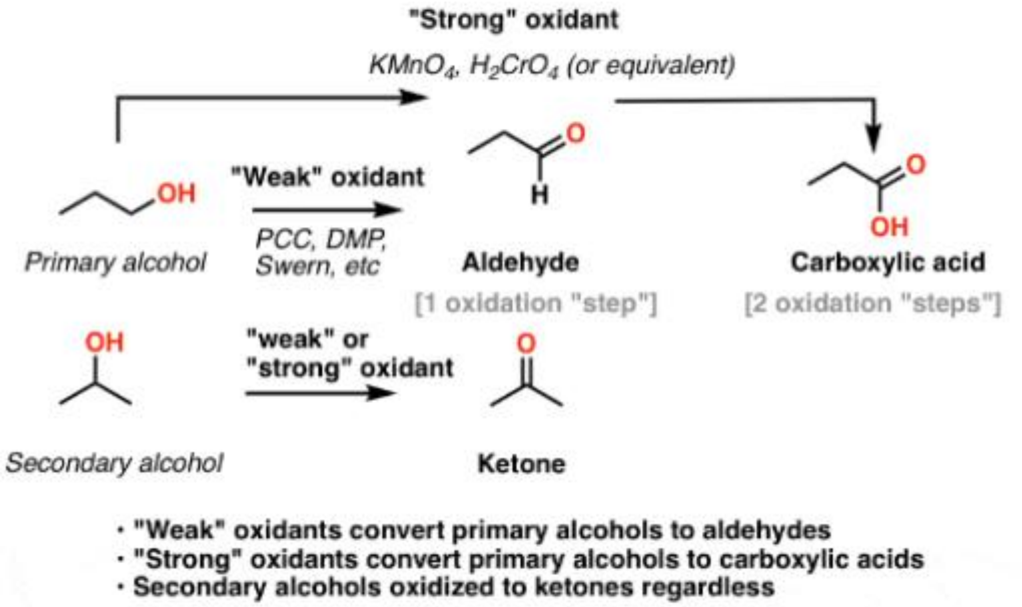
ii) Chromic acid is formed when chromium trioxide reacts with water. Chromium trioxide is crystalline, light red or brown in colour and is deliquescent and fully soluble in water. Chromic acid is a very weak acid and its salts can be dissociated even by acetic acid.



Chromium trioxide Chromic acid

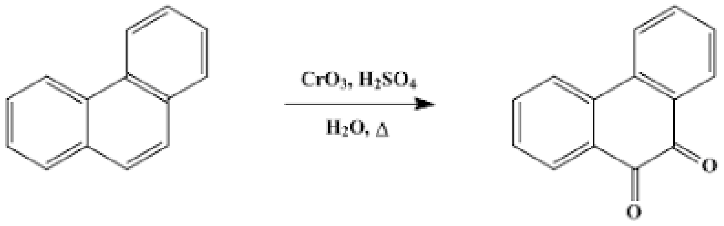
B) Silent features of Chromic Acid

- The polymer supported chromic acid (H_2CrO_4) and has been used to oxidise primary and secondary alcohol to carbonyl compounds and also oxidizes allylic and benzylic halides to aldehydes and ketones.



- "Weak" oxidants convert primary alcohols to aldehydes
- "Strong" oxidants convert primary alcohols to carboxylic acids
- Secondary alcohols oxidized to ketones regardless
- Tertiary alcohols not oxidized at all

- The another example is,Phenthracence also oxidised with Chromic Acid to give 9,10 – di keto Phenthracence **.**



Phenthracence 9,10 – di keto Phenthracence

6.4.3.3. Poly-N-Bromosuccinimide (PNBS)

N-Bromosuccinimide or NBS is a chemical reagent used in radical substitution, electrophilic addition, and electrophilic substitution reactions in organic chemistry. NBS can be a convenient source of Br •, the bromine radical.

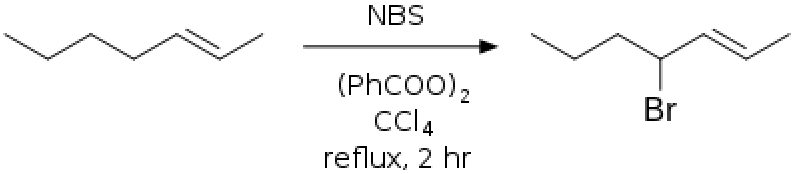
A) Method of formation

NBS is commercially available. It can also be synthesized in the laboratory. To do so, sodium hydroxide and bromine are added to an ice-water solution of succinimide. The NBS product precipitates and can be collected by filtration.

B) Silent features of Poly-N-Bromosuccinimide (PNBS)

- **Allylic and benzylic bromination**

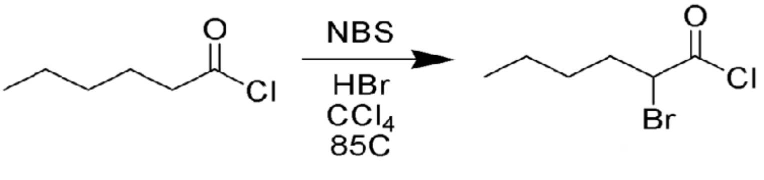
Standard conditions for using NBS in allylic and /or benzylic bromination involves refluxing a solution of NBS in anhydrous CCl_4 with a radical initiator—usually azo bisisobutyronitrile (AIBN) or benzoyl peroxide, irradiation, or both to effect radical initiation. The allylic and benzylic radical intermediates formed during this reaction are more stable than other carbon radicals and the major products are allylic and benzylic bromides. This is also called the Wohl–Ziegler reaction.



The carbon tetrachloride must be maintained anhydrous throughout the reaction, as the presence of water may likely hydrolyze the desired product. Barium carbonate is often added to maintain anhydrous and acid-free conditions. In the above reaction, while a mixture of isomeric allylic bromide products are possible, only one is created due to the greater stability of the 4- position radical over the methyl-centered radical.

- **Bromination of carbonyl derivatives:**

NBS can α-brominate carbonyl derivatives via either a radical pathway (as above) or via acid-catalysis. For example, hexanoyl chloride can be brominated in the alpha-position by NBS using acid catalysis.

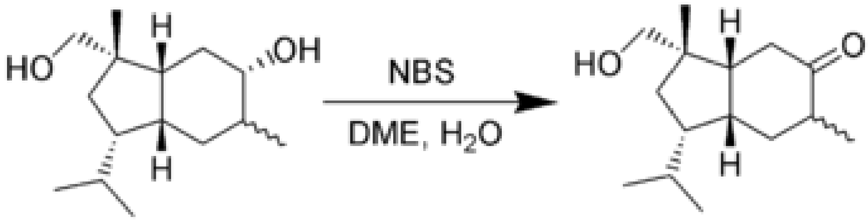


Hexanoyl chloride 2- Bromo hexanoyl chloride

The reaction of enolates, enol ethers, or enol acetates with NBS is the preferred method of α-bromination as it is high-yielding with few side-products

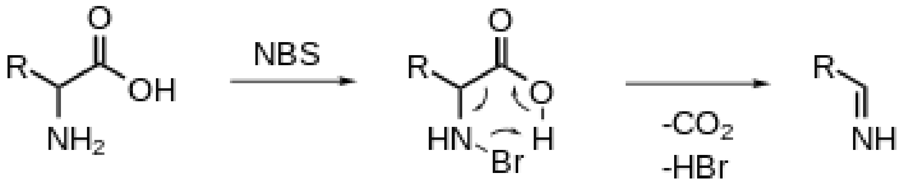
- **selective oxidation of alcohols:**

It is uncommon, but possible for NBS to oxidize alcohols, found that one can selectively oxidize secondary alcohols in the presence of primary alcohols using NBS in aqueous dimethoxyethane (DME).



- **Oxidative decarboxylation of α-amino acids**

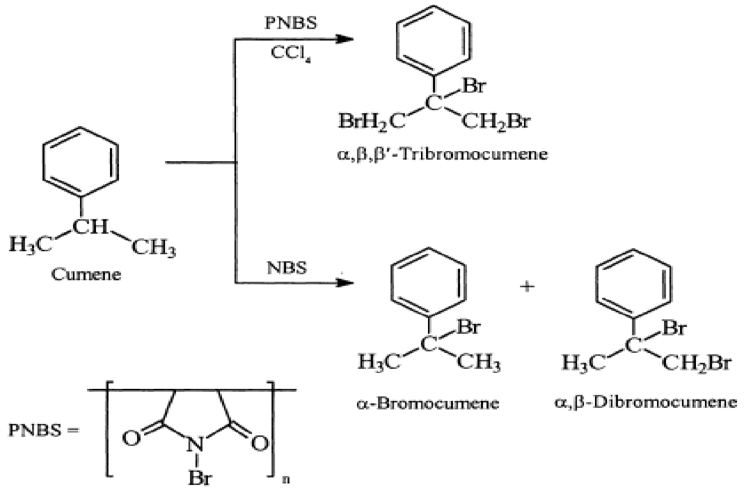
NBS electrophilically brominates the amine, which is followed by decarboxylation and release of an imine. Further hydrolysis will yield an aldehyde and ammonia.



imine

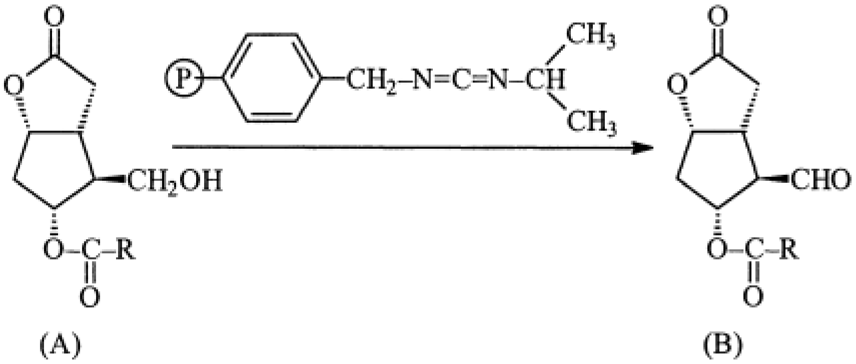
- **Bromination on cumene**

On bromination of cumene yield α, β, β ' tribromocumene .However, bromination with NBS gives α, β -dibromocumene and α -bromocumene.



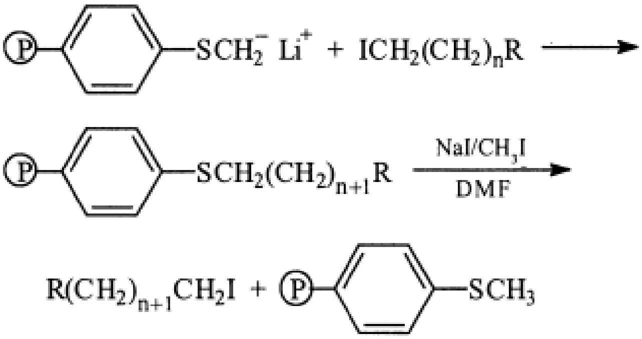
6.4.3.4 Polystyrene carbodiimide

Polystyrene carbodiimide is useful for the synthesis of anhydrides. It can also be used for the Moffatt oxidation of alcohols to aldehydes and ketones. Even the labile prostaglandin intermediate (A) is readily converted to the desired aldehyde (B)



6.4.3.5 Polymeric phenylthiomethyl lithium reagent

The polymeric phenylthiomethyllithium reagent is useful for lengthening of side chain of alkyl iodide in good yield.



6.5 GREEN CATALYST PHASE TRANSFER CATALYSIS FOR GREEN SYNTHESIS

6.5.1 Catalysis and green chemistry

In general, catalysis plays a major role in making industrial processes more efficient and economically profitable. This can be quite obviously attributed to three general characteristics of catalysts:

a. Catalytic reagents reduce the energy of the transition state, thereby reducing the energy input required for a process.

b. Catalysts are required in small quantities. In the case of biocatalysts, the number of catalysts (generally enzymes) needed compared to the quantity of reactants is very low.

c. The regeneration and reversibility of catalysts are good for green processes

6.5.2 Green catalyst

As much as it is a key in achieving economic objectives, catalyst is also a powerful tool in realizing the goals of green chemistry. Innovation in the field of catalysis is driven by both profit motives and efforts to make more eco-efficient processes. Most often profits are markedly improved with the development of green processes. An important concept of green chemistry that can be addressed by the use of catalysis is atom-efficiency, also known as atom-economy.

The term “green catalyst” has no single definition. Currently, it is most commonly associated with catalysts that are recoverable or prepared from readily available starting materials. In green Chemistry we will look different type of catalyst these are mainly:

(a) Acid Catalyst (b) Basic Catalyst c) Oxidation Catalyst

(d) Bio Catalyst (e) Phase transfer Catalyst

(a) Acid Catalyst

Acid catalyst are highly corrosive, due to this property it is hazardous and toxic. So in order to get rid of this problem we can be used in different ways so, that they become greeners majorly used.For example : HF used as a acid catalyst and it is mostly used in many different industries, petroleum industries as well as production of linear alkyl benzene but , it has corrosive , hazardous , and toxic properties. So in order to overcome this properties we can replace HF by fluorided silica-alumina catalyst.

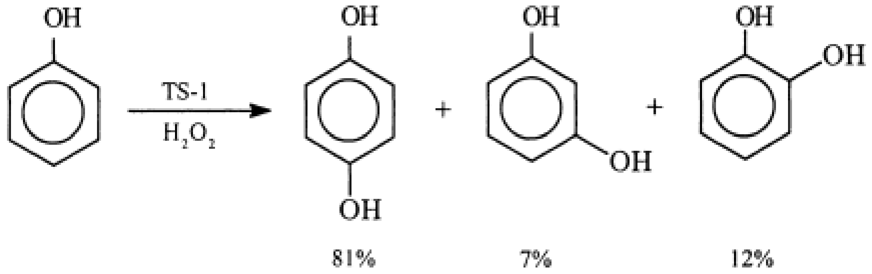
Similarly, Scandium trifluoromethane sulfonate, commonly called scandium triflate, $Sc(SO_3CF_3)_3$, Lewis acid used in different type of reactions as a acid catalyst. But is corrosive in nature, to overcome this problem, Wako has produced a micro encapsulated $Sc(OTF)_3$ that is recoverable and reusable. It is water-stable Lewis Acid that is useful in many synthetic reactions. It demonstrates higher activity than monomeric Lewis Acid in reactions such as Imino Aldol Reactions, Quinoline Synthesis, Friedel-Crafts Acylation, etc.

(b) Basic Catalyst

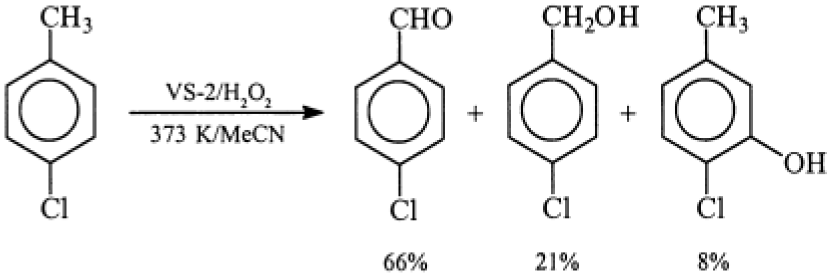
Base catalyst possesses the following advantages over acid catalyst: ability to complete the transesterification at higher speed, and decrease reaction temperature and pressure. Base catalyst has few side reactions, and it does not undergo oxidation. They are readily available at low cost. The rate of transesterification reaction is very much fast when base catalyst is used. Base catalyst gives good result when the acid value (free fatty acid content) of the source is less than two. The disadvantages of base catalyst are that it does not give good results when water is present in the source and acid value of the source is high. Most widely used heterogeneous base catalysts are alkaline earth metal oxides such as MgO, BaO, SrO, CaO, zeolites, and KNO_3 loaded on Al_2O_3. The industrial applications of basic catalysts are in the alkylation of phenol, side chain alkylation and isomerisation reactions.

(c) Oxidation Catalyst:

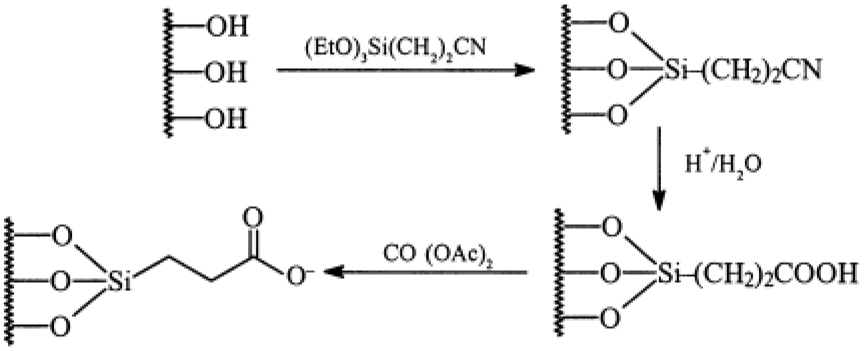
A large number of supported reagents have been used in the liquid phase partial oxidation of organic substrates .There has been considerable success in the use of molecular sieves (titanium and vanadium) in commercial. The most important application of titanium silicates (TS-I) is the hydroxylation of phenol, giving mixtures of hydroquinone and catechol. The process is clean, giving excellent conversion to product with very little waste.



Vanadium silicate molecular sieves are capable of selectively oxidizing 4-chlorotoluene to 4-chlorobenzaldehyde using hydrogen peroxide as the source of oxygen in acetonitrile solvent.



Recent reports of oxidation catalysts based on chemically modified support materials include cobalt, copper and iron. Effective catalysts include cobalt immobilized on silica which has been derivatised with carboxylic acid functions.



(d) Bio Catalyst

Biocatalyst is defined as the use of natural substances that include enzymes from biological sources or whole cells to speed up chemical reactions. Enzymes have played votal role in the catalysis of hundreds of reactions that include production of alcohols from fermentation and cheese by breakdown of milk proteins. Recent advances in the field of scientific research has helped to understand the structure and functional activities of enzymes, which has in turn led to an increase in their stability, activity, sustainability, and substrate specificity. Currently, there are hundred different biocatalytic processes that have been implemented in various pharma, chemical, food, and agro-based industries.

6.5.3. Phase transfer catalysis (PTC)

The Phase transfer catalyst to reaction between two substance located in different immiscible phase in the presence of catalyst is known as Phase transfer catalyst and this process is known as Phase transfer catalysis (PTC). Phase-transfer catalysts are especially useful in green chemistry by allowing the use of water; the need for organic solvents is reduced. Contrary common perception, PTC is not limited to systems with hydrophilic and hydrophobic reactants. PTC is sometimes employed in liquid/solid and liquid/gas reactions and it is a special form of heterogeneous catalysis.

6.5.3.1. Principle of phase-transfer catalysis

The principle of phase transfer catalysis (PTC) is brought forth well by Reuben and Sjoberg (1981). The principle of PTC is based on the ability of certain phase-transfer agents (the PT catalysts) to facilitate the transport of one reagent from one phase into another (immiscible) phase wherein the other reagent exists. Thus, reaction is made possible by bringing together the reagents which are originally in different phases. However, it is also necessary that the transferred species is in an active state for effective PT catalytic action, and that it is regenerated during the organic reaction.

6.5.3.2 Mechanisms of PTC

The mechanism of PTC reaction was first proposed in 1971. According to Starksí original work, a quaternary ammonium halide dissolved in the aqueous phase (Q +X -) undergoes anion exchange with the anion of the reactant dissolved in the aqueous solution. The ion-pair formed (Q +X -) can cross the liquid-liquid interface due to its lipophilic nature and diffuses from the interface into the organic phase, this step being the ëphase-transferí. In the organic phase, the anion of the ion-pair being quite nucleophilic undergoes a nucleophilic substitution reaction with the organic reagent forming the desired product (RY). The catalyst subsequently returns to the aqueous phase and the cycle continues. An overview of PTC reactions is given below:

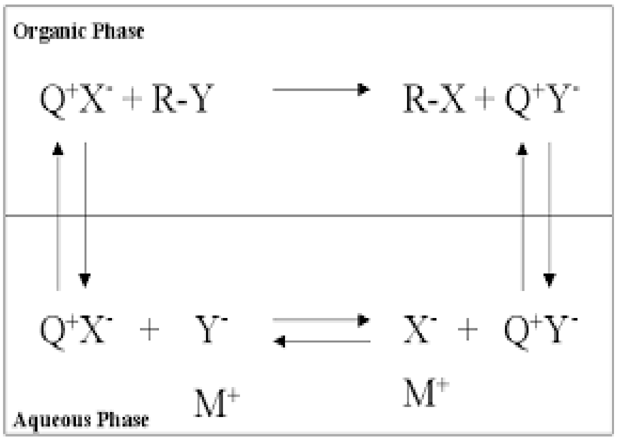


Fig. 6.2 Mechanisms of PTC

A prerequisite for a substance to function as a PT-Catalyst is to form ion-pairs soluble in the organic phase and to be transferred in a highly active state. Other mechanisms that can be considered as phase-transfer catalytic are:

6.5.3.3 PTC of uncharged species

- Complexation and transfer of uncharged protic species or metal salts into the organic medium as complexes of the phase -transfer agent.
- Electron-transfer catalysis for Redox systems.

- Metal ion-transfer from aqueous solutions into waterimmiscible ionic liquids containing neutral complexing agents.
- Pyrolytic alkylation process, whereby thermal decomposition of a quaternary ammonium salt yields avolatile alkyl derivative in the heated injector of a gas chromatography.

6.5.3.4 Types of phase-transfer catalysts

There are many types of phase transfer catalysts, such as quaternary ammonium and phosphonium salts, crown ethers, cryptands, etc. Among these, the quaternary ammonium salts are the cheapest and hence the most widely used in the industry.

Some of the PTC’S normally used are:

a. Tetra-n-butyl ammonium chloride, bromide, chlorate or hydroxide ions, $N^+(n\text{-}Bu)_4Y^-$ (Y = CI, Br, CIO_4, OH).

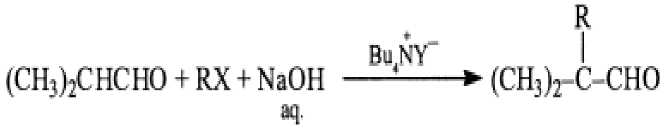
b. Trimethyal benzyl ammonium chloride (TMBA)

c. Aliquat 336 (Methyl trioctyl ammonium chloride) / stark’s catalyst

d. Crown ethers

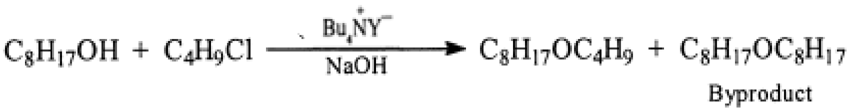
A. Tetra-n-butyl ammonium chloride, bromide, chlorate or hydroxide, $N^+(n\text{-}Bu)_4Y^-$ (Y = CI, Br, $CI0_4$, OH)

Tetra-n-butyl ammonium ions used in various different type of reactions aldehydes which are disubsituted α carbon atom like isobutyl aldehydes react with alkyl halide in presence of NaOH the product formation will be difficult because both reactants soluble in organic solvent while NaOH soluble in aqueous medium, but we are adding, $N^+(n\text{-}Bu)_4Y^-$ now we get trisubsituted aldhedydes .Now alkylation is done easily by Tetra-n-butyl ammonium ions. e.g. Isobutyraldehyde, can be alkylated with alkyl halides in presence of 50% aq. NaOH and catalytic amount of tetrabutyl ammonium ions



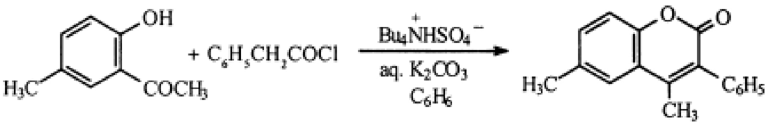
$$(CH_3)_2CHCHO + RX + \underset{aq.}{NaOH} \xrightarrow{Bu_4\overset{+}{N}Y^-} (CH_3)_2\text{–}\overset{\overset{\displaystyle R}{|}}{C}\text{–}CHO$$

Similarly, it is used in **Williamson ether synthesis** reaction. When we can added octanol to butyl chloride in presence of NaOH , but when we can adding $N^+(n\text{-}Bu)_4Y^-$ we get desired ether in a larger quantities and it has a bi products also be obtained in a smaller quantities.

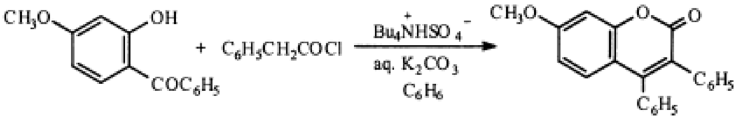


$$C_8H_{17}OH + C_4H_9Cl \xrightarrow[NaOH]{Bu_4\overset{+}{N}Y^-} C_8H_{17}OC_4H_9 + \underset{\text{Byproduct}}{C_8H_{17}OC_8H_{17}}$$

It is also be reported to use to synthesis of optical brightners such as coumarins or coumarins derivatives.



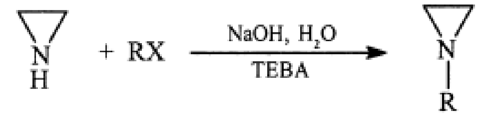
4,6-Dimethyl-3-phenyl coumarin (96%)



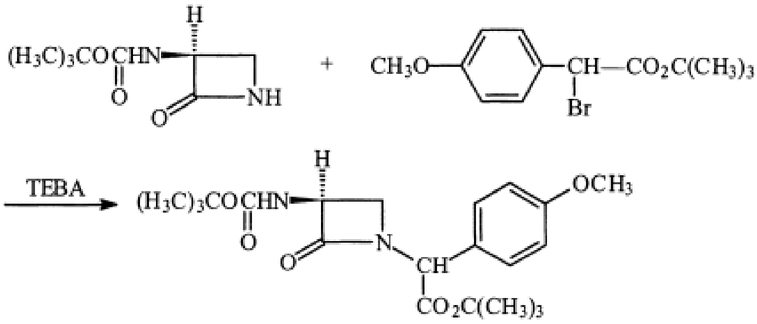
3,4-Diphenyl-7-methoxy coumarin (80%)

B. Trimethyal benzyl ammonium chloride (TMBA)

These are utilizing for different types of reaction like alkylation of Aziridines. When TMBA using in alkyl halide, in Presence of NaOH this reaction proceed in aqueous medium and very rapidly we get alkylated product. This is very difficult reaction in normal phase, because desired product is very less without TMBA.

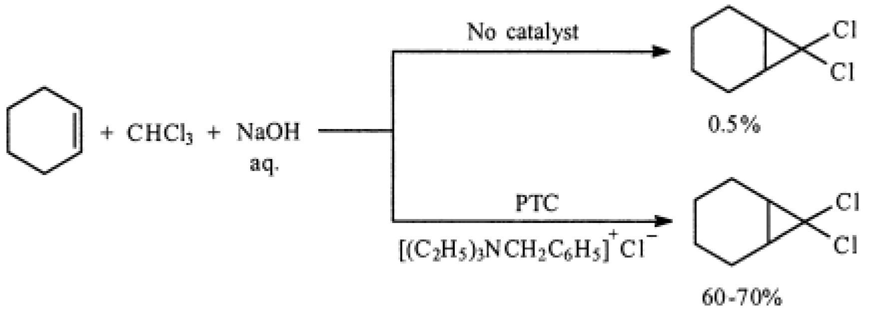


Similarly N- Alkylation β lactums reported using TMBA; without opening ring reaction is proceed out. For example:



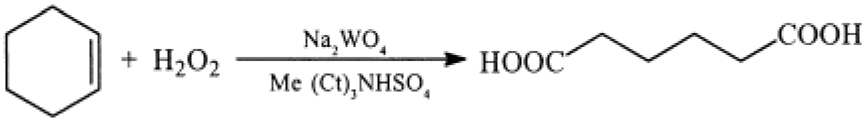
Nacardicin -A

TMBA also being reported is used in carbon intermediated reactions. Like when we reacting cyclohexene with chloroform and NaOH , if there is no catalyst is used obtained negligible amount of product is obtained (0.5%) but when we are using TMBA catalyst , same but approximate 60 to 7o% product is obtained.



C. Aliquat 336 (Methyl trioctyl ammonium chloride) / stark's catalyst

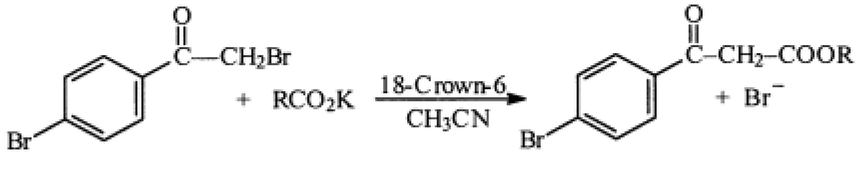
Aliquat 336 (Starks' catalyst) is a quaternary ammonium salt used as a phase transfer catalyst and metal extraction reagent. It contains a mixture of C_8 (octyl) and C_{10} (decyl) chains with C_8 predominating. Aliquat 336 (Starks' catalyst) is a quaternary ammonium salt used as a phase transfer catalyst and metal extraction reagent. It contains a mixture of C_8 (octyl) and C_{10} (decyl) chains with C_8 predominating. So the availability of anion in the organic medium is the one which creat problem for uses of this H_2O_2 as a oxidant but by using But by using Aliquat 336 it has been reported that, this H_2O_2 can be made available in organic medium. Like for example: Noyori's synthesis of adipic acid.



D. Crown ethers

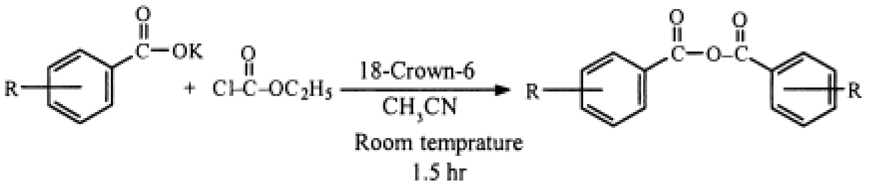
Crown ethers strongly bind certain cations, forming complexes. The oxygen atoms are well situated to coordinate with a cation located at the interior of the ring, whereas the exterior of the ring is hydrophobic. The resulting cations often form salts that are soluble in nonpolar solvents, and for this reason crown ethers are useful in phase transfer catalysis. The denticity of the polyether influences the affinity of the crown ether for various cations. For example, 18-crown-6 has high affinity for potassium cation, 15-crown-5 for sodium cation, and 12-crown-4 for lithium cation. The high affinity of 18-crown-6 for potassium ions contributes to its toxicity. The smallest crown ether still capable of binding cations is 8-crown-4.

Now we have been reported many different types of reaction catalysis by crown ether. For example: Esterification reaction in presence of, 18-crown-6 and actonitrile we will get a product as esters. This Reaction p-bromophenacyl bromide with potassium salt of a carboxylic acid using 18-crown-6 as the solubilizing agent have been used to prepare p-bromophenacyl esters

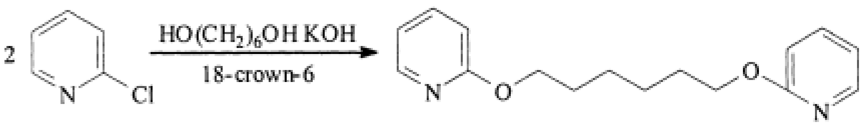


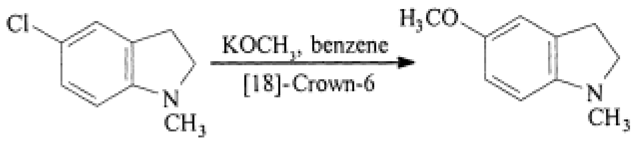
R = H, CH_3, CH_3CH_2, $CH_3CH_2CH_2$, C_6H_5, 2-$CH_3C_6H_4$,
2,4,6-trimethylbenzoyl, 4-t-butyl C_6H_4

Similarly , we can used in a convenient synthesis of anhydride, when potassium or sodium salts of acid react with acetyl chloride in presence of 18-crown-6 , acetonitrile solvent in presence of room temperature , the reaction brought about 1 and half hour .This process, used for cinnamic acid, p-nitrobenzoic acid, benzoic acid, acetic acid and propionic acid converted into their anhydrides.

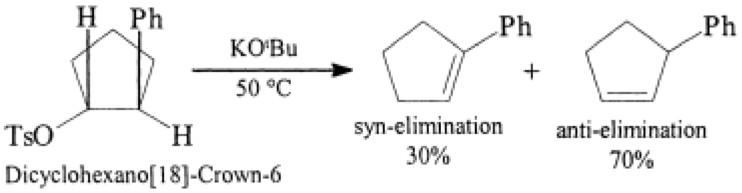


Similarly, in aromatic substitution of 2-chloropyridine by 1,6-dihydroxyhexane in good yield was carried out using 18-crown-6 as a catalyst. Furthermore, the electron rich ring undergoes methoxide substitution in excellent yield using the same catalyst.





Crown ethers ability to enhance or alter the reaction is significantly important. This is depicted in



In the absence of crown ether syn-elimination takes place in 91 % yield along with 9% of anti-elimination.

6.6 CHOICE OF STARTING MATERIALS

In many cases, the selection of a starting material from which the final product will be the most significant factor in determining the impact o f a chemical manufacturing process on the environment. There are a number of criteria that can be used in evaluating the potential environmental impacts of materials.

The criteria for a starting material include:

1. Its persistence in the environment
2. Its bioaccumulation potential
3. Its ecotoxicity
4. Human toxicity
5. Scarcity of materials
6. Renewable or non-renewable

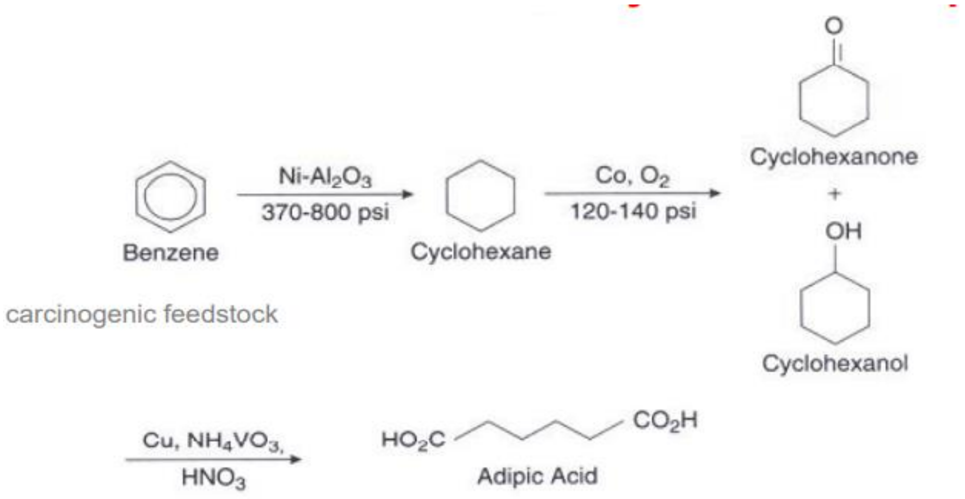
6.6.1. How do we identify alternative raw materials can improve environmental performance

a) Adipic Acid manufacturing

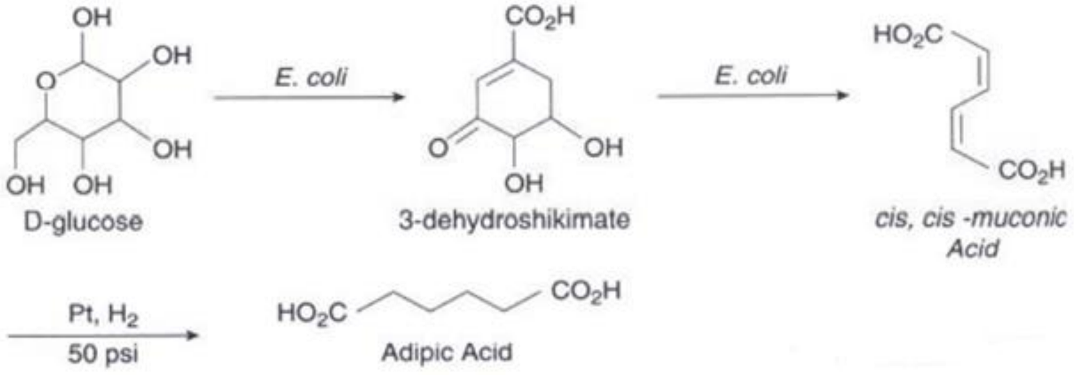
- Traditional method for adipic acid manufacture uses benzene, a fossil-fuel based, carcinogenic feedstock (Designer may wish to consider feed-stocks which are renewable or less toxic)
- One potentially environmentally preferable alternative uses glucose, a renewable feedstock which is innocuous.

- Thus, adipic acid pathway using glucose (Draths and Frost, 1998), shown in Figure 7.2-1, has some advantages.
- However, a complete evaluation would need to consider the environmental issues associated with glucose and benzene environmental issues associated with glucose and benzene production and purification

Traditional Feedstock used in the synthesis of Adipic acid



Scheme 1: Alternative Feedstock used in the synthesis of Adipic acid

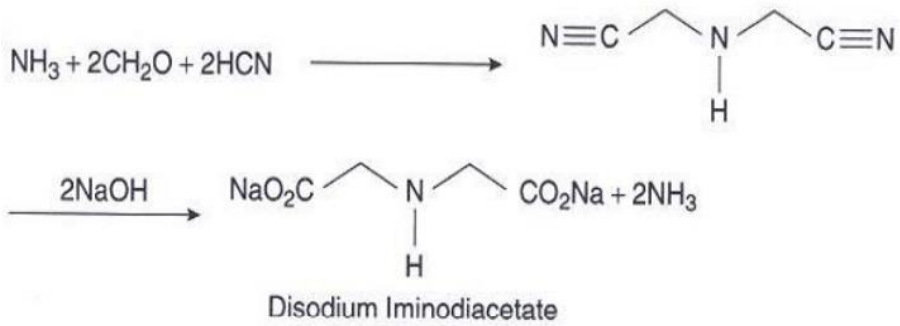


Scheme 2: Traditional and alternative synthesis pathways for adipic acid.

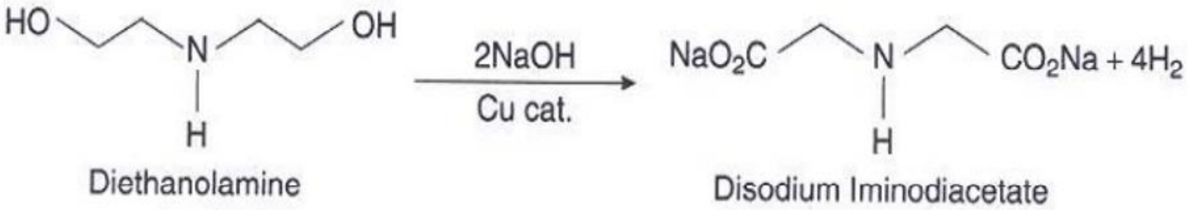
Second example of the use of less hazardous materials is provided by the synthesis of by the synthesis of disodium iminodiacetate.

- Traditional synthesis uses hydrogen cyanide.
- Alternative route uses diethanolamine to avoid using HCN.

Traditional Synthesis of Disodium Iminodiacetate (Strecker Process)



Scheme 3: Alternative Synthesis of Disodium Iminodiacetate (Catalytic Dehydrogenation):



Scheme 4: Traditional and alternative synthesis pathways for disodium iminodiacetate

6.6.2 General principles and guidelines for selection of starting materials or feedstocks

These few examples can be expanded into a set of more general principles and guidelines, which are described below:

a) Innocuous

b) Generates Less Waste

c) Selective

d) Efficient

a) Innocuous

i. The selection of starting materials should start with an evaluation the material themselves, to determine they possess any hazardous.

ii. Inherent to this analysis is determining whether the process o r reaction step requiring hazardous material is necessary or whether the final target compound be obtained from an alternative pathway that uses a less hazardous material.

b) Generates Less Waste

i. An important point the use of a particular raw material is whether it is responsible for the generation of more or less waste than other materials.

ii. It cannot be only consideration to eliminate the amount of waste.

iii. The type of waste generated must also be assessed as all chemical products are not equal in terms of their hazard, neither are chemical waste. Waste streams therefore must also be assessed for any hazardous properties that they posses

c) Selective

a. Utilizing a raw material or reaction reaction pathway that is more selective means that more of the starting material will be converted into the desire d product. High product selectivity does not always translate into high product yield. Both high conversion and high selectivity must be achieved for a synthetic transformation to generate little.

b. Using highly selective reagents can mean that separation, isolation, and purification of the product will be significantly less difficult. Since a substantial portion of the burden to the environment that chemical manufacturing processes incur result from separation an d purification processes, highly selective materials and reaction pathways are very desirable.

d) Efficient

a. Reaction efficiency, much like product selectivity, has long been a goal of synthetic design, and even prior to the advent of green chemistry principles, has offered benefits. When the overall yield of a process is increases by 10 or 20 %, less material ends up in waste streams and more is converted into product.

b. However, yield and selectivity are not entirely adequate as a measure of reaction efficiency. Synthetic transformation can achieve 100 % selectivity produce and still generate a substantial amount of waste if the transformation is not “atom economical”.

c. Atom economy, a ratio of the molecular weight of the starting materials and regents to the molecular weight of the target molecule, provides a measure of the intrinsic efficiency of the transformation.

6.7 *ORGANIC SYNTHESIS IN SOLID PHASE REAGENTS*

The earlier belief that no reaction is possible without the use of a solvent is no more valid. It has been found that a large number of reactions occur in solid state without the solvent. In fact in a number of cases, such reactions occur more efficiently and with more selectivity compared to reactions carried out in solvents. Such reactions are simple to handle, reduce pollution, comparatively cheaper to operate and are especially important in industry. It is believed that solvent-free organic synthesis and transformations are industrially useful and largely green. In the present discussion, the organic synthesis will be presented in two parts:

a. Solid phase organic synthesis without using any solvent.

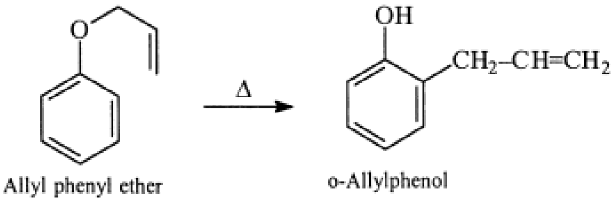
b. Solid supported organic synthesis.

6.7.1. Solid phase organic synthesis without using any solvent

The following gives a brief account of solid phase organic synthesis without the use of any solvent (dry state).

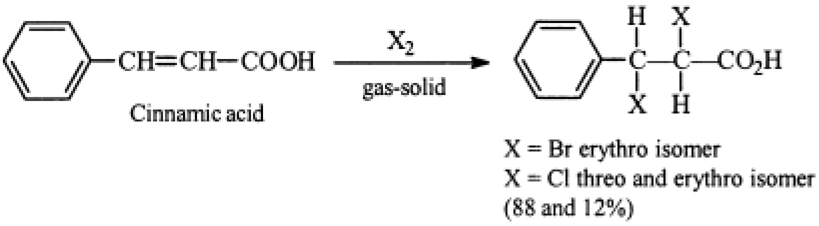
(i) Claisen rearrangement

It has been observed that an organic reaction in without the use of any solvent (dry state) is carried out in Claisen rearrangement of allyl phenylether to o-allylphenol.

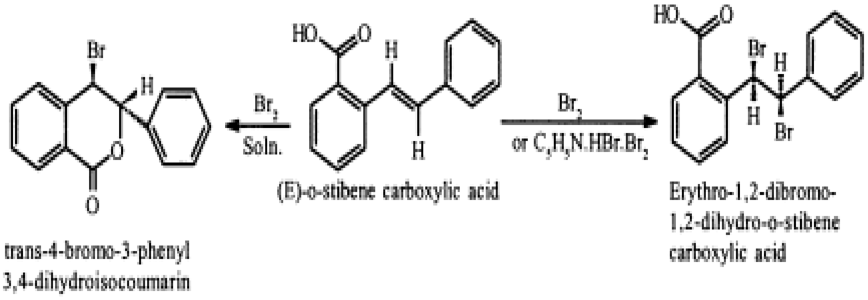


(ii) Halogenation

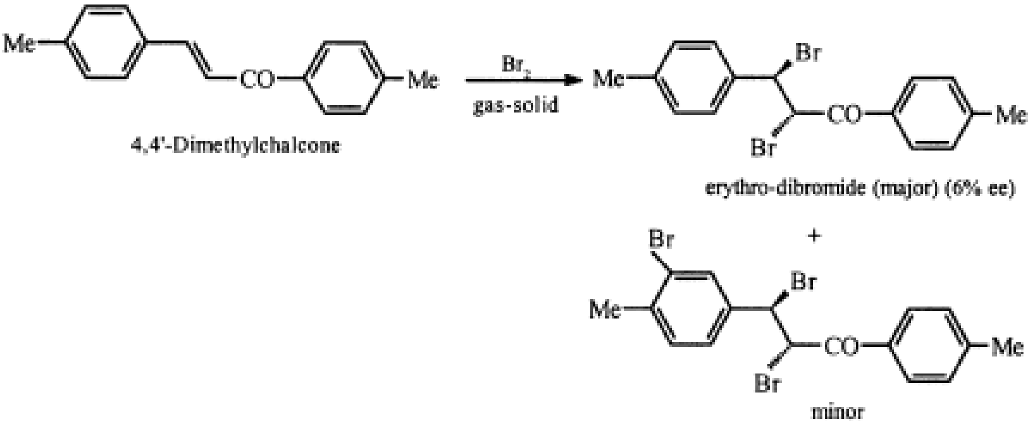
The systematically solid phase bromination work was done in 1987.It was found that crystalline cinnamic acid on bromination (gas solid phase) gives exclusively the erythro isomer, but its chlorination gives the threo and erythro isomers in 88 and 12% yields, respectively.



In a similar way bromination of powdered (E)-o-stilbene carboxylic acid with bromine vapour or with powdered pyridine. $HBr.Br_2$ complex in solid state at room temperature gave selectively erythro-l ,2-dibromo-l ,2-dihydroo-stilbene carboxylic acid. However, bromination with bromine in solution gives 4-bromo-3-phenyl-3,4-dihydroisocoumarin as the major product.

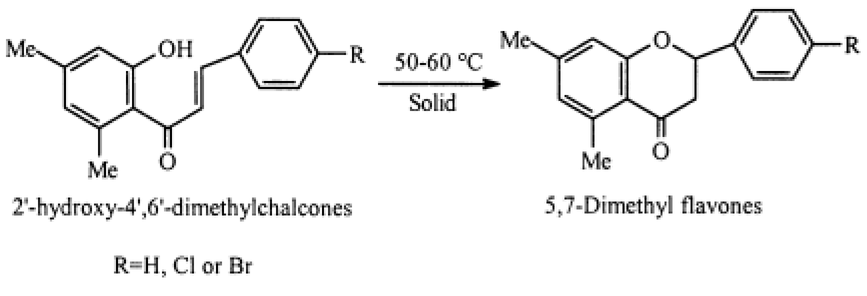


While in case, Bromination of 4,4'-dimethylchalcone with bromine (gas-solid reaction) gave optically active erythro-dibromide (6%) along with minor amount of a product.

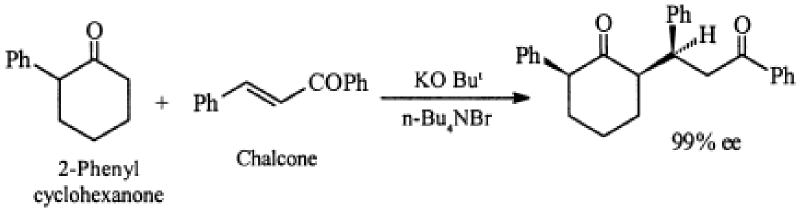


(iii) Michael Addition

In Michael addition a number of 2'-hydroxy-4',6'-dimethylchalcones undergo a solid state to yield the corresponding flavonones.

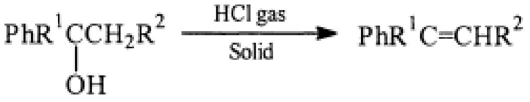


Similarly, Michael addition of chalcone to 2-pheny1cyc1ohexanone under PTC conditions give 2,6-disubstituted cyclohexanone derivative in high distereoselectivity (99%).

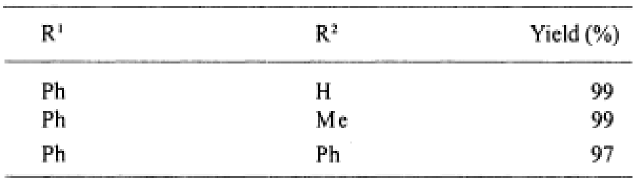


(iv) Dehydration of Alcohols to Alkenes

The dehydration of alcohols proceeds efficiently in the solid state. The dehydration is carried out by keeping the powdered alcohol PhR^{1}C(OH)CH$_2$R^2 in a desiccators filled with HCI gas for 5-6 hr, alcohols on dehydration gives PhR^{1}C=CHR^2 alkenes.



$$\mathrm{PhR^1\underset{\displaystyle OH}{\underset{|}{C}}CH_2R^2} \xrightarrow[\text{Solid}]{\text{HCl gas}} \mathrm{PhR^1C{=}CHR^2}$$

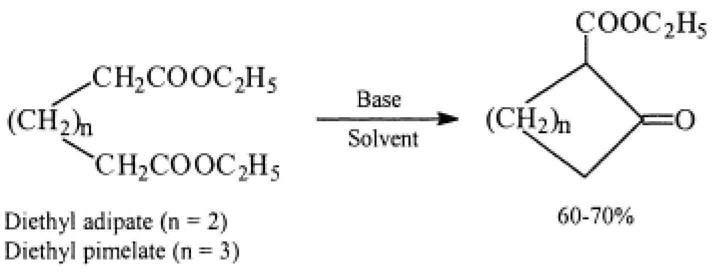


R^1	R^2	Yield (%)
Ph	H	99
Ph	Me	99
Ph	Ph	97

If benzene is used as solvent in the above reaction gave much lower yields (65-75%), and dehydration proceeded much faster by using Cl$_3$CCOOH catalyst.

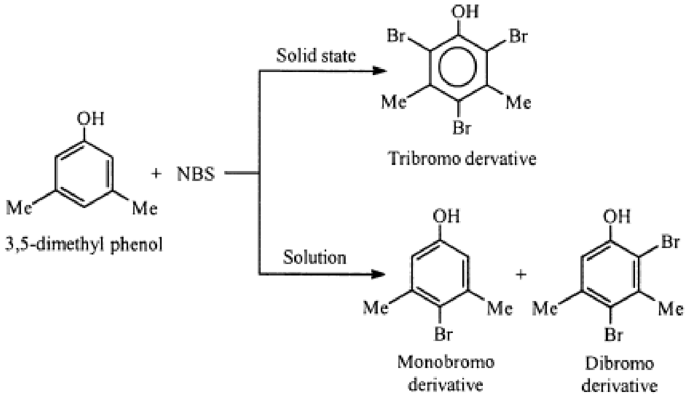
(v) Dieckmann Condensation

Dieckman condensation reactions of diesters have been carried out in solid state in presence of base (like Na or NaOEt) using high-dilution conditions in order to avoid intermolecular reaction. In this condensation diethyl adipate and pimelate proceed very well in absence of the solvent; the reaction products were obtained by direct distillation of the reaction mixture. In this method the diester and powdered But OK were mixed using a pestle and mortar for 10 min. The solidified reaction mixture was neutralised with p-TsOH. Hp and distilled to give cyclic compounds. The other bases like BuOK, ButONa, EtOK or EtONa could also be used in this reaction.



(vi) Armoatic Substitution Reactions

In aromatic Nuclear Bromination of phenols with N-bromosuccinimide (NBS) is accomplished in the solid state. Thus, the reaction of 3,5-dimethylphenol with 3 mol equivs of NBS in the solid state for 1 min gave the tribromo derivative in 45% yield. However, if the reaction is conducted in solution a mixture of mono and dibromo derivatives is obtained.



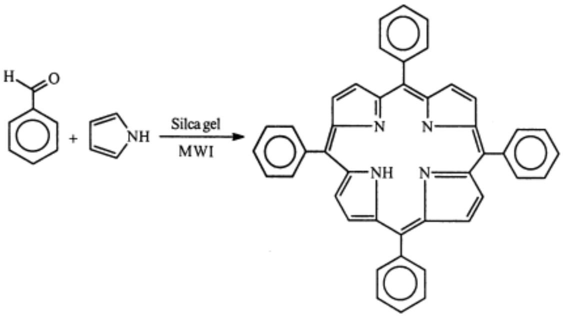
6.7.2 Solid supported organic synthesis

These types of reactions, the reactants are stirred in a suitable solvent, like water, alcohol, methylene chloride etc. After that solution is stirred thoroughly with a suitable adsorbent or solid support like silica gel, alumina, phyllosilicate. After stirring, the solvent is removed in vacuo and the dried solid supports on which the reactants have been adsorbed are used for carrying the reaction under microwave irradiation.

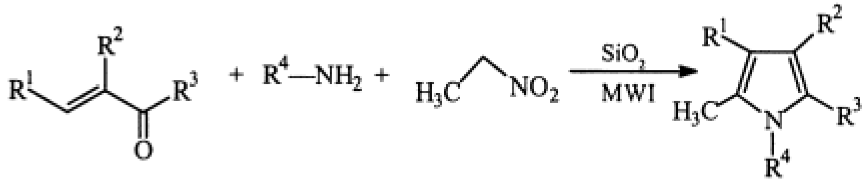
Some of the important examples of solid support synthesis are given as follows:

(i) Synthesis of Pyrroles:

A simple and fast synthesis of a tetrapyrrolic macrocycle under dry media conditions with microwave activation was performed. Pyrrole and benzaldehyde adsorbed on silica gel afforded tetrahydroporphyrin within 10 min, whereas conventional method needed 24 hr .

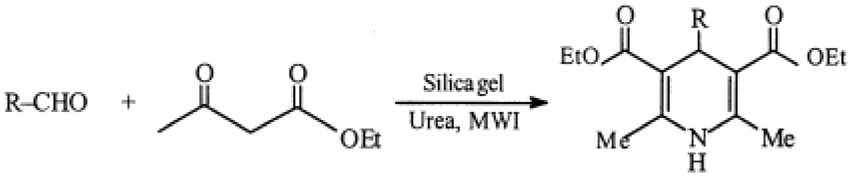


Synthesis of substituted pyrrole over silica gel under microwave irradiation has been given below:



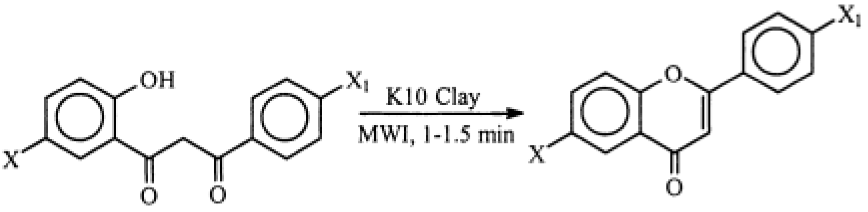
(ii) Synthesis of Pyridines

The synthesis of, 4-dihydropyridine in the presence of silica gel under microwave irradiation (MWI) has been given below. This is rapid and high yielding method.



(iii) Synthesis of Flavones

A solvent-free synthesis of flavones which involves the MWI of o-hydroxydibenzoyl methanes absorbed on montmorillonite K10 clay for 1 to 1.5 min has been achieved. Rapid and exclusive formation of cyclized flavones occurs in good yields.



$X = H, OCH_3; X_1 = H, Me, OMe, NO_2$

6.8 IONIC LIQUID

6.8.1 Introduction

Ionic liquids are compounds that have revolutionized the chemical industries. These compounds are the part of green chemicals likes, solvent have very important role in reducing the uses of hazardous, toxic and environmentally harmful. Due to their unique characteristics ionic liquid taking part in various new syntheses. An ionic liquid is a salt in the liquid state, whose melting point is below some arbitrary temperature, such as 100°C. While ordinary liquids such as water and gasoline are predominantly made of electrically neutral molecules, ionic liquids are largely made of ions and short-lived ion pair. These substances are variously called liquid electrolytes, ionic melts, ionic fluids, fused salts, liquid salts, or ionic glasses.

6.8.2 Advantages and characteristics of ionic liquid

The most important advantage of ionic liquids includes the following:

a) They are highly polar.

b) They have low vapor pressure and are non –volatile.

c) They are generally stable and resistant to heat up to 300^0C.

d) They are liquid in a wide range of temperatures, up to 200^0C.

e) The electrical conductivity of these compounds is very high.

f) These compounds are incompatible with many common organic solvents.

6.8.3 Properties of ionic liquid

a) Ionic liquids with solvent use

The presence of volatile and toxic solvent in the chemical industry is the biggest environmental problem. An attempt has been made to find a suitable alternative to volatile solvents, the following materials have recently been identified as suitable for this purpose, and these are: Supercritical CO2 Fluorinated solvent, Ionic liquids.

Ionic liquids are a class of compounds that are now considered the best alternative volatile solvents. In addition to being green, ionic fluids can dissolve a wide range of organic, inorganic, metalorganic compounds, vital molecules, and metal ions. Due to their ionic structure, these compounds are highly polar and are therefore incompatible with many organic solvents. By increasing the length of the alkyl chain attached to the cation, water insoluble ionic liquids can be made, and these ionic liquids can be used as organic phases.

b) Purity ionic liquids

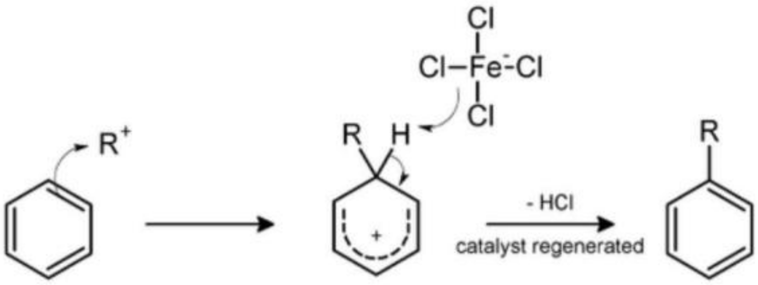
The physical and chemical properties of ionic liquids can change with the presence of impurities. Therefore, the purification of ionic liquids is essential. The most important ionic liquid pollutants are halides or organic and water based substrates, which usually come from unreacted materials. . Ionic liquids have a strong tendency to absorb moisture, so hydrophobic ionic liquids are also moisture-absorbing. In general, ionic liquids are dried by heating under vacuum, but it is difficult to completely remove water (due to the strong hydrogen bonding). The presence of water reduces the density and viscosity and modulates the chemical properties.

6.8.4 Applications of ionic liquid

Ionic liquids have many potential applications. Because of these unique properties, ionic liquids have a number of useful applications. For example, because they have a low volatility, they can dissolve many different things, they have been used as 'green' solvents in different industrial practices. Their properties also make ionic liquids useful for gas transport and storage. Instead of using pressurized containers, gases can be dissolved into ionic liquids and easily removed when needed. Ionic liquids can also be useful in recycling, aiding in the separation of similar but different materials from one another. For example, separating polymers from plastics. The most important use of ionic liquids is to act as a green solvent instead of volatile solvents. Today, ionic liquids have a wide range of other uses, some of which are briefly mentioned.

a) Catalytic reactions

Ionic liquids are used as a two- phase catalyst or substrate to stabilize other catalysts. In the presence of ionic liquids, it is possible to reuse the catalyst. The general state of this reaction is shown below:



b) Electrochemistry

Some ionic fluids were the best examples for electrochemical devices such as power storage, fuel cells, photovoltaic cells, and electric hydration. This is due to the very high electrochemical stability, high conductivity, and wide temperature performance range. The need for high-power batteries for various applications, led to the search for more non-aqueous electrolytic solutions. The competition for rechargeable lithium-ion batteries has led to the introduction of high-conductivity electrolytes that are electrochemically stable and have a high capacity for reuse. The ionic liquid appears to be good electrolytes for rechargeable lithium batteries. Their wide range of electrochemical potential prevents the electrode from regenerating or oxidizing. For example, their conductivity in lithium batteries is 5 times higher than in mixed and lithium salts in non-aqueous solvents.

c) Liquid-liquid extraction

Aqueous ionic liquids are a good alternative to the organic phase. Ionic liquids are mainly used in the extraction of valuable metal ions such as gold, lanthanides, and actinides or toxic metal ions of drinking water such as mercury and cadmium.

d) Solvent

One of the most important benefits of using ionic liquids is increasing the speed of reactions and improving orientation relative to other solvents.

e) Stability of nanocatalysts in an ionic liquid medium:

Metal nanocatalysts such as gold, platinum, palladium, rhodium, and ruthenium are widely used in organic reactions. The problem with nanocatalysts is that they bind together in reaction environments and become clumpy, greatly reducing their activity. A variety of ionic liquids are used to prevent this. Nanocatalyst Rhodium (Rh) for example, is more active in the ionic liquids mentioned in the hydrogenation reaction of alkenes and rains.

6.9 *SAQS TYPES QUESTIONS*

A. Multiple Choice Questions:

(1) The term “green chemistry” was introduced by

a. Rachel Carlson

b. Paul. T. Anastas

c. Marteel

d. Livio Desimone ,Treaty

2) What is the full form of DMC:

a. Dimethyl Carbonate

b. Dimethyl Chloride

c. Dodamethyl chlorate

d .Decamethyl Carbonate

(3) N- Alkylation β lactums,without opening ring reaction is proceed out. In presence of Catalyst:

a .TMCA

b .TMBA

c. Stark’s catalyst

d. Iron catalyst

B) Fill in the blanks:

(1) The green synthesis methods should have _______________.

(2) According to the green chemistry, the chemical involved in the production must be _______.

(3) We must use feedstock derived from annually renewable resources or from____

(4) Liquid in a wide range of temperatures, up to __________ .

5) In aromatic Nuclear Bromination of phenols with ___________ is accomplished in the solid state.

6) Hydroxylation of phenol,in presence of) titanium silicates (TS-I) giving mixtures of _______ and ______ .

(7) m-CPBA forms ___________when added to alkenes.

(8) Baeyer-Villiger oxidation with m-CPBA ketone converted into __________.

(9) Ionic liquids are used as a __________ catalyst.

(10) The dehydration of alcohols proceed efficiently in the ______ state.

(11) Using ionic liquids is _______ the speed of reactions.

(12) The bromination of cumene with NBS gives _____ α, β dibromocumene and _____α bromocumene.

C. True/False:

(1) The twelve principles of Green Chemistry can be grouped into "Reducing Risk" and "Maximizing the Environmental Footprint. True/False

(2) Polystyrene carbodiimide is used for the Moffatt oxidation of alcohols to aldehydes and ketones. True/False

(3) Atom economy is equal to formula of all of the reactants is devided by formula weight of product. True/False

(4) Addition of hydrogen to olefin is 100% atomic economical reaction . True/False

(5) Green Chemistry aims to replace the hazardous reagents. True/False

(6) Phase transfer catalysis (PTC) is a special form of homogeneous catalysis. True/False

(7) Dieckman condensation reactions of diesters have been carried out in solid state in presence of an acid. True/False

(8) Ionic liquids are largely made of ions and short-lived ion pair. True/False

Answer Key: (A)

1. b	**2. a**	**3. b**	**4. c**

(B)

1. Low energy requirements	**2.** Non toxic	**3.** Abundant waste	**4.** 200^0C	**5.** N -bromo succinimide	**6.**Hydroquinone, catechol
7. Epoxide	**8.** Ester	**9.** Two- phase	**10.** Solid	**11.** Increasing	**12.** α-bromocumene

(C)

1.False	**2.**True	**3.**False	**4.**True	**5.**True	**6.**False	**7.**False	**8.** True

6.10 *GLOSSARY*

DMC = Dimethyl carbonate

m –CPBA = meta chloro per benzoic acid

PNBS = Poly-N-Bromosuccinimide

PTC = Phase transfer catalysis

TMBA = Trimethyal benzyl ammonium chloride

TS-I = Titanium silicates

6.11 REFERCENCES

1. Basics of Green Chemistry | US EPA https://www.epa.gov › greenchemistry › basics-green-chemistry.
2. Anastas, P. T. and Warner, J. C. *Green Chemistry: Theory and Practice*. Oxford University Press: New York, 1998, p. 30. By permission of Oxford University Press.
3. An introduction to environmental chemistry, M.Fazal-ur-Rehman , Chemistry Department
4. Dimethyl Carbonate - an overview | ScienceDirect Topic https://www.sciencedirect.com › topics › chemistry › dime...
5. Green Reagent - Springer LINK https://link.springer.com › content › pdf
6. Reagent Friday: m-CPBA (metachloroperoxybenzoicacid) https://www. masterorganicchemistry.com › 2011/06/17
7. N-Bromosuccinimide – Wikipedia https://en.wikipedia.org › wiki › N-Bromosuccinimide
8. Green Oxidation Catalyst - Chemistry LibreTexts https://chem.libretexts.org › Exemplars › Green_Oxidat...
9. Biocatalysis - an overview | ScienceDirect Topicshttps://www.sciencedirect.com › topics › biocatalysis.
10. International Journal of Scientific & Technology Research Volume 1, Issue 3, April 2012 ISSN 2277-861661IJSTR©2012 www.ijstr.org The Basic Principle of Phase-Transfer Catalysis, Some Mechanistic Aspects and Important Applications Senthamizh Selvi, R 1 , Nanthini, R 2 and Sukanyaa, G.
11. Green Chemistryhttps://ocw.snu.ac.kr › sites › default › files › NOTE
12. Fine Chemical Engineering http://ojs.wiserpub.com/index.php/FCE/
13. Review :Ionic Liquids: Properties, Application, and Synthesis Ehsan Kianfar1,2* , Sajjad Mafi Fine Chemical Engineering http://ojs.wiserpub.com/index.php/FCE/

6.12 *SUGGESTED READING*

1. Green Chemistry and Processes Mukesh Doble Professor, Department of Biotechnology, India Institute of Technology, Madras, India Anil Kumar Kruthiventi Associate Professor, Department of Chemistry Sri Sathya Sai University, India.

2. New Trends in GREEN CHEMISTRY V. K. Ahluwalia Visiting Professor Dr. B. R. Ambedkar Centre for Biomedical Research University of Delhi. Delhi - J 10007. India M.Kidwai Coordinator International Chapter of Green Chemistry in India Department of Chemistry. University of Delhi. Delhi - llO 007. India.

6.13. TERMINAL QUESTIONS

1. What is Green Chemistry? What are the first listed 12 Principles of green Chemistry?
2. Green Chemistry is sustainable Chemistry. Explain the statement.
3. What is a Green reagent? Write down the preparation and properties of at least one green reagent?
4. How we prepare Polymer support chromic acid? Explain its silent feature also.
5. What are General Principles and Guidelines for Selection of Starting Materials or Feedstocks?
6. Write a short notes on solid phase organic synthesis in dry state on the following :

   a) Claisen rearrengment b) Dieckmann condensation c) Michael addition
7. What is the basic Principle and mechanism of Phase transfer catalysis (PTC)?
8. What is Ionic Liquid? Write its properties and application.
9. How do we identify alternative raw materials can improve environmental performance?
10. By Solid Supported Organic Synthesis how we prepare pyrroles and pyridines?