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Brief and Intensive Notes

Short & Long Answer Type Questions

Based On NEP 2020

PHOTOCHEMISTRY

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CHEMISTRY

Photochemistry

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SYLLABUS

Photochemistry

Unit-I Photochemical Reaction: Interaction of electromagnetic radiation with matter, types of excitations, fate of excited molecule, quantum yield, transfer of excitation energy, actinometry.

Unit-II Determine of Reaction mechanism: Classification, rate constants and life times of reactive energy states – determine of rate constant of reactions. Effect of light intensity on the rate of photochemical reaction – types of photochemical reactions photodissociation, gas-phase photolysis.

Unit-III Photochemistry of Alkenes: Intramolecular reaction of the olefinic bond – geometrical isomerism, cyclisation reactions, rearrangement of 1,4 and 1,5 -dienes.

Unit-IV Photochemistry of Carbonyl Compound: Intramolecular reaction of carbonyl compounds saturated, cyclic and acyclic, saturated and unsaturated compound. Cyclo-hexa-dienes.

Intramolecular cycloaddition reaction – dimerization and oxetane formation.

Unit-V Photochemistry of Aromatic Compounds: Isomerization, and addition and substitutions.

Unit-VI Miscellaneous photochemical Reactions: Photo-Fries reactions of anilids. Photo-Fries rearrangement.

Borton reaction. Singlet molecular oxygen reaction. Photochemical formation of smog. Photo degradation of polymers. Photochemistry of vision.

Unit-I

Photochemical Reaction:

“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*.

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

(b) Secondary reaction

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

$A^* \rightarrow B$

A. 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

Number of Einstein’s absorbed $= q / (Nhc/ \lambda) = q \lambda / Nhc$

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

In CGS units,

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

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 and dissociated to produce one H and one I. This is followed by the second reaction as shown below:

HI + hγ → H*+ I* Primary reaction

H* + HI → H2 + I* Secondary reaction

I*+ I* → I2

Overall reaction: 2HI + hv → H_2 + I_2

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

Formation of HCl: In the primary step, one Cl_2 molecule absorbs a photon

And discussed into two Cl atoms. This is followed by the secondary reaction as shown

below:

Cl_2 + hv → 2Cl* Primary reaction

Cl* + H_2 → HCl + H*

H* + Cl_2 → 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*→ Cl_2

Thus, the quantum yield varies from 104 to 106.

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 Di anthracene

$2C_{14}H_{10}$ + hv → $C_{28}H_{20}$

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

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 × 106 photons of light per second. Calculate the quantum yield of the reaction. (Avogadro number N = 6.02 × 1023)

SOLUTION:

Number of molecules of A reacting = 0.002 × 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 = $2.0 \times 10^{6} \times 1204$

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

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

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

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 × 1023).

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.

CH3CH2CHO +hv → CH3CH3 + 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

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

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

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

$$= 0.54$$

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

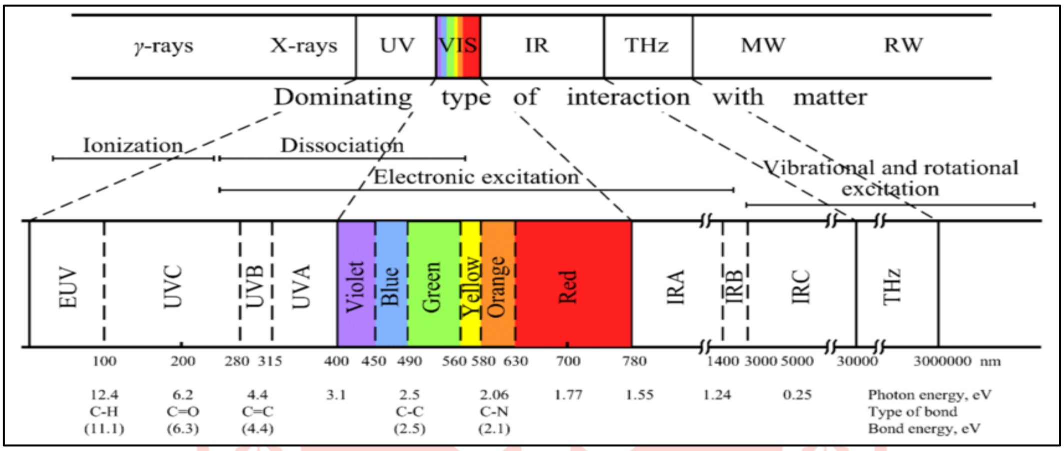
$= 2.04 \times 10^{-9}$ mole

B. Interaction of Electromagnetic Radiation with Matter

According to quantum mechanics, EM radiation can behave as a wave and as a particle. Therefore, EM radiation can be characterized by its energy, *E*, momentum, *p*, wavelength, *λ*, and frequency, *f*:

$$E = pc = \frac{hc}{\lambda} = hf$$

At high energies and short wavelengths, EM radiation typically behaves like particles, called photons. An example of these energy quanta are gamma rays. At low energies and long wavelengths, EM radiation behaves more like a wave. Examples include radio- and micro-waves.



There are several ways that EM radiation and matter interact:

- Absorption: EM radiation can be completely absorbed by an electron, boosting it into an excited state or removing it from an atom completely.
- Scattering: Like particle-particle scattering, photons can transfer some of its energy to a particle causing them to scatter.

EM radiation can also be emitted by a particle, if it changes energy states, if a reaction between particles releases energy, or if that particle accelerates. There are many ways in which EM radiation will interact with a medium. All have the net effect of transferring some or all of the initial energy to the surrounding medium. These interactions can result in the production of free or excited electrons, possibly causing further release of radiation. The presence of these free electrons can serve as a detectable signature of a photon-matter interaction. Also, the energy transferred to a conducting medium by an electromagnetic wave can be detected by electronic circuits. Examples of EM Radiation Interacting with Matter

Photo absorption

The most significant interaction mechanism of EM radiation with matter, especially at low energy and long wavelengths, is the absorption of energy by electrons. When a bound electron absorbs energy; it enters an excited state. If the transferred energy is greater than a specific threshold, the photoelectric effect is observed. The photoelectric effect describes the effect of a material absorbing a photon, then subsequently emitting an electron, often termed a photoelectron. This effect occurs when the photon's energy, hf, exceeds the binding energy of the electron within its atomic orbital, E_b. The kinetic energy of the ejected photoelectron, E_{e^-}, can be determined by the following equation**:**

$$\boxed{E_{e^-} = hf - E_b}$$

The ejection of an electron leaves the atom in an ionized state. This vacancy is quickly filled by another electron from a higher energy level within the atom or from a neighbouring atom. This atomic relaxation process often results in the emission of characteristic X-rays. Measuring these X-rays can tell you a lot about a material. If the energy absorbed by the electron is below the threshold for the photoelectric effect, the excited electron will typically relax back into a lower energy state. The excess energy released during this relaxation is typically lower, emitting EM radiation within the UV, visible, or infrared range. This process is called photoluminescence, which includes fluorescence and phosphorescence**.**

C. Types of excitations

The electronic transitions that occur in UV and visible 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**.**

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:

$$\boldsymbol{\sigma \rightarrow \sigma^* > n \rightarrow \sigma^* > \pi \rightarrow \pi^* > n \rightarrow \pi^*.}$$

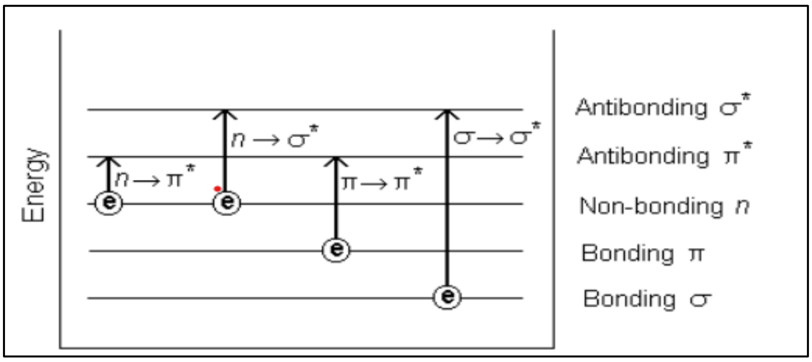


Fig.- Generalised ordering of molecular orbital energies for organic molecules and electronic transitions with light.

The possible electronic transitions of p, s, and n electrons are as in -

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, halogens etc. 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 appear at occur longer wavelengths in near UV region. Infect 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 ($n \rightarrow \sigma*$). In simple alkenes several transitions are available but $n \rightarrow \pi*$ 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 nonbonding atomic orbital to the π *MO are called n— π * transitions. The energy gap for an $n \rightarrow \pi*$ 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, $n \rightarrow \pi*$ transitions around 280 nm are the lowest energy transition. $n \rightarrow \pi*$ is forbidden by symmetry consideration. Thus, the intensity of the band due to this transition is low, although the wavelength is long.

D. Fate of excited molecule OR 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 labelled as S0. The thicker lines on the left labelled S1, S2, and S3 represent the excited electronic states for the molecule in the singlet state. The thicker lines on the right labelled T1, T2, and T3 represent excited triplet states.

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) can occur from the ground singlet electronic state (So) 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.

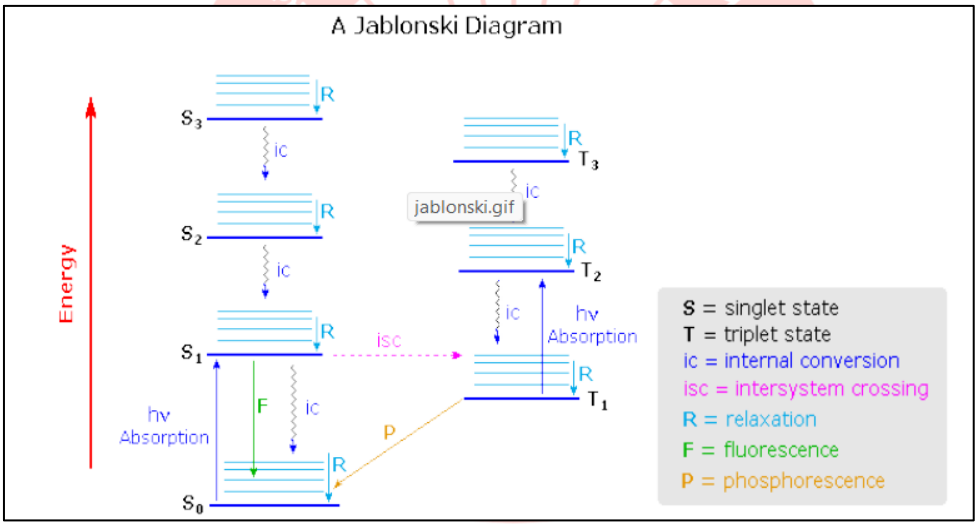


Fig.- Jablonski Diagram, depicting various Photophysical Processes

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

- When the molecule absorbs UV light radiations it gets promotes to excited singlet state S1, S2, S3. In the above state molecules are collides and after 10-13 to 10-11second it returns back to the S1, 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 S1 is long hence in this state has done many physical and chemical processes. Molecules returns to its ground state, S0 from excited singlet S1, S2 state by release energy as heat, but this is generally quite slow because the amount of energy is large between S0 and S1. This process is called **internal conversion**.

- When molecules return to its ground state S0 from excited state S1, S2 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 fluorescent light is of lower energy than absorbance light.

- Most molecules in the S1 state may drop to triplet state (T1) (S1→T1). This is energetically slow process. However, if the singlet state S1 is long lived, the S1 →T1conversion 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 (S0) to triplet state (T1) 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 S1 → T1 energy gap. When this energy difference is small their intersystem crossing is efficient, if energy difference is large, spin forbiddances quite important and efficiency is low or zero.

When molecule in the T1 state may return to the So state by giving up heat or light this is called **Phosphorescence**. Intersystem crossing and phosphorescence are very slow process (10–3 to 101 sec). This means that T1 state generally have much longer lifetime than S1 states (lifetime of S1 s 10–9 to10–15 sec, lifetime of T1 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 S1 and S0 than between T1and So and is longer-lived.

- For many molecules intersystem crossing (S1 → T1) is not very efficient. If this is the only way to produce T1 then T1 would be rather very-very limited.

E. Actinometry

actinometry is a technique used to determine the number of photons absorbed or emitted by a system by measuring the rate of a known photochemical reaction or using a physical device that converts photon energy into a quantifiable signal.

It's used to quantify the number of photons absorbed or emitted, which is crucial for understanding and characterizing photochemical processes.

Actinometry can be performed using either chemical or physical methods.

- **Chemical Actinometry:** Uses a photochemical reaction with a known quantum yield as a standard to measure photon flux.
- **Physical Actinometry:** Employs physical devices (e.g., photodiodes, photomultiplier tubes) to directly measure photon flux.

F. Transfer of excitation energy

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).

Electronic excited state

According to Pauli Exclusion principle, two electrons in an atom cannot have the same four quantum numbers (n, l, ml, ms). 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. $S1 = ½$ or $S2 = – ½$

So that, $S = S1 + S2 = ½ - ½ = 0$

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

Hence, the spin multiplicity of the molecules the molecule is said to be in the singlet ground state, denoted by S0. Figure(a)

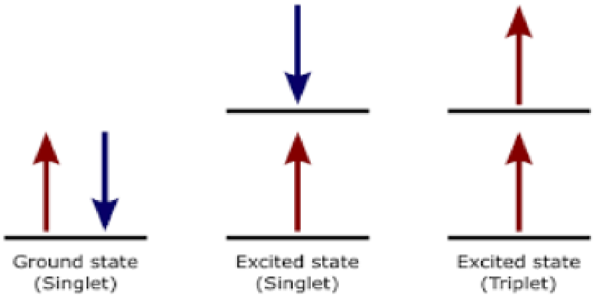


Figure:- (a) (b) (c)

When by the absorption of a quantum (photon) of suitable energy “hu”, 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(c) or anti-parallel as shown in. figure(b)

If, the spin is parallel, as shown in figure(b) then,

spin multiplicity = 2S + 1 = 2(s1 + s2) + 1

So, s1 = ½ s2= – ½ (antiparallel)

= 2 (½ - ½) + 1 = 2 (0) + 1 = 1

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

If, the spin is antiparallel, as shown in Figure(c), then,

Then spin multiplicity = 2S + 1 = 2(s1 + s2) + 1

So, s1 = ½ s2 = 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 (4)

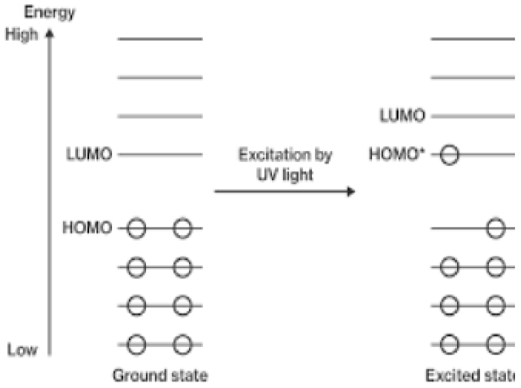


Figure: - Transition between molecule

Short & Long Answer type Questions-

Q. What is meant by quantum yield of photochemical reaction? How is low and high quantum yield explained? (CSJMU2020,15)

Ans. 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

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

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 and dissociated to produce one H and one I. This is followed by the second reaction as shown below:

$HI + hv \rightarrow H^* + I^*$ Primary reaction

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

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

Overall reaction: $2HI + hv \rightarrow H_2 + I_2$

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 Di anthracene

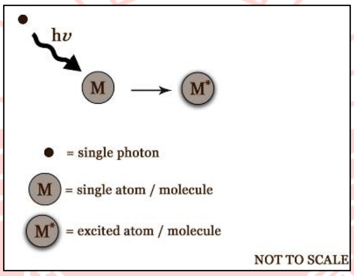
$$\mathbf{2C_{14}H_{10} + hv \rightarrow C_{28}H_{20}}$$

Q. Explain basic low of photochemistry? (CSJMU2020,17)

Ans. There are two basic laws governing photochemical reactions:

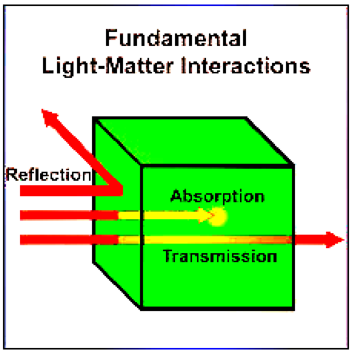
1. Grotthuss -Draper Law, named after the researchers that cemented this concept in the early 1800's.
This seems rather intuitive to our understanding of how light interacts with matter. There are only 3 fundamental choices a photon must make when it encounters a molecule. It could be reflected, absorbed, or transmitted through.
"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. Naturally light that is reflected or passed through a molecule will not have any effect. Only absorbed light can have an effect.



2. The Stark–Einstein law is named after German-born physicists Johannes Stark and Albert Einstein, who independently formulated the law between 1908 and 1913. It is also known as the photochemical equivalence law or photo equivalence law. In essence it says that every photon that is absorbed will cause a (primary) chemical or physical reaction.

The photon is a quantum of radiation, or one unit of radiation. Therefore, this is a single unit of EM radiation that is equal to the Planck constant (*h*) times the frequency of light.



The photochemical equivalence law is also restated as follows: for every mole of a substance that reacts, an equivalent mole of quanta of light are absorbed. The formulais:

$$\boxed{\Delta E_{\mathrm{mol}} = N_{\mathrm{A}} h\nu}$$

where N_A is the Avogadro constant.

Q. What is the fate of the molecule? Explain on the basis of Jablonski diagram. (CSJMU2019,18,17)

Ans. The "fate of a molecule" refers to what happens to a molecule after it is exposed to certain conditions, such as being excited by light or undergoing chemical reactions. This can include processes like dissociation, reaction, or simply relaxation back to its ground state.

Examples of a molecule's fate:

1. Electronic excitation:

When a molecule absorbs light (photoexcitation), its electrons can be promoted to higher energy levels.

2. Photolysis (splitting by light):

As seen in photosynthesis, water molecules (H2O) can be split into hydrogen ions (protons), electrons, and oxygen.

Jablonski diagram-

In molecular spectroscopy, a Jablonski diagram is a diagram that illustrates the electronic states and often the vibrational levels of a molecule, and also the transitions between them. The states are arranged vertically by energy and grouped horizontally by spin multiplicity. Nonradiative transitions are indicated by squiggly arrows and radiative transitions by straight arrows. The vibrational ground states of each electronic state are indicated with thick lines, the higher vibrational states with thinner lines. The diagram is named after the Polish physicist Aleksander Jabłoński who first proposed it in 1933.

Transitions

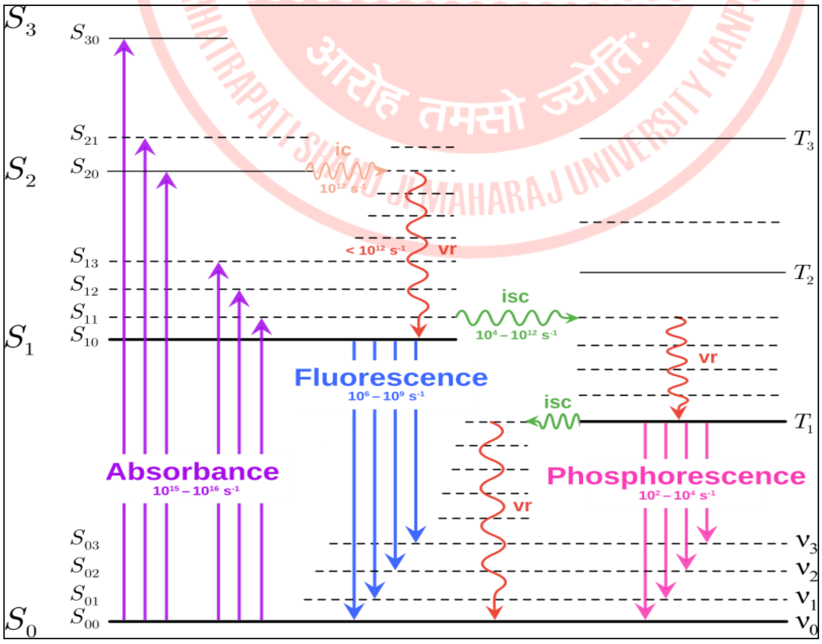
When a molecule absorbs a photon, the photon energy is converted and increases the molecule's internal energy level. Likewise, when an excited molecule releases energy, it can do so in the form of a photon. Depending on the energy of the photon, this could correspond to a change in vibrational, electronic, or rotational energy levels. The changes between these levels are called "transitions" and are plotted on the Jablonski diagram.

Radiative transitions involve either the absorption or emission of a photon. As mentioned above, these transitions are denoted with solid arrows with their tails at the initial energy level and their tips at the final energy level.

Nonradiative transitions arise through several different mechanisms, all differently labeled in the diagram. Relaxation of the excited state to its lowest vibrational level is called vibrational relaxation (VR). This process involves the dissipation of energy from the molecule to its surroundings, and thus it cannot occur for isolated molecules.

A second type of nonradiative transition is internal conversion (IC), which occurs when a vibrational state of an electronically excited state can couple to a vibrational state of a lower electronic state. The molecule could then subsequently relax further through vibrational relaxation.

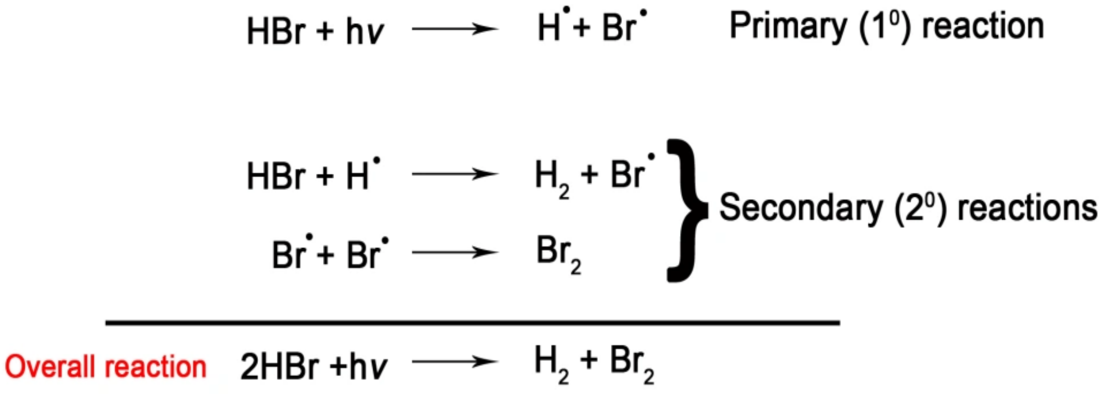
A third type is intersystem crossing (ISC); this is a transition to a state with a different spin multiplicity. In molecules with large spin-orbit coupling, intersystem crossing is much more important than in molecules that exhibit only small spin-orbit coupling. ISC can be followed by phosphorescence.



Q. Write consequences of light absorption primary and secondary process. (CSJMU2015,14)

Ans. Primary And Secondary Processes-

We studied in the earlier posts that the Stark-Einstein law holds true only for the primary process of a photochemical reaction. However, we never studied what exactly a primary process means. Thus, this post is dedicated to discussing the primary and secondary processes of photochemical reactions. A primary process of a photochemical reaction refers to what happens immediately after absorption of light. This can be thought of as the first step of the photochemical reaction. The subsequent chemical changes are termed secondary processes. Let us try to understand this with an example – the decomposition of hydrogen bromide (HBr).



Q. When irradiated with light of 5000Å wavelength, 1×10^{-4} mole of a substance is decomposed. How many photons are absorbed during the reaction if it's quantum efficiency is 10? (CSJMU2015,14)

Ans.

Solution

Reacted mole = 1×10^{-4}

Reacted Molecule = $1\times 10^{-4} \times 6.023\times 10^{-34}$

λ = 5000Å

Φ = 10

$$E = \frac{hc}{\lambda}$$

$$= \frac{6.626 \times 10^{-27} \times 3 \times}{5 \times 10^{-10}}$$

$= 3.97 \times 10^{-9}$

$$\text{Absorbed molecule} = \frac{\text{No. of mole reacted}}{\text{Quantum yield}}$$

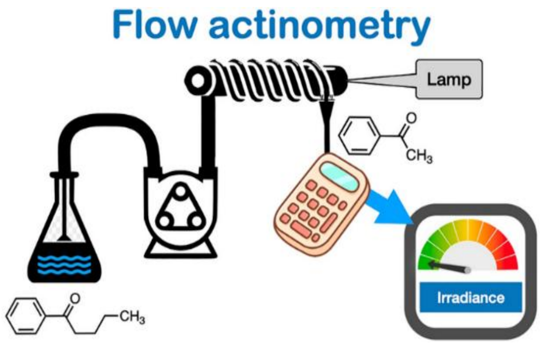
$$= \frac{1 \times 10^{-4} \times 6.023 \times 10^{-34}}{10}$$

$$= \frac{0.602 \times 10^{-38}}{3.97 \times 10^{9}}$$

$\text{Absorbed molecule} = 0.151 \times 10^{-29}$

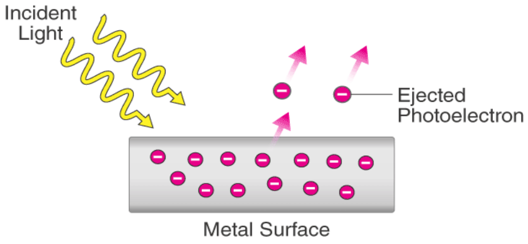
Q. Write a short note on actinometry. (CSJMU2017,16)

Ans. An actinometer is an instrument that can measure the heating power of radiation. An actinometer is a chemical system or physical device which determines the number of photons in a beam integrally or per unit time. This name is commonly applied to devices used in the ultraviolet and visible wavelength ranges. For example, solutions of iron(III) oxalate can be used as a chemical actinometer, while bolometers, thermopiles, and photodiodes are physical devices giving a reading that can be correlated to the number of photons detected.



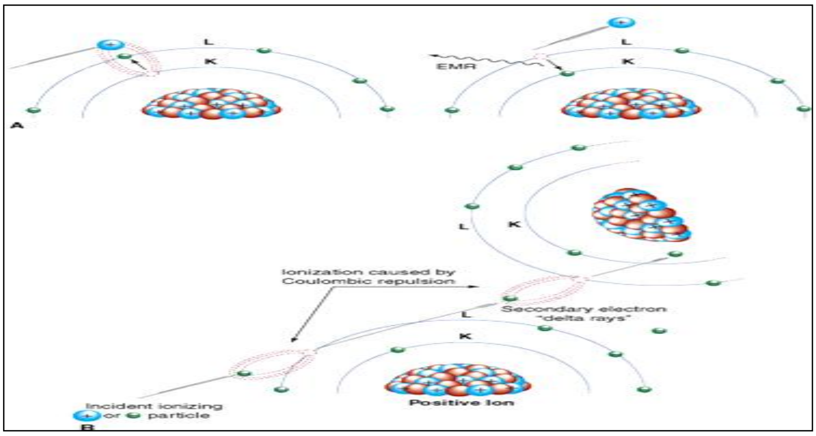
Q. Write a short note on photoelectric effect. (CSJMU2015,14)

Ans. The photoelectric effect is a phenomenon in which electrons are ejected from the surface of a metal when light is incident on it. These ejected electrons are called photoelectrons. It is important to note that the emission of photoelectrons and the kinetic energy of the ejected photoelectrons is dependent on the frequency of the light that is incident on the metal's surface. The process through which photoelectrons are ejected from the surface of the metal due to the action of light is commonly referred to as photoemission. The photoelectric effect occurs because the electrons at the surface of the metal tend to absorb energy from the incident light and use it to overcome the attractive forces that bind them to the metallic nuclei. An illustration detailing the emission of photoelectrons as a result of the photoelectric effect is provided below.



Q. - What is photochemistry interaction of radiation with matter? (CSJMU2016,20,22)

Ans. Photochemistry, a branch of chemistry, focuses on the interaction of electromagnetic radiation, especially light, with matter, leading to physical or chemical changes. This interaction involves the absorption of photons, which can excite molecules, ultimately causing them to undergo reactions or undergo changes in their physical properties. Example - Photochemistry is fundamental to processes like photosynthesis, vision, and the formation of vitamin D.



Q. - What is the quantum yield of a photochemical reaction? (CSJMU2017,18)

Ans. The quantum yield (also known as quantum efficiency) of a photochemical reaction is a measure of how efficiently a light-induced chemical reaction proceeds. It is defined as the number of molecules that react or are formed per photon of light absorbed. In essence, it quantifies the reaction's efficiency by relating the number of reaction events to the number of photons used.

Understanding the Concept:

Definition:

The quantum yield (Φ) is calculated as: Φ = (Number of molecules reacted or formed) / (Number of photons absorbed).

Efficiency:

A quantum yield of 1 indicates that for every photon absorbed, one molecule reacts or is formed. A quantum yields greater than 1 signifies a chain reaction where one photon can trigger multiple reactions.

Light Absorption:

Photochemical reactions are initiated by the absorption of light by the reactant molecules.

Measuring Efficiency:

The quantum yield is a key parameter for understanding and characterizing the efficiency of photochemical reactions.

Q.- What is an example of a photochemical reaction? (CSJMU2019,22)

Ans. A common example of a photochemical reaction is photosynthesis, where plants use sunlight to convert carbon dioxide and water into glucose and oxygen. Another example is the decomposition of silver chloride in light, which is used in photography.

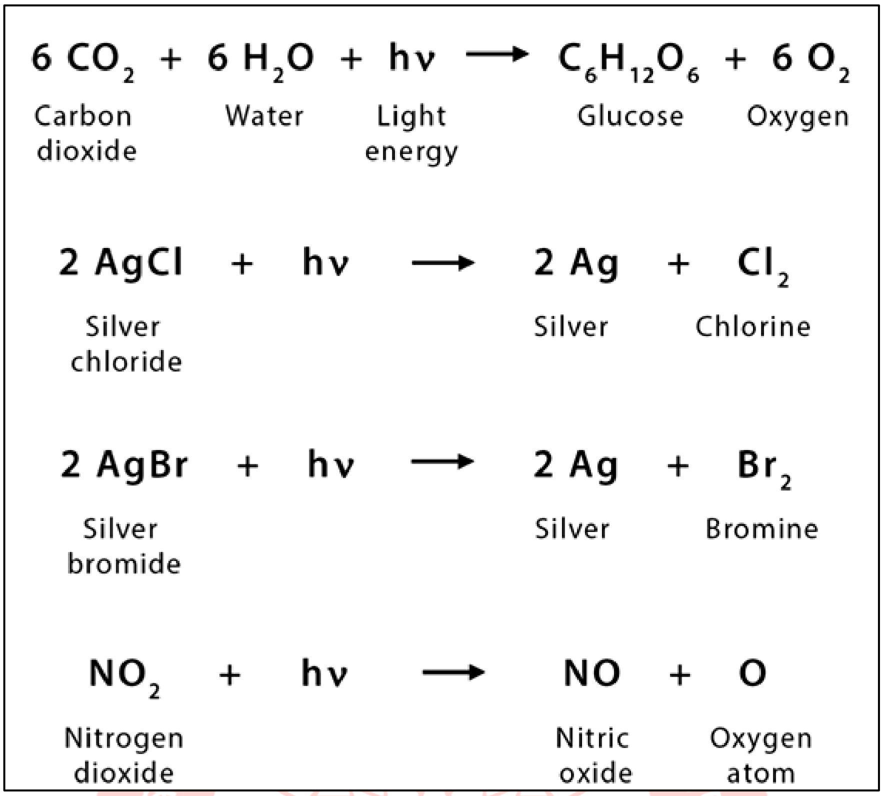
Examples –

- **Photosynthesis:**

Plants utilize light energy to drive the synthesis of carbohydrates from carbon dioxide and water, releasing oxygen as a byproduct.

- **Decomposition of Silver Chloride:**

When silver chloride is exposed to light, it decomposes into silver and chlorine, which is the principle behind photographic film.



$$6\,CO_2 + 6\,H_2O + h\nu \longrightarrow C_6H_{12}O_6 + 6\,O_2$$

$$2\,AgCl + h\nu \longrightarrow 2\,Ag + Cl_2$$

$$2\,AgBr + h\nu \longrightarrow 2\,Ag + Br_2$$

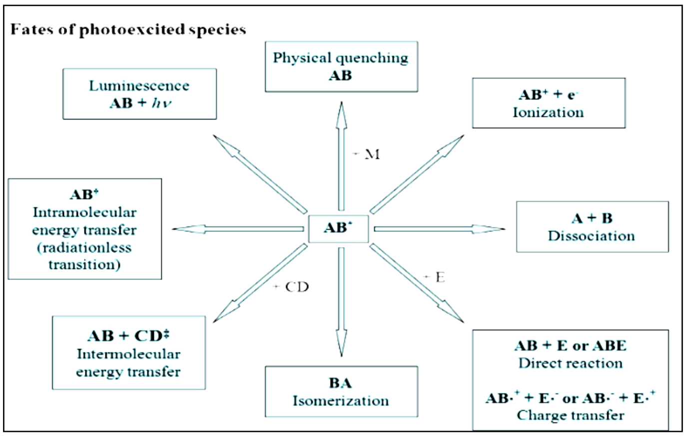
$$NO_2 + h\nu \longrightarrow NO + O$$

Q. - Who is the father of photochemistry?

Ans. Giacomo Luigi Ciamician, an Italian chemist, is widely considered the "father of photochemistry". He was a pioneer in the study of photochemical reactions, investigating them in a systematic way, especially utilizing sunlight in his research at the University of Bologna.

Q.- What is the fate of an excited molecule in photochemistry?

Ans. In photochemistry, an excited molecule can follow several paths after absorbing light. It can release energy as heat and return to the ground state, or it can undergo chemical reactions. The excited molecule can also release light (fluorescence) or transfer energy to another molecule, leading to various photochemical processes.



Q. 6- What is the excited state in photochemistry?

Ans. In photochemistry, an excited state refers to a higher energy state of a molecule that is achieved when it absorbs a photon of light, causing an electron to jump to a higher energy level or orbital. This excited state is less stable than the molecule's ground state and can lead to various chemical reactions or physical processes.

Example:

- **Fluorescence and Phosphorescence:** An excited molecule can return to its ground state by emitting light (fluorescence or phosphorescence).

Unit-II

Photochemical Reaction Equation

In photochemical reactions, light is absorbed by reactants. If we talk about black and white photography, AgBr gets decomposed due to light and forms Ag and bromine gas, which is given as

2AgBr + sunlight⟶2Ag + Br22AgBr + sunlight⟶2Ag + Br2

Mechanism of Photochemical Reaction (Photosynthesis)

Photosynthesis, which sustains life on planet earth, is one of the important topics discussed worldwide. It is a photochemical process by which green plants absorb light energy from the sun directly and utilize it to convert atmospheric carbon dioxide to food and oxygen in the presence of water. Using this process, plants can convert the sunlight energy into chemical energy, form carbohydrates using water and carbon dioxide and release oxygen. Oxygen is used by humans and other animals, as the life of living beings is sustained with the aid of oxygen and carbohydrates.

The chemical reaction of this process is

6CO2 + 6H2O+ sunlight⟶C6H12O6 + 6O26CO2 + 6H2O+ sunlight⟶C6H12O6 + 6 O2

Laws of Photochemistry

There are two basic laws of photochemistry, and these are as follows:

Grothaus's-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, Grothaus's and Draper studied a number of photochemical reactions and enunciated a generalization. This is known as Grothaus's-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 Grothaus's-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.

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.

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)** 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:

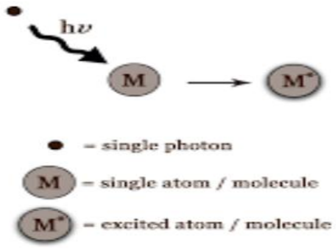


Figure: - Stark-Einstein law of photochemical equivalence

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

$$M^* \rightarrow B$$

$$\text{Overall } M + h\nu \rightarrow B$$

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:

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

Difference Between Photochemical and Thermal Reaction

Following are the key differences between a photochemical and a thermal reaction:

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 (hv) 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.

Electronically exited state - life time-

Life times of reactive energy 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 S1 (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:

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

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, τ0 is 10^{-6} to10^{-3} s. Lifetime of radiative T1 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).

Excited singlet - state lifetime:

The competing intramolecular photophysical processes that can occur fromS1 (v = 0) undergoes fluorescence, intersystem crossing and internal conversion, with first - order rate constants of, k_f, k_{isc}, k_{ic} respectively **(Figure-2)**.

Applying a standard treatment of first - order chemical kinetics, the rate of disappearance of the excited molecules, S1, J total, is given by:

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

(the sign shows that the excited state S1 decays with time; that is, its concentration decreases with time).

Solution of this equation gives the exponential decay form of the transient excited S1molecule:

$[S1]t = [S1]0 \exp(- t / \tau)$

where [S1]0 is the concentration of excited S1molecules at time t = 0 resulting from the initial exciting pulse, [S1] t is the concentration of excited S1molecules at time t and τ is the excited singlet - state lifetime of the S1 excited state.

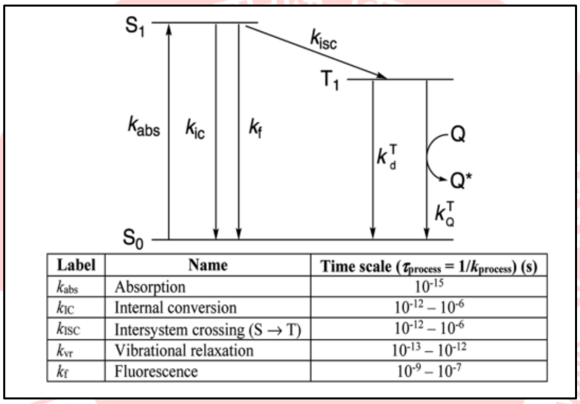
Where,

t = τ

[S1] t = [S1]0 exp (- 1) = [S1]0 / e

Thus, τ is given by the time for the concentration ofS1 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 S1 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- Excited Singlet - State Lifetime

The Technique of time - correlated single - photon counting

The technique of time-correlated single - photon counting **(Figure-3)** 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.

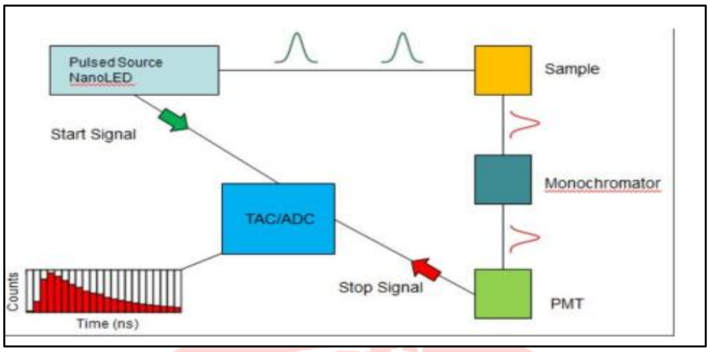


Figure- Schematic diagrams of the principal components of a time - correlated single - photon counting apparatus

Excited singlet - state radiative lifetime

The excited singlet - state radiative lifetime, τ_0, of S1 is the lifetime of S1 in the absence of any radiation less transitions; that is, the only deactivation 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_{tatal} is greater than k_f, 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 S1 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 Jabs

$\Phi_f = J_f / J_{abs}$

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;

$\Phi_f = J_f / J_{abs}$

$\Phi_f = J_f / J_{total}$

$\Phi_f = k_f[S1] / k_{total}[S1]$ $\phi_f = k_f / k_{total}$

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 S1 is given by:

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

Where τ_0 has units of s and εmax has units of $mol^{-1}\ cm^{-1}$.

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

Lifetimes of the T1 excited state

Similar considerations apply to the T1 triplet state as to theS1 singlet state. By analogy with the expressions for the lifetimes of S1, the values for T1 are given by:

$\tau = 1/k_p$

$\tau = 1/k_{tortal} = 1/k_p + k_{isc}$

An order - of - magnitude estimate of the radiative lifetime of T1 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 T1 states will have a longer lifetime than S1 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 (~1μs) 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.

Effect of light intensity on the rate of photochemical reaction

"The law states that each molecule takes one quantum of radiation for its activation and subsequent chemical reaction. So, the rate of Photochemical reaction increases with increasing intensity of light and is independent of the concentration of the reactant and product."

There are two main effects of light intensity as given:

1. **Absorption of single photon:** When a molecule is excited by the absorption of one proton, particle or quanta, such type of the reaction is called monophotonic photochemical chemical reaction.

The rate of reaction depends upon:

a) **If reaction is unimolecular:** In unimolecular reaction, the rate of photochemical reaction is directly proportional to the intensity of light (I).
b) **If reaction is bimolecular:** During the reaction, when atoms or radical recombine bimolecularly; the reaction rate gets equal to under rate of intensity of light ($\sqrt{I}$).

2. **Absorption of two photons:** When single or more molecules absorb two photons' particles of incident light, these reactions are called biphotonic photochemical reaction. It occurs by the interaction of two excited molecules and the rate of rection is directly proportional to the square of the light intensity as I^2.

Photochemical Processes:

Photochemical Reactions: We know that according to Einsteins law of photochemical equivalence, every reacting molecule absorbs one quantum of radiation and clearly, the number of reacting molecules should be equal to the number of quanta absorbed. But it is not fully true and, in many cases, it has been observed that

$$\boxed{A \quad + \quad h\nu \longrightarrow \quad A^*}$$

Atom One quantum Excited atom

(i) A small amount of light absorbed can brings about only a large amount of reaction.
(ii) A large amount of light absorbed brings about only a small amount reaction.

This anomaly is explained on the basis of the fact that a photochemical reaction consists of two processes. M. Bodenstein proposed that photochemical processes involve two distinct processes.

1. Primary Process: Primary processes are those processes in which quantum of energy (hv) is absorbed by a molecule, resulting in the excitation of the molecule. Thus, the absorption of radiation by an atom or a molecule to form an excited atom or molecule is known as primary process in photochemistry. The excited atom or molecule form by the absorption may then behave in different ways. There are four distinct possibilities of excitation of the molecule.

(i) In Type I, the energy absorbed raises the molecule to excited state, which is unstable. The molecule breaks up into atoms or radicals immediately on absorption of photon, i.e., dissociation of the molecule takes place. The fragments obtained are associated with different kinetic energy and a continuous spectrum is obtained without any fine spectrum.

(ii) In Type II, the electronic transition from a stable ground state to stable excited state. There will be no direct dissociation of the molecule. This is indicated by the corresponding spectrum consisting of discontinuous band with a fine structure.

(iii) In Type III, the molecule is raised to a higher level. The energy acquired is more than the binding energy. Therefore, molecule would undergo dissociation and the spectrum will be continuous throughout.

(iv) In Type IV, transition occurs from lower level to a stable upper level. During the course of vibration, the molecule may shift from the stable state to the unstable state. When a shift of this type takes place, the molecule would dissociate producing atoms or radicals. This type of behaviour is referred to as predissociation. The spectrum would show fine structure. In the region of predissociation, the rotational lines are absent and the rotational bands have a diffuse appearance.

The molecule which absorbs light may get dissociated yielding excited state atoms or free radicals. The primary process may also involve loss of vibrational energy of excited molecules by collision with other molecules as well as by fluorescence and phosphorescence.

Secondary Process:

The excited molecule during the primary process may undergo one of the following changes to complete the reaction.

1. It may react to form the final product.
2. It can be partly or fully deactivated and no more reaction occurs.
3. It may start a chain reaction.

As the law of photochemical equivalence is applicable to primary processes, light radiations are essential only for the primary process. It is important to note that the secondary process may take place in the dark provided the products of primary reactions are available. Secondary photochemical processes. The activated molecules or the products of primary process may react with other molecules to form products or the activated molecules may emit the radiation of either the same or the different frequency. These processes are known as secondary processes. In the light of above discussion, mechanism of some important photochemical reaction is given below:

Photochemical decomposition of hydrogen iodide in the gaseous phase (Photolysis of hydrogen iodide): on the exposure to radiations having wavelength in the range 207-252 nm, the decomposition of hydrogen iodide takes place. The quantum yield of the reaction is 2. This has been explained with the help of mechanism given below.:

(a) Primary process: $HI + hv \rightarrow H + I$ …(i)

(b) Secondary process: $H + HI \rightarrow H_2 + I$ …(ii)

$I + I \rightarrow I_2$ …(iii)

Possibility of other secondary processes such as

$I + HI \rightarrow I_2 + H$ …(iv)

$H + H \rightarrow H_2$ …(v)

$I + H \rightarrow HI$ …(vi)

is ruled out because the reactions (iv) are endothermic and takes place slowly and reactions (v) and (vi) are highly exothermic. The heat produced results into dissociation of the product of these reactions. The overall reaction is, therefore, obtained by adding reactions, (i), (ii), (iii).

$2HI + hv \rightarrow H_2 + I_2$

Thus, for every one quantum of light absorbed, two molecules of HI are decomposed. Hence, the quantum yields of reaction is 2. It may be noted that while adding the equations (i), (ii), and (v), no distinction has been made between the excited iodine atom and normal iodine atom. The quantum yield for the photochemical decomposition of HBr is also 2 which suggests that the mechanism of this reaction is exactly similar to that of photolysis of HI.

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

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 ^{0}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.

Non radiative processes

These transitions involve the return of the activated molecule from the higher (activated states) excited state (S$_3$, S$_2$ or T$_3$, T$_2$) 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 Intersystem 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:4) 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 v ′= 0. From this stage it returns back singlet. S_0 state through producing Phosphorescence.

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 v ′ = 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:4).

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 v ′ = 0 to ground state S_0 is spectroscopically forbidden because the selection rule ΔS is not applicable, but this transition occurs in slower rate than allowed electronic transition. The emission of this transition is called Phosphorescence. The time period of Phosphorescence is 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.

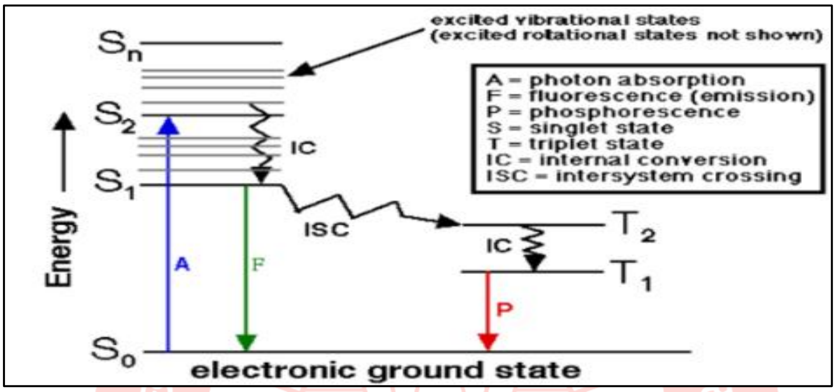


Figure: Phosphorescence

Photochemical Reaction

As the name of photochemical reactions suggests, these are concerned with light. So we can define these reactions of chemistry as the chemical reactions that deal with the rate of reaction and whose mechanisms result from the exposure of reactants to light radiations. Photochemical reactions depend upon the number of protons which are known to activate these reactions. One of the most common examples of these reactions is photosynthesis which is the base for all types of life forms.

Photochemical reaction deals with the chemical effects of light. Trommsdorff was the first person to describe the photochemical reaction in 1834. He observed the reaction on crystals of santonin, which when exposed to sunlight turned yellow and burst. Those reactions which occur by absorption of light energy are called photochemical reactions. The diagram of the photochemical reaction is given below:

Photochemical reactions are of five types which are as follows:

(I) Photo-Dissociation

Photolysis is also called photo fragmentation or photodissociation, or photodecomposition. It is a chemical reaction in which photons break down molecules of a chemical compound. It is one or more photons interacting with a single target molecule and is not limited to visible light. Flash photolysis is an example of photo-dissociation.

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).

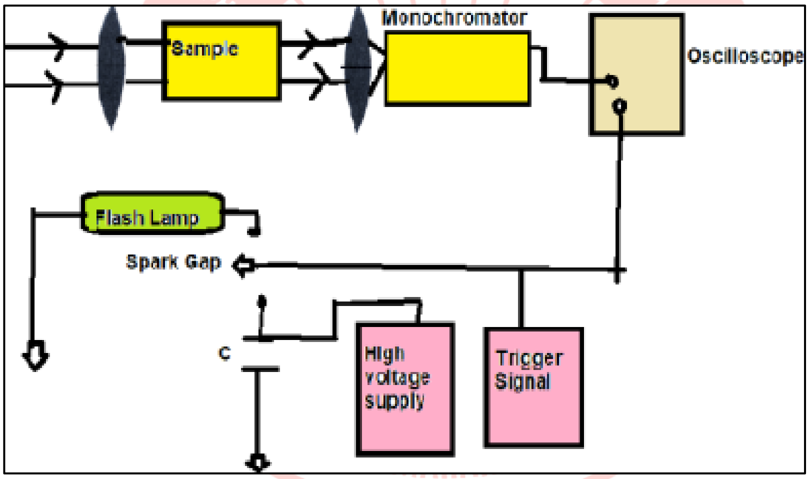
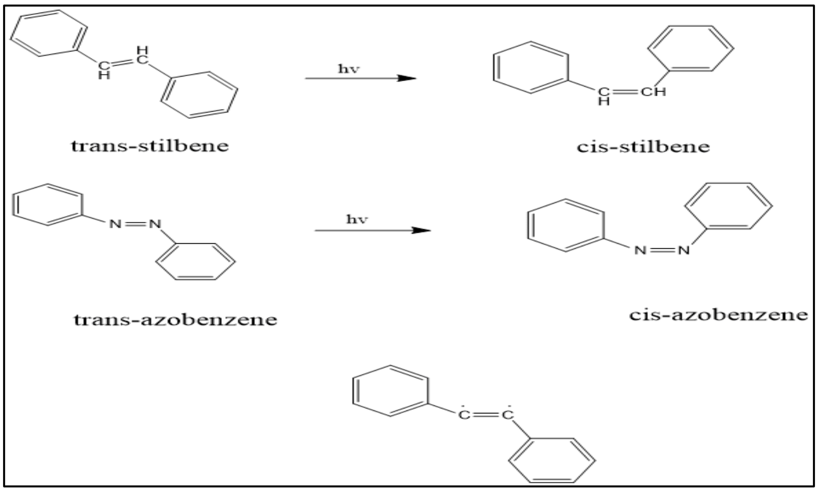


Figure: Experimental Techniques: Flash Photolysis

(II) Photo-Induced Rearrangements, Isomerization

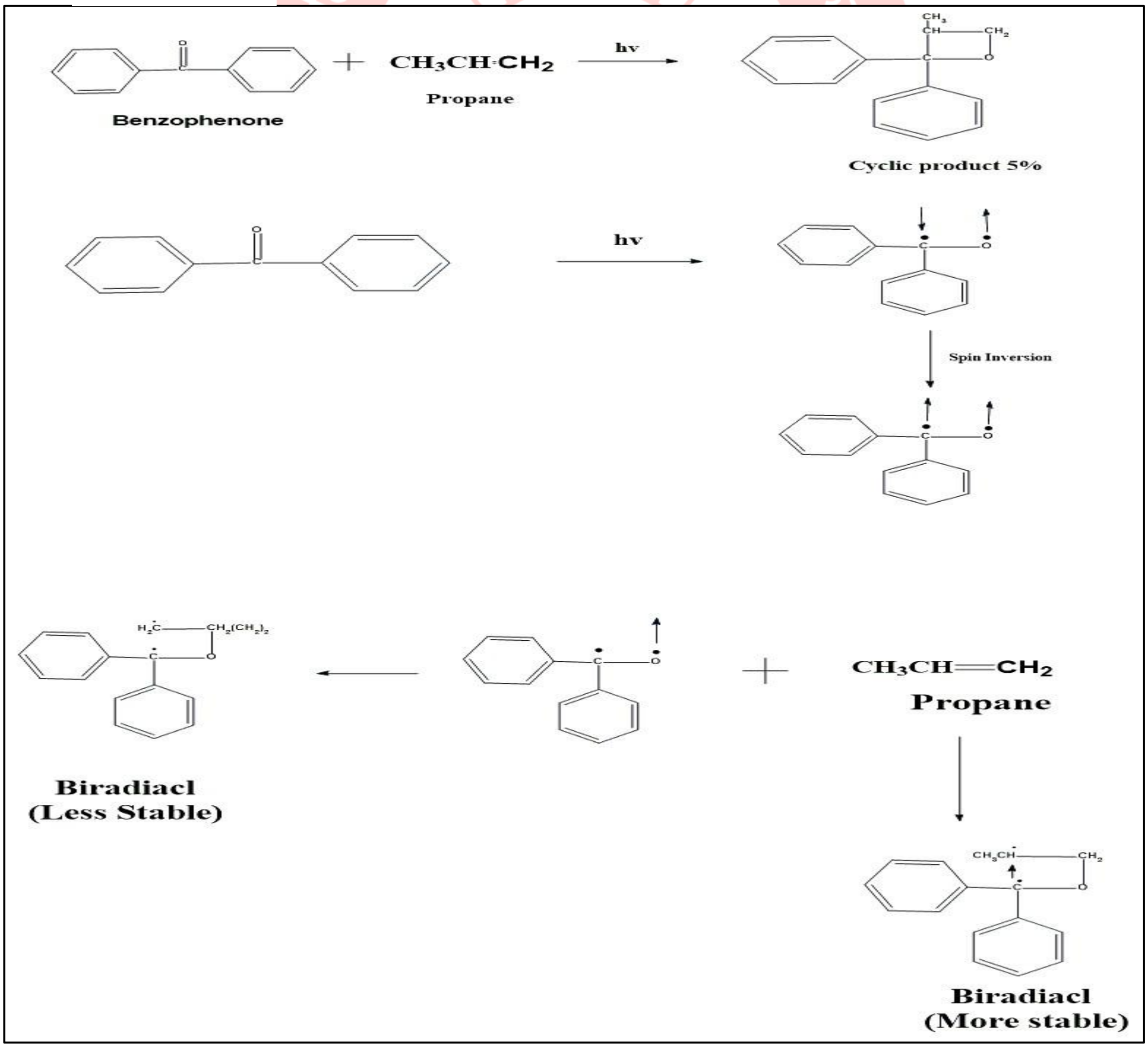
Photoisomerization is the photochemical cis-trans isomerization induced by photo-excitation (which is the reason for structural change between isomers). It is the isomerization of organic molecules with a double bond in their structure. This reaction is a common photo-reaction, during which one isomer is converted into another by light. Both reversible and irreversible isomerization reactions exist. However, photoisomerization usually refers to a reversible process.



(III) Photo-Addition

It is a bimolecular photochemical process in which, by electronically excited unsaturated molecules, a single product is formed and occurs under the influence of light.

Mechanism:



(IV) Photo-Substitution

Photo-substitution reactions are substitution reactions performed in the presence of sunlight. An example of this reaction is the chlorination of CH_4CH_4 using HCl.

$$CH_4 + HCl \rightarrow CH_3Cl + H_2CH_4 + HCl \rightarrow CH_3Cl + H_2$$

Aquation is the most common in photo substitution reactions. It refers to the ligand exchange between the primary and secondary coordination spheres with conservation of the oxidation state and coordination number of the metal ion.

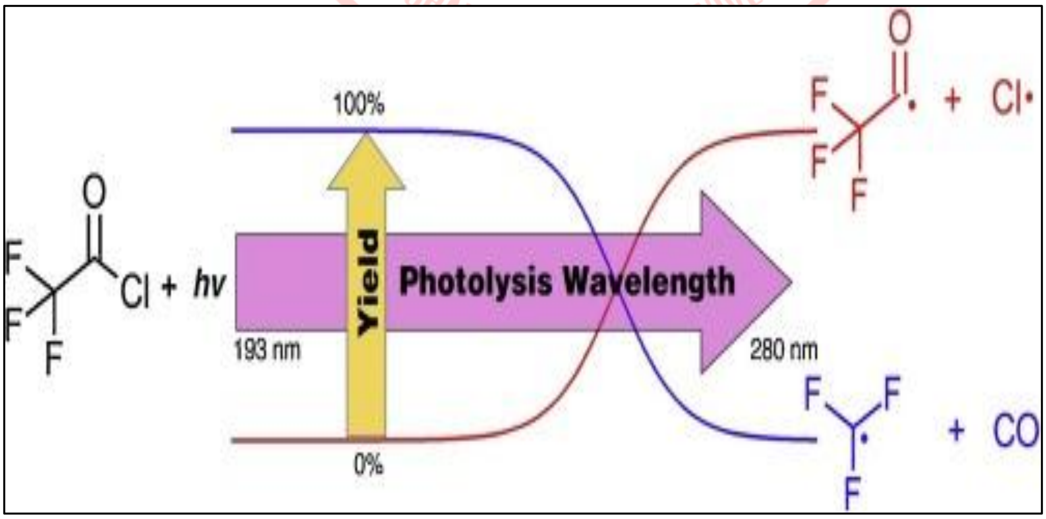
(V) Photo-Redox Reaction

Photo-redox catalysis is an important field both in environmental applications as well as in organic synthesis. It is the branch of photochemistry that uses single electron transfer. Photo-redox catalysts are generally taken from three classes of materials which are

semiconductors, transition-metal complexes, and organic dyes.

Gas-phase photolysis:

Gas-phase photolysis is a chemical process where molecules in the gaseous state break down or transform due to the absorption of light (photons). This absorption excites the molecule to a higher energy state, which can then lead to a variety of outcomes, including bond breaking, fragmentation, or reaction with other molecules.



Short & Long Answer Type Questions

Q. What is meant by the classification of reaction mechanisms in chemical kinetics?(CSJMU2022,23)

Ans. Reaction mechanisms describe the step-by-step sequence of elementary reactions by which an overall chemical change occurs. They are classified into:

- **Elementary reactions** – occur in a single step and involve one transition state.
- **Complex reactions** – consist of multiple elementary steps. These can be:
    - **Consecutive reactions** – one product becomes the reactant for the next step.
    - **Parallel reactions** – a reactant gives multiple products simultaneously.
    - **Chain reactions** – involve initiation, propagation, and termination steps often

Q. What is the effect of light intensity on the rate of a photochemical reaction?

Ans. In photochemical reactions, light provides the energy to initiate the reaction by exciting molecules. Increasing light intensity increases the number of photons absorbed, thereby raising the number of molecules in excited states and increasing the reaction rate-up to a point of saturation where all molecules are already excited.

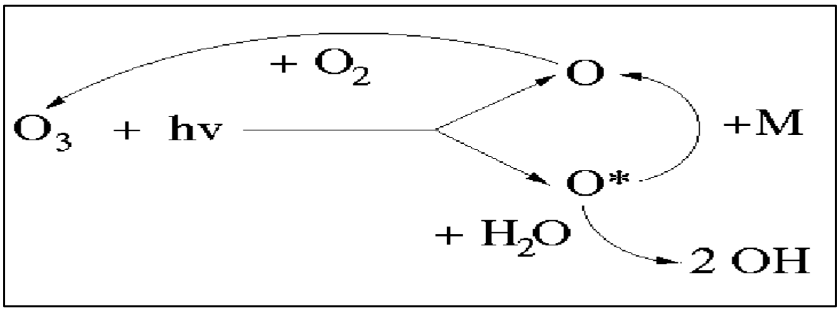
Q: What are the major types of photochemical reactions?(CSJMU216.18,22)

Ans.

- **Photodissociation** – light breaks chemical bonds.
- **Gas-phase photolysis** – gas molecules absorb light and decompose.
- **Photoionization** – light ejects electrons from atoms/molecules.
- **Photosensitized reactions** – a photosensitizer absorbs light and transfers energy to the reactant.

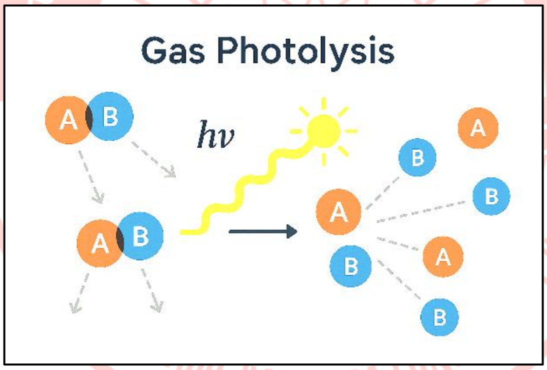
Q. What is photodissociation and give an example?

A: Photodissociation is a chemical process in which a molecule absorbs a photon and breaks into smaller fragments (often radicals).



Q. Describe gas phase photolysis. (CSJMU2014,16,20,17)

Ans. Gas-phase photolysis is a photochemical process where gaseous molecules absorb light energy—typically ultraviolet (UV) or visible radiation—and undergo chemical transformations. This phenomenon is pivotal in atmospheric chemistry, influencing the formation and degradation of various compounds.



How Gas-Phase Photolysis Works

When a gas-phase molecule absorbs a photon, it becomes electronically excited. This excitation can lead to:

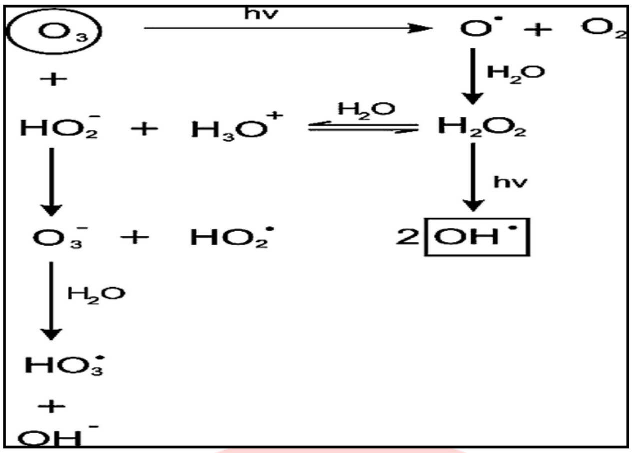
- **Bond Cleavage**: The molecule breaks into smaller fragments or radicals.
- **Isomerization**: The molecule rearranges its structure without breaking bonds.
- **Ionization**: The molecule loses or gains electrons, forming ions.

The specific outcome depends on the molecule's structure and the photon's energy.

Atmospheric Significance

In the Earth's atmosphere, gas-phase photolysis plays a crucial role in:

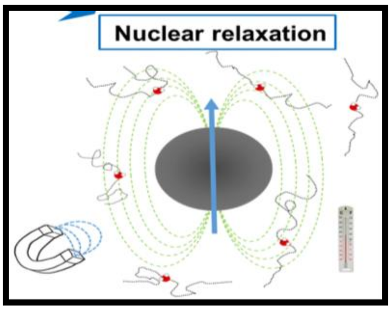
- **Ozone Formation and Depletion**: Photolysis of oxygen molecules (O_2) leads to ozone (O_3) formation, while ozone photolysis contributes to its breakdown.



- **Pollutant Degradation**: Compounds like nitrogen dioxide (NO_2) and volatile organic compounds (VOCs) undergo photolysis, leading to secondary pollutants like ozone and particulate matter.
- **Radical Generation**: Photolysis produces reactive radicals (e.g., hydroxyl radicals) that drive many atmospheric reactions.

Q. Discuss Which factors effect nuclear relaxation. (CSJMU2019,21)

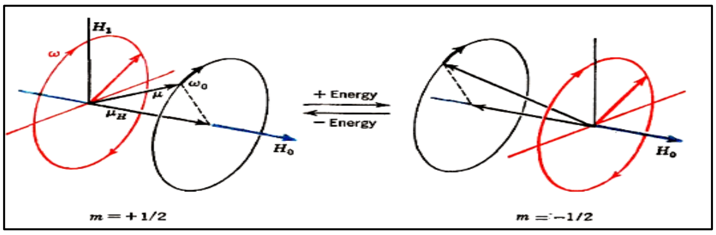
Ans. In the context of nuclear magnetic resonance (NMR), the term relaxation indicates the process by which the magnetic atomic nuclei reach thermal equilibrium with the chaotic molecular environment. In NMR, this process can be very slow, requiring between a fraction of a second to many minutes, depending on the sample and the environmental conditions. To NMR spectroscopists, relaxation is a friend, since it generates the nuclear magnetisation from which all NMR signals are derived; at the same time, relaxation can be a foe, since it limits how long any different forms of spin order last. For many years, it was generally thought that relaxation was intrinsic to the sample, and could not readily be manipulated or overcome. However, recent experiments have shown that in some cases the nuclear spin systems may be held in special configurations called long-lived states that are to some extent protected against relaxation.



Factors Affecting Nuclear Relaxation:

1. Magnetic Field Strength:

The strength of the magnetic field (H_0) impacts relaxation times, with different magnetic fields leading to varying relaxation rates.



2. Molecular Properties:

- Size and Shape: Larger molecules and those with restricted motion tend to have longer relaxation times due to slower molecular tumbling, which affects the efficiency of relaxation mechanisms.
- Molecular Mobility: The rate of molecular motion influences the efficiency of relaxation processes.
- Chemical Environment: The chemical environment surrounding a nucleus, including the presence of nearby atoms and functional groups, affects relaxation through factors like chemical shifts and spin-spin coupling.

3. **Viscosity**

- High viscosity = slower molecular motion = longer T_1, shorter T_2.
- Low viscosity = faster motion = more efficient T_1 relaxation.

4. **Dipolar Interactions**

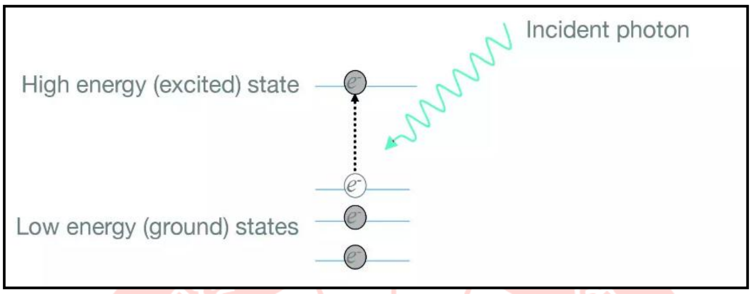
- Magnetic interactions between neighbouring nuclear spins.
- Strong dipolar coupling (common in solids) enhances T_2 relaxation.

5. **Chemical Shift Anisotropy (CSA)**

- Particularly significant in solids or partially aligned systems.
- CSA contributes to relaxation, especially T_2.

Q. Explain the effect of light intensity on rate of photochemical reactions. (CSJMU2019,23)

Ans. In photochemistry, an excited state refers to a higher energy level of a molecule that is reached when it absorbs a photon of light, causing one or more electrons to jump to a higher energy orbital. This process is fundamental to many photochemical reactions, as the excited state molecule possesses different chemical properties and is more reactive than its ground state counterpart.



Explanation:

- **Ground State:**

A molecule's normal, lowest energy state.

- **Excitation:**

When a molecule absorbs a photon of light with the right energy (wavelength), an electron can be promoted to a higher energy level (excited state).

- **Excited State Properties:**

The excited state molecule has a different electronic structure compared to its ground state, which can lead to changes in:

  - **Bonding:** Single bonds might gain double bond character, and vice versa.
  - **Dipole Moment:** The distribution of electron density changes, affecting the molecule's polarity.
  - **Acidity/Basicity:** The molecule's ability to donate or accept protons can be altered.

- **Photochemical Reactions:**

These altered properties make the excited state molecule more susceptible to chemical reactions that might not occur in the ground state.

- **Excited State Lifetimes:**

The excited state is typically short-lived and will eventually return to the ground state through various deactivation processes, often releasing energy as light or heat.

- **Singlet and Triplet States:**

Excited states can be classified as singlet or triplet states, depending on the spin of the electrons. These different states have varying lifetimes and reactivity.

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 or a phonon) 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). This return to a lower energy level is known as de-excitation and is the inverse of excitation.

Q. Describe the rate of formation of HBr from the photochemical reaction of H_2 and Br_2. (2015,13)

Ans. The hydrogen-bromine or the H_2-Br_2 reaction is a typical case of photochemical reactions for which

the overall reaction can be written as given below.

$$H_2 + Br_2 \xrightarrow{h\nu} 2HBr$$

Since it is a chain reaction, the elementary steps for the same can be proposed as

Initiation: $Br_2 + h\nu \xrightarrow{k_1} 2Br$

Propagation: $Br + H_2 \xrightarrow{k_2} HBr + H$

$H + Br_2 \xrightarrow{k_3} HBr + Br$

Inhibition: $H + HBr \xrightarrow{k_4} H_2 + Br$

Termination: $Br + Br \xrightarrow{k_5} Br_2$

The net rate of formation of HBr must be equal to the sum of the rate of formation and the rate of disappearance of the same i.e.

$$\frac{d[\mathrm{HBr}]}{\mathrm{dt}} = k_2[Br][H_2] + k_3[H][Br_2] - k_4[H][HBr]$$

Now, in order to obtain the overall rate expression, we need to apply the steady-state approximation on the H and Br first i.e.

$$\frac{\mathrm{d[H]}}{\mathrm{dt}} = k_2[Br][H_2] - k_3[H][Br_2] - k_4[H][HBr] = 0$$

Similarly,

$$\frac{\mathrm{d[Br]}}{\mathrm{dt}} = 2k_1[Br_2] - k_2[Br][H_2] + k_3[H][Br_2] + k_4[H][HBr] - 2k_5[Br]^2 = 0$$

Taking negative both side of equation, we have

$$-k_2[Br][H_2] + k_3[H][Br_2] + k_4[H][HBr] = 0$$

Using the above result in equation, we get

$$2k_1[Br_2] + 0 - 2k_5[Br]^2 = 0$$

$$2k_5[Br]^2 = 2k_1[Br_2]$$

Similarly, rearranging equation again

$$k_3[H][Br_2] + k_4[H][HBr] = k_2[Br][H_2]$$

$$[H] = \frac{k_2[Br][H_2]}{k_3[Br_2] + k_4[HBr]}$$

Now using the value of [Br] from equation, the above equation takes the form

$$[H] = \frac{k_2(k_1/k_5)^{1/2}[Br_2]^{1/2}[H_2]}{k_3[\mathrm{Br_2}] + k_4[\mathrm{HBr}]}$$

Now rearranging equation again in different mode i.e.

$$k_2[Br][H_2] - k_4[H][HBr] = k_3[H][Br_2]$$

Using the above result in equation, we have

$$\frac{d[\mathrm{HBr}]}{\mathrm{dt}} = k_3[H][Br_2] + k_3[H][Br_2]$$

$$d[\mathrm{HBr}]/\mathrm{dt} = 2k_3[H][Br_2]$$

After putting the value of $[H]$ from equation -

$$\frac{d[\mathrm{HBr}]}{\mathrm{dt}} = \frac{2k_3k_2(k_1/k_5)^{1/2}[Br_2]^{3/2}[H_2]}{k_3[\mathrm{Br}_2] + k_4[\mathrm{HBr}]}$$

Taking $k_3[\mathrm{Br}_2]$ as common in the denominator and then canceling out the same form numerator, we get

$$\frac{d[\mathrm{HBr}]}{\mathrm{dt}} = \frac{2k_2(k_1/k_5)^{1/2}[Br_2]^{1/2}[H_2]}{1 + (k_4/k_3)[\mathrm{HBr}]/[Br_2]}$$

Now since $2k_1[Br_2] = 2I_{ab}$, then

$$k^{1/2}[Br_2]^{1/2} = (I_{ab})^{1/2}$$

Using the above result in equation , we get

$$\frac{d[\mathrm{HBr}]}{\mathrm{dt}} = \frac{2k_2(I_{ab}/k_5)^{1/2}[H_2]}{1 + (k_4/k_3)[\mathrm{HBr}]/[Br_2]}$$

Hence, the rate of hydrogen-bromine reaction is directly proportional to the square root of the intensity of absorbed radiation.

Q. Propose the mechanism and rate of photo-chemical decomposition of hydrogen peroxide in presence of carbon monoxide. (2014,12)

Ans.

When hydrogen peroxide is irradiated (UV/near-UV), the dominant primary step is homolytic photolysis:

1. Primary photolysis

$$H_2O_2 + h\nu \xrightarrow{J} 2\ \cdot OH$$

where J is the first-order photolysis rate constant (depends on light intensity, wavelength, H_2O_2 absorbance and quantum yield).

2. Fast secondary reactions of •OH
   In the presence of dissolved CO the hydroxyl radical reacts rapidly with CO to give the HOCO (formyl) radical:

$$\boxed{\cdot OH + CO \xrightarrow{k_1} HOCO\cdot}$$

HOCO· (often written HOCO or HCOO· depending on notation) has several possible fates depending on conditions (pH, O_2 presence, solvent):

- HOCO· → CO_2 + H· (decomposition / decarboxylation)
- HOCO· + O_2 → HOCOO· (peroxy adduct) → further propagation / termination
- HOCO· + ·OH / other radicals → termination products

Chain propagation / H_2O_2 as radical sink
Hydroxyl radicals also react with H_2O_2 (self-reaction channel):

$$\boxed{\cdot OH + H_2O_2 \xrightarrow{k_2} H_2O + HO_2\cdot}$$

HO_2· can either terminate (HO_2 + HO_2 → H_2O_2 + O_2) or react further to produce H_2O_2 or O_2 depending on conditions. Thus, there are chain and termination branches: some radical pathways regenerate H_2O_2 (via HO_2 dimerization) but many lead to net consumption (via CO oxidation to CO_2 and radical recombination).

Steady-state for $[\cdot OH]$ (d[•OH]/dt ≈ 0):

$$\text{formation} = \text{loss}$$

$$J[H_2O_2] \;=\; k_1[CO][\cdot OH] \;+\; k_2[H_2O_2][\cdot OH] \;+\; k_r[\cdot OH]^2$$

If radical concentration is low, quadratic term small; then

$$[\cdot OH] \approx \frac{J[H_2O_2]}{k_1[CO] + k_2[H_2O_2]}$$

Rate of net H_2O_2 loss has two main contributions:

1. direct photolysis: $-J[H_2O_2]$
2. reaction of produced •OH with H_2O_2: $-k_2[H_2O_2][\cdot OH]$ (this is a chain step consuming additional H_2O_2)

Photolysis produces •OH from H_2O_2; in presence of CO most •OH are trapped forming HOCO· which changes the radical chain balance. Kinetics can be approximated by

So:

$$\frac{d[H_2O_2]}{dt} = -J[H_2O_2] \;-\; k_2[H_2O_2][\cdot OH]$$

Substitute [•OH]:

$$\frac{d[H_2O_2]}{dt} = -J[H_2O_2]\left(1 + \frac{k_2[H_2O_2]}{k_1[CO] + k_2[H_2O_2]}\right) = -J[H_2O_2] \cdot \frac{k_1[CO] + 2k_2[H_2O_2]}{k_1[CO] + k_2[H_2O_2]}$$

$$\frac{d[H_2O_2]}{dt} = -J[H_2O_2]\frac{k_1[CO] + 2k_2[H_2O_2]}{k_1[CO] + k_2[H_2O_2]},$$

Q. Effect of light intensity on the rate of photochemical reaction. (CSJMU2012)

Ans. Primary photochemical step-

In a photoreaction, the rate of primary excitation (photon absorption) is:

$$R_{\text{abs}} = I \cdot (1 - 10^{-\varepsilon c l}) \cdot \phi$$

where:

- III = incident light intensity (photons per second per area)
- ε\Var epsilon (ε) = molar absorptivity of reactant
- ccc = concentration
- lll = path length
- ϕ\phiϕ = quantum yield of the primary process

2. Low intensity (linear regime)

- At low/moderate light intensity, the rate of reaction is directly proportional to the light intensity.
- Reason: each absorbed photon initiates one event, and radicals/excited states are few enough that bimolecular radical–radical recombination is negligible.

$$\text{Rate} \propto I$$

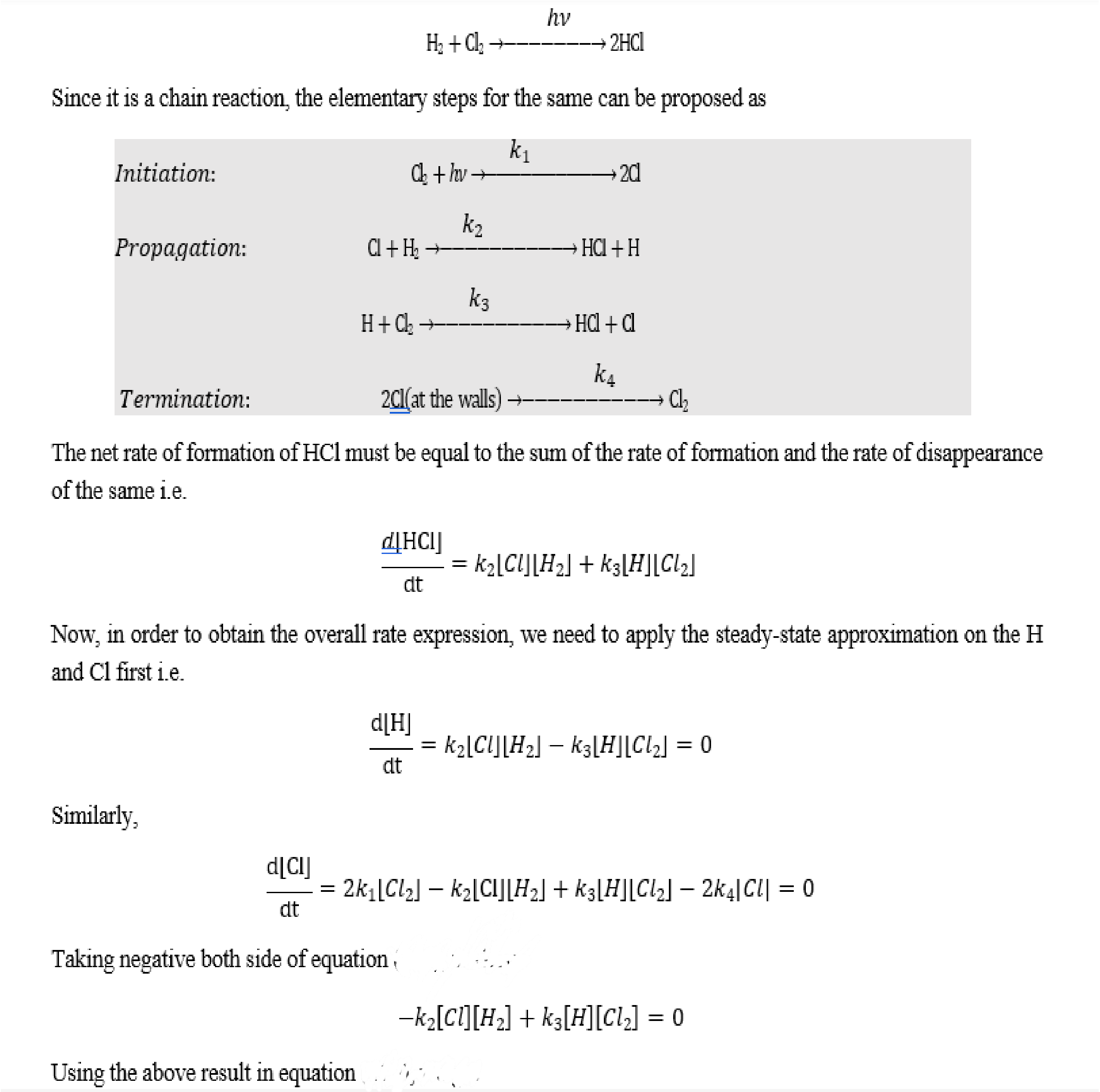
3. High intensity (square-root regime in chain reactions)

- At very high intensity, many radicals are generated simultaneously.
- Radical–radical termination becomes important.
- In a steady-state approximation:

$$[R\cdot] \propto \sqrt{I}$$

Q. Discuss kinetics of the following photochemical reaction: (CSJMU2022,23)

$$H_{2(g)} + Cl_{2(g)} \xrightarrow{hv} 2HCl_{(g)}$$



$$H_2 + Cl_2 \xrightarrow{hv} 2HCl$$

Since it is a chain reaction, the elementary steps for the same can be proposed as

Initiation: $Cl_2 + hv \xrightarrow{k_1} 2Cl$

Propagation: $Cl + H_2 \xrightarrow{k_2} HCl + H$

$H + Cl_2 \xrightarrow{k_3} HCl + Cl$

Termination: $2Cl(\text{at the walls}) \xrightarrow{k_4} Cl_2$

The net rate of formation of HCl must be equal to the sum of the rate of formation and the rate of disappearance of the same i.e.

$$\frac{d[HCl]}{dt} = k_2[Cl][H_2] + k_3[H][Cl_2]$$

Now, in order to obtain the overall rate expression, we need to apply the steady-state approximation on the H and Cl first i.e.

$$\frac{d[H]}{dt} = k_2[Cl][H_2] - k_3[H][Cl_2] = 0$$

Similarly,

$$\frac{d[Cl]}{dt} = 2k_1[Cl_2] - k_2[Cl][H_2] + k_3[H][Cl_2] - 2k_4[Cl] = 0$$

Taking negative both side of equation ([illegible]

$$-k_2[Cl][H_2] + k_3[H][Cl_2] = 0$$

Using the above result in equation [illegible]

$$|Cl| = \frac{k_1}{k_4}|Cl_2|$$

Similarly, rearranging equation (

$$k_2[Cl][H_2] - k_3[H][Cl_2] = 0$$

or

$$|H| = \frac{k_2[Cl][H_2]}{k_3[Cl_2]}$$

Now using the value of [Cl] from equation (

$$|H| = \frac{k_2[H_2]}{k_3[Cl_2]}\frac{k_1}{k_4}|Cl_2| = \frac{k_1k_2[H_2]}{k_3k_4}$$

Using values of $[Cl]$ and $[H]$ from equation (

$$\frac{d\,[\mathrm{HCl}]}{\mathrm{dt}} = k_2\frac{k_1}{k_4}|Cl_2|\,|H_2| + k_3\frac{k_1k_2[H_2]}{k_3k_4}|Cl_2|$$

or

$$\frac{d\,[\mathrm{HCl}]}{\mathrm{dt}} = \frac{k_1k_2[Cl_2]\,[H_2]}{k_4} + \frac{k_1k_2[H_2]\,[Cl_2]}{k_4}$$

Now since $2k_1[Cl_2] = 2I_{ab}$, then

$$k_1[Cl_2] = I_{ab}$$

Using the above result in equation

$$\frac{d\,[\mathrm{HCl}]}{\mathrm{dt}} = \frac{k_2I_{ab}[H_2]}{k_4} + \frac{k_2I_{ab}[H_2]}{k_4}$$

$$2k_1[Cl_2] + 0 - 2k_4[Cl] = 0$$

or

$$2k_1[Cl_2] = 2k_4[Cl]$$

or

or

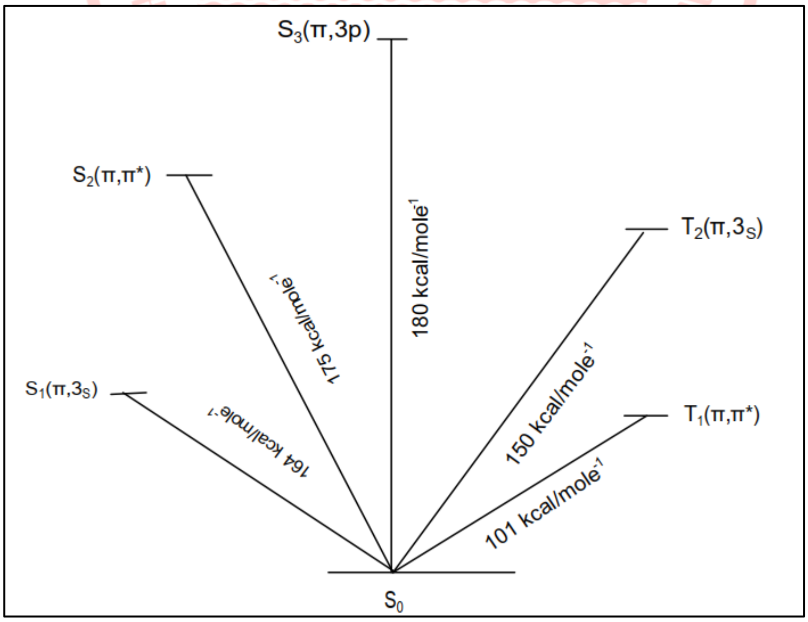
$$\frac{d\,[\mathrm{HCl}]}{\mathrm{dt}} = \frac{2k_2 I_{ab}[H_2]}{k_4}$$

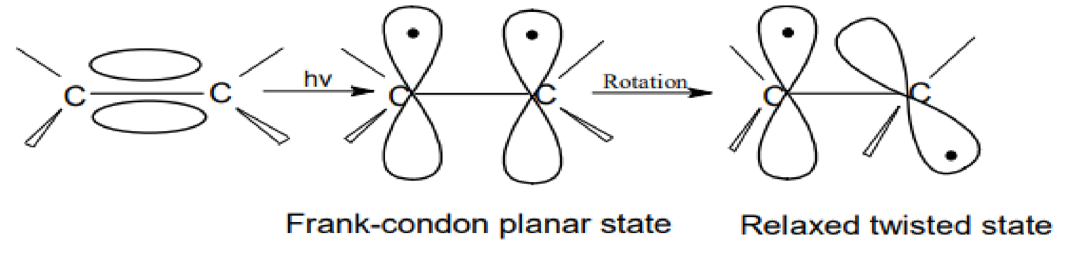
Hence, we can conclude that the rate of hydrogen-bromine reaction is directly proportional to the intensity of absorbed radiation. It is also worthy to note that the quantum yield of the hydrogen-chlorine reaction is much higher than that of hydrogen-bromine reaction which may simply be attributed to the exothermic nature of the second step in H_2-Cl_2 reaction which makes it spontaneous in nature.

Unit-III

Photochemistry of Alkenes:

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.



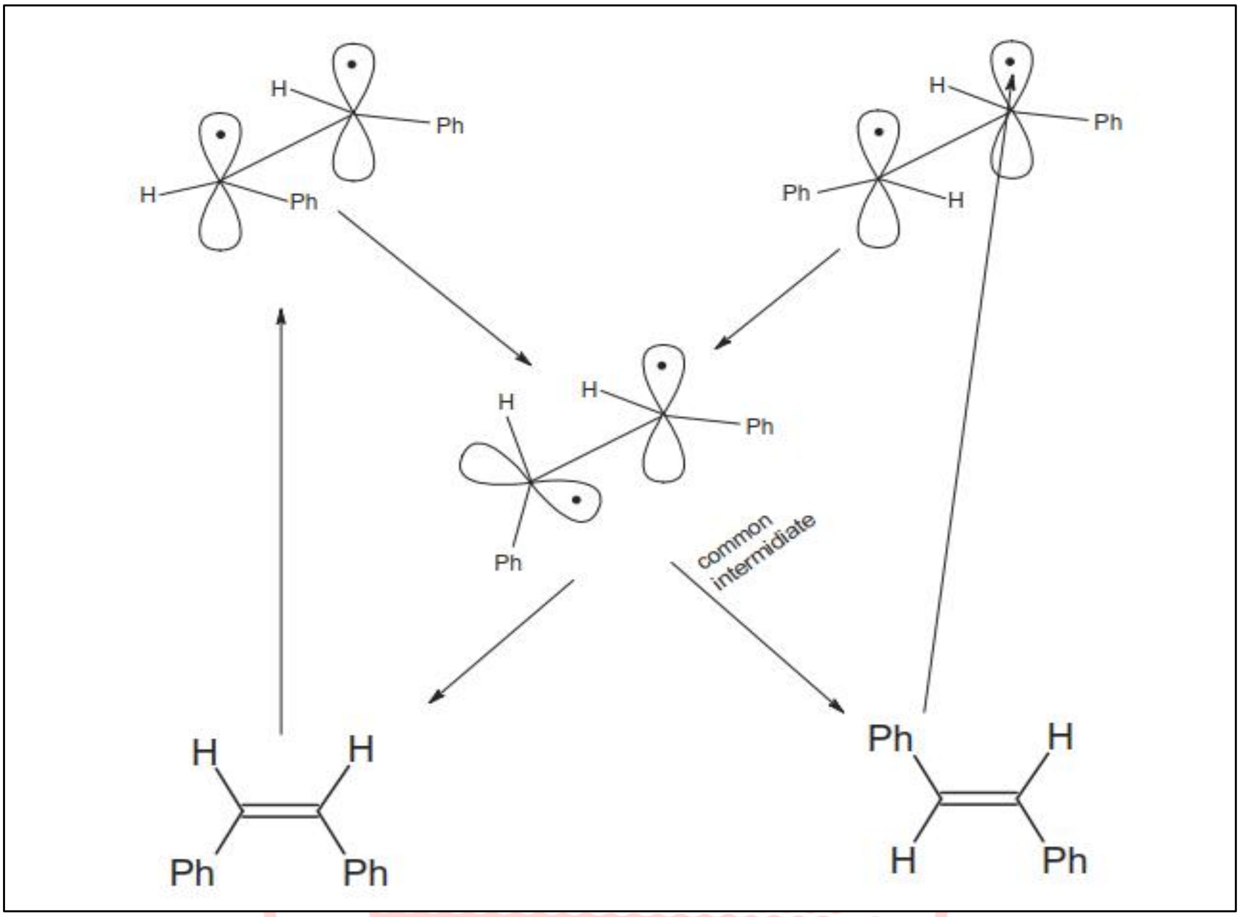


Cis-Trans isomerisation in alkenes:

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.

1. Cis-Trans isomerisation of alkenes by direct irradiation:

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 photo stationary state. 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 affected 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. However, as previously stated, the trans form absorbs more light at the exciting wavelength (εmax trans = 16300) than the cis form (max cis = 2880), and as a result, the trans isomer is almost fully transformed to the cis isomer.

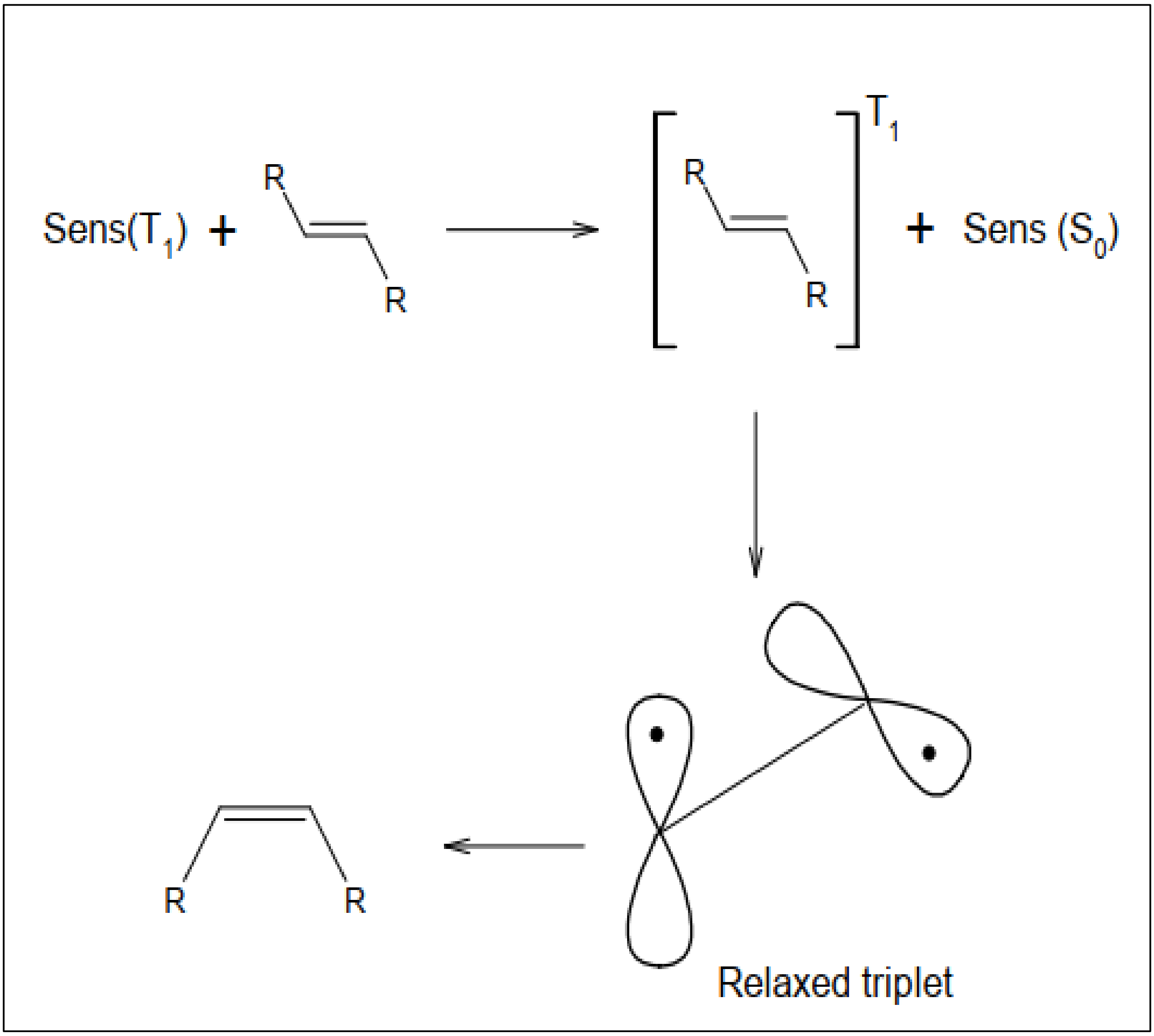


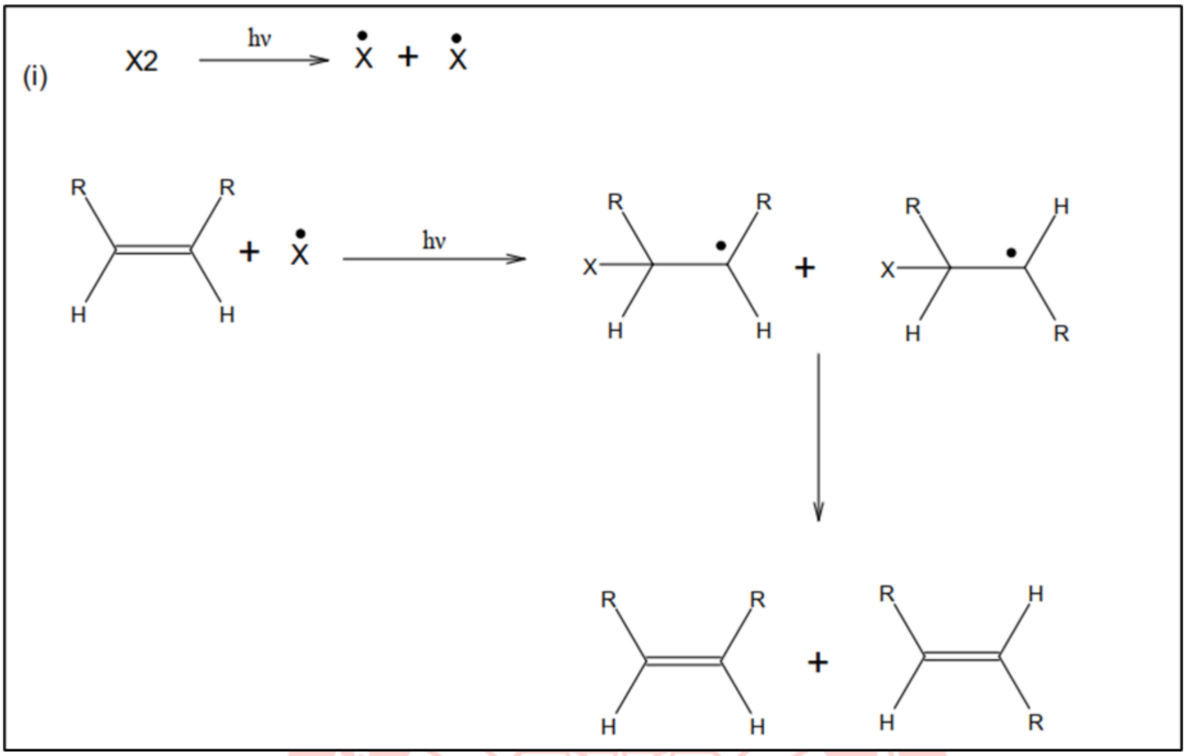
2. Sensitised cis-trans isomerisation:

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.

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 (S0), they form a mixture of isomers. The proportion of cis-trans isomer in the photo stationary 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 photo stationary 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.

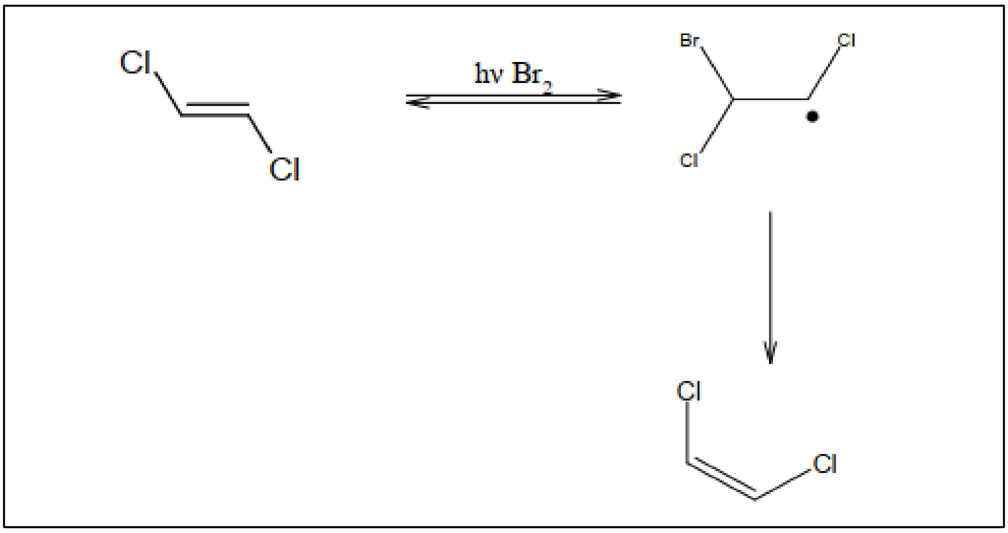
$$\textbf{Sens (S0) hv} \xrightarrow{\textbf{hv}} \textbf{Sens (S1)} \xrightarrow{\textbf{ISC}} \textbf{ISC Sens(T1)}$$





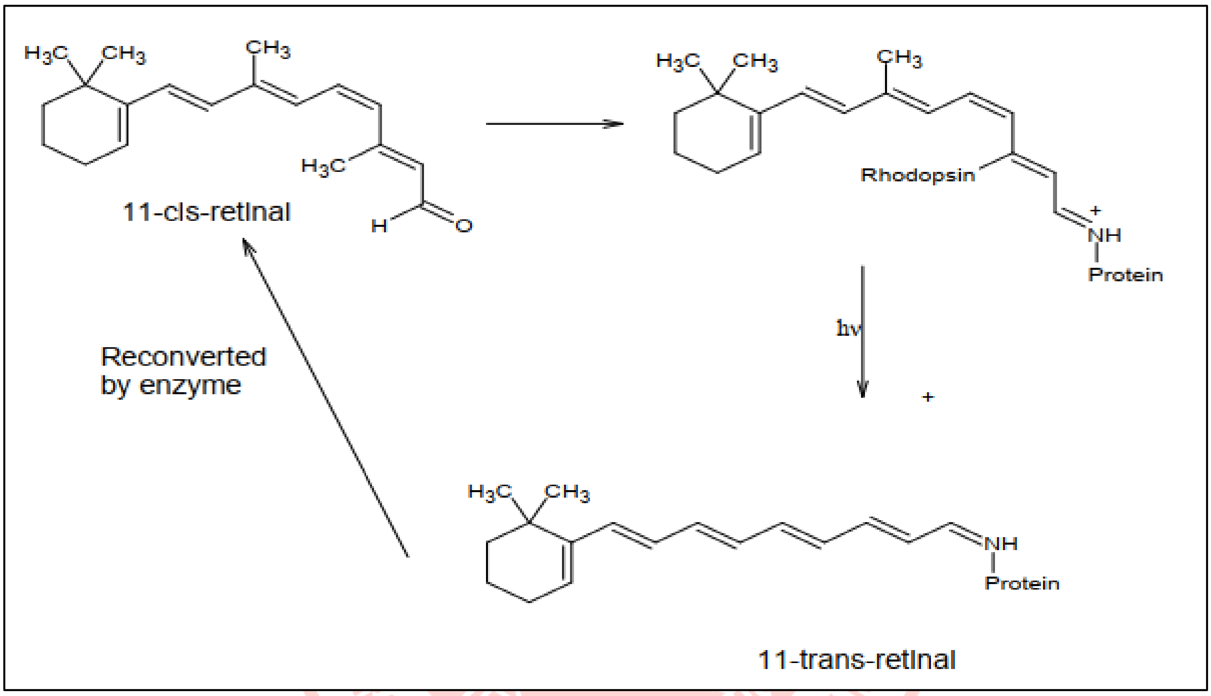
3. Catalysed method:

Photoisomerization 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, photoisomerization 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.



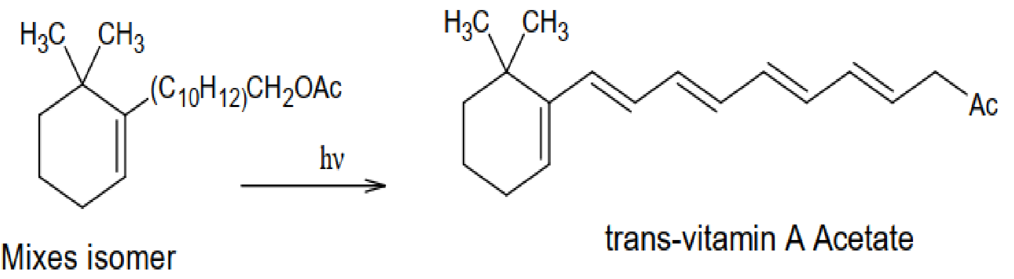
Biological importance:

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.



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.

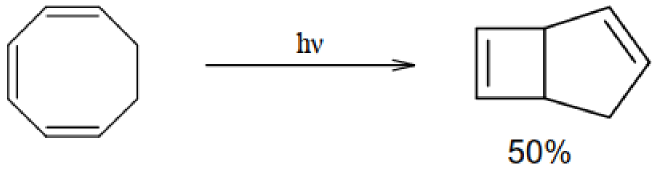
3.

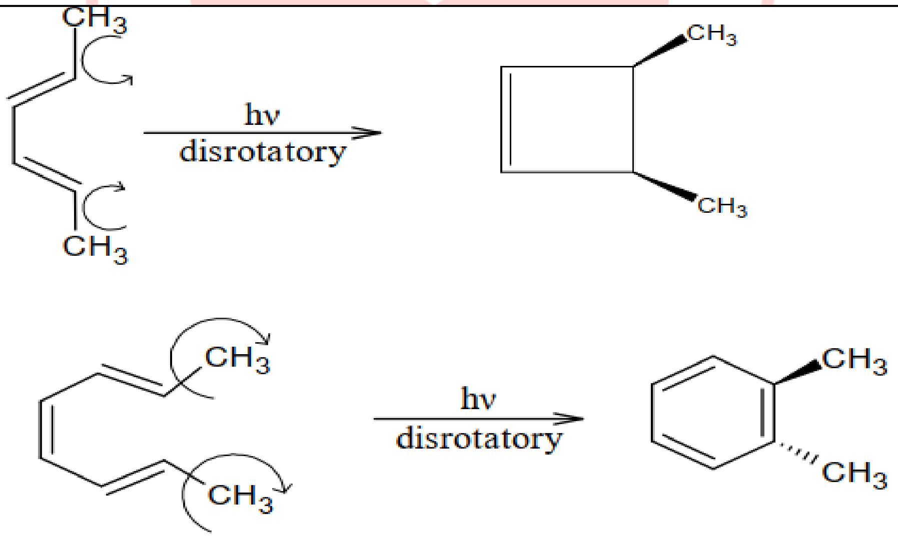


Cyclisation Reactions:

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 derogatory 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).

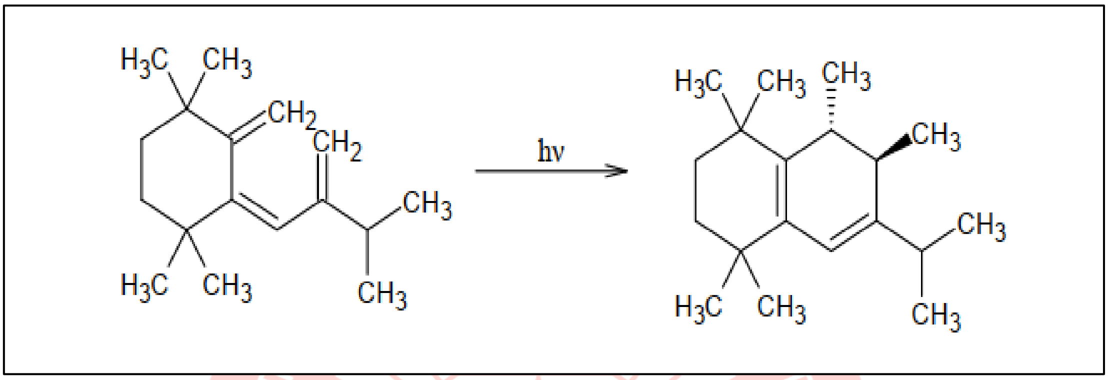
Example:





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.

1.



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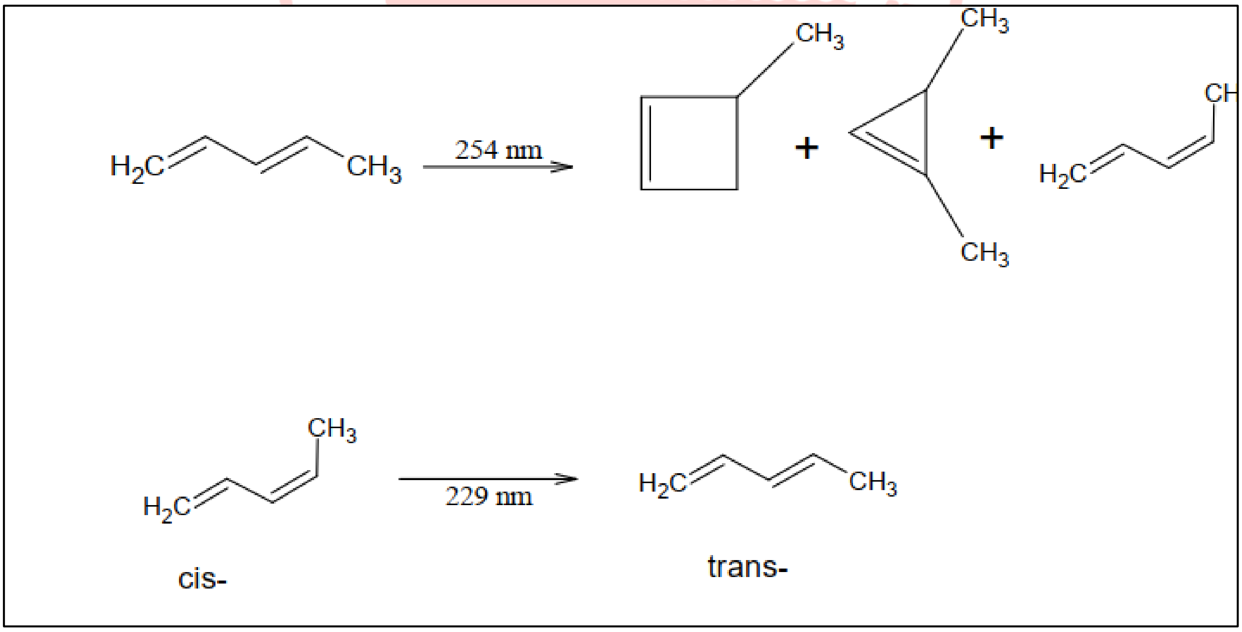
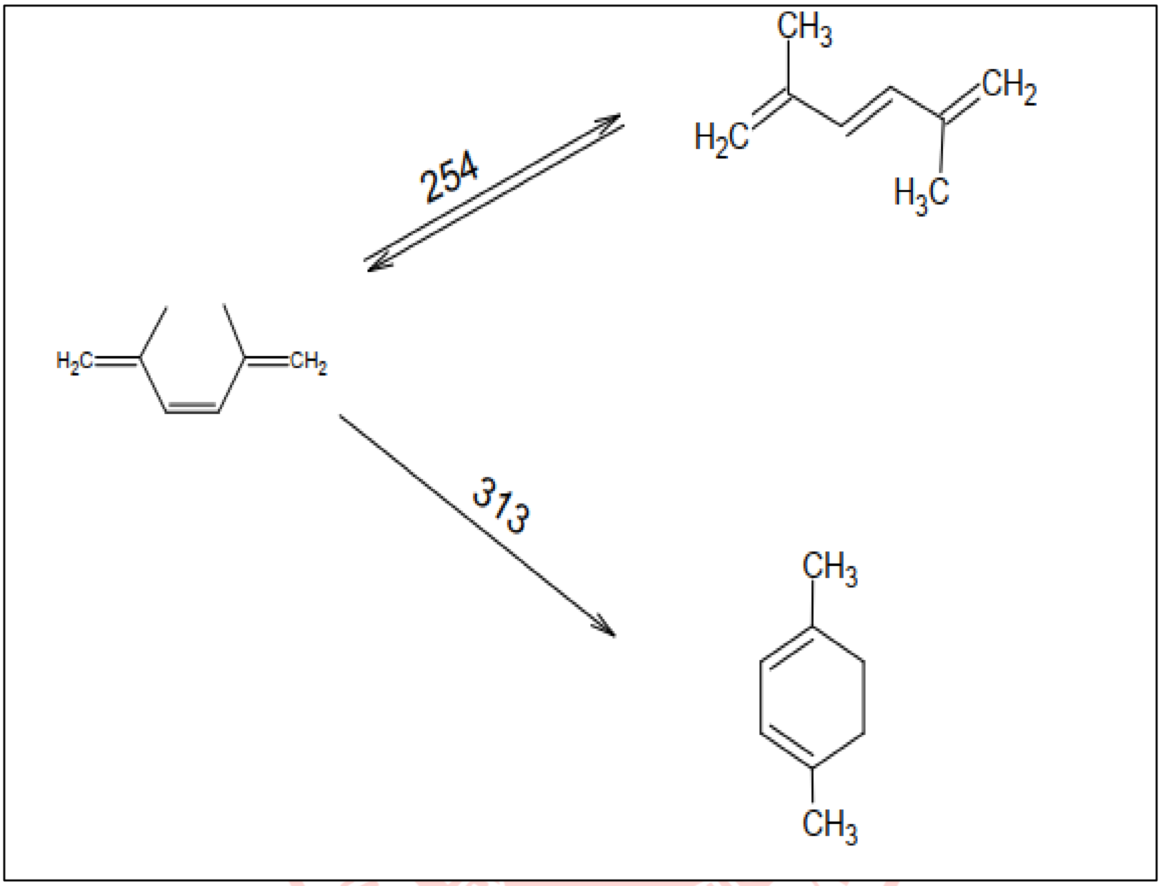
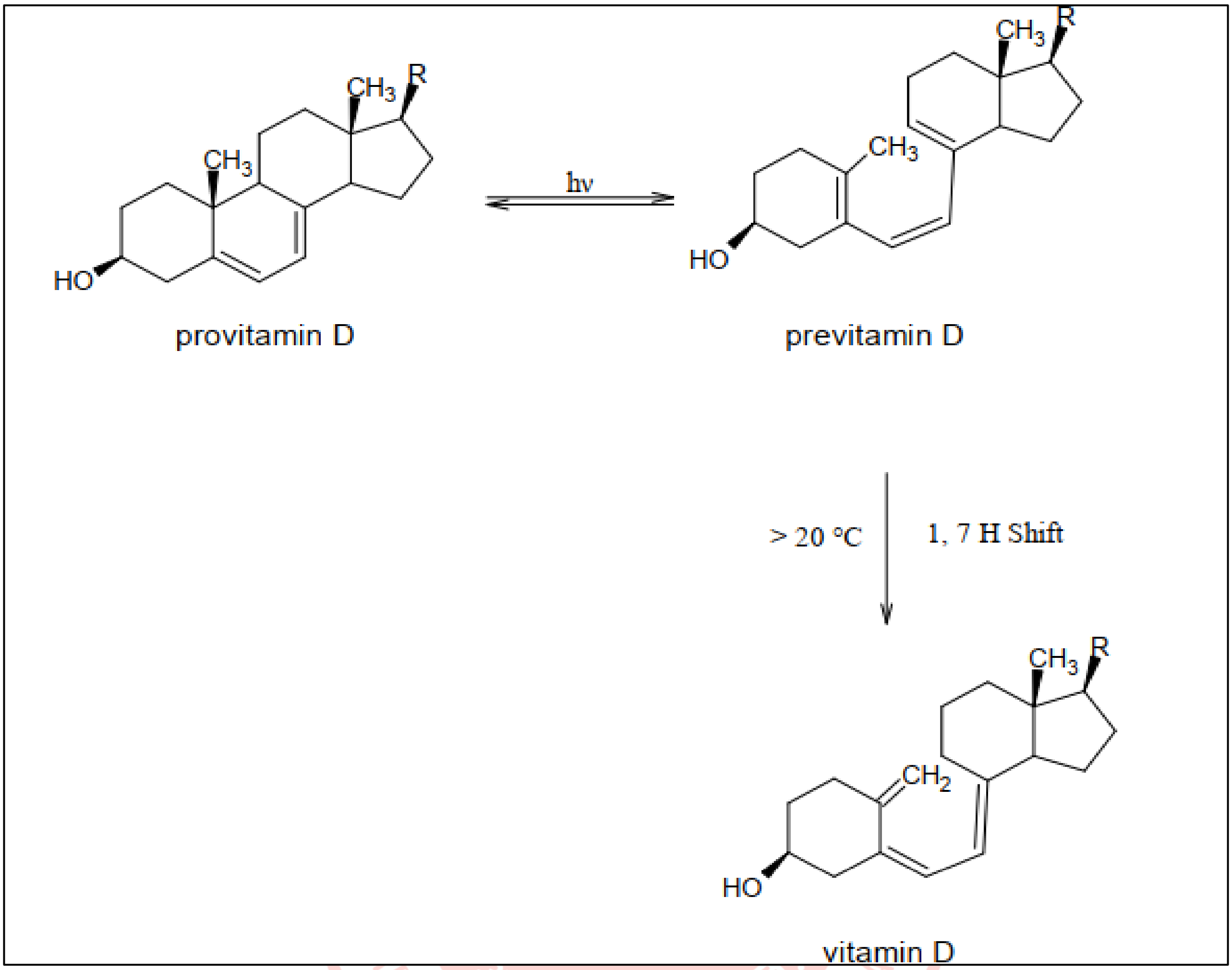


3. At 254 nm, the conjugated triene 2,5-dimethylhexa-1,3,5-trine exhibits effective cis-trans isomerization, but at 313 nm, it cyclizes to a cyclohexadiene.

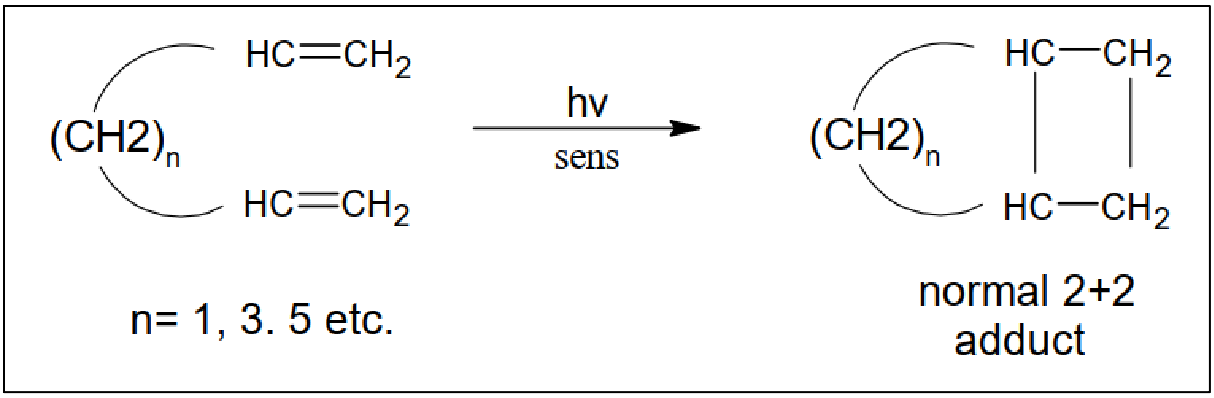


4. Some foods contain both vitamin D2 and vitamin D3. Vitamin D3 can also be made in keratinocytes from 7-dehydrocholesterol (provitamin D), which undergoes a photochemical six electron conrotatory electrocyclic ring opening at 280 nm to provitamin D3, which then spontaneously isomerizes to vitamin D in a thermal antarafacially hydride [1,7]- sigma tropic shift.

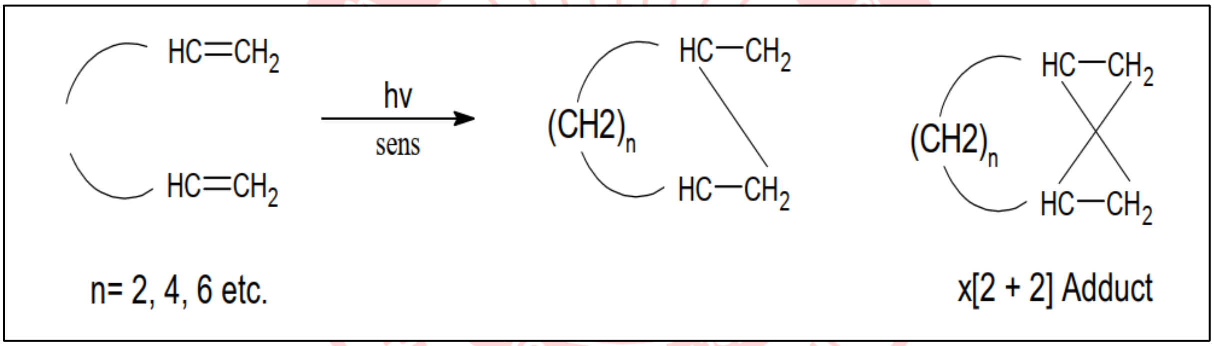


Intramolecular dimerization:

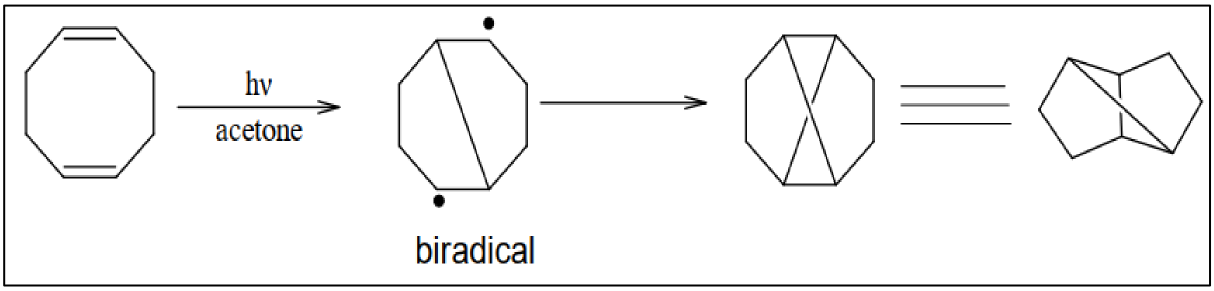
Nonconjugated dienes with isolated double bonds have a photochemistry similar to simple alkenes. Intramolecular [2 + 2] cycloaddition events occur in such alkenes, resulting in bicyclic compounds. The quantity of —CH2— groups between the two double bonds affect the results of sensitized intermolecular 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.



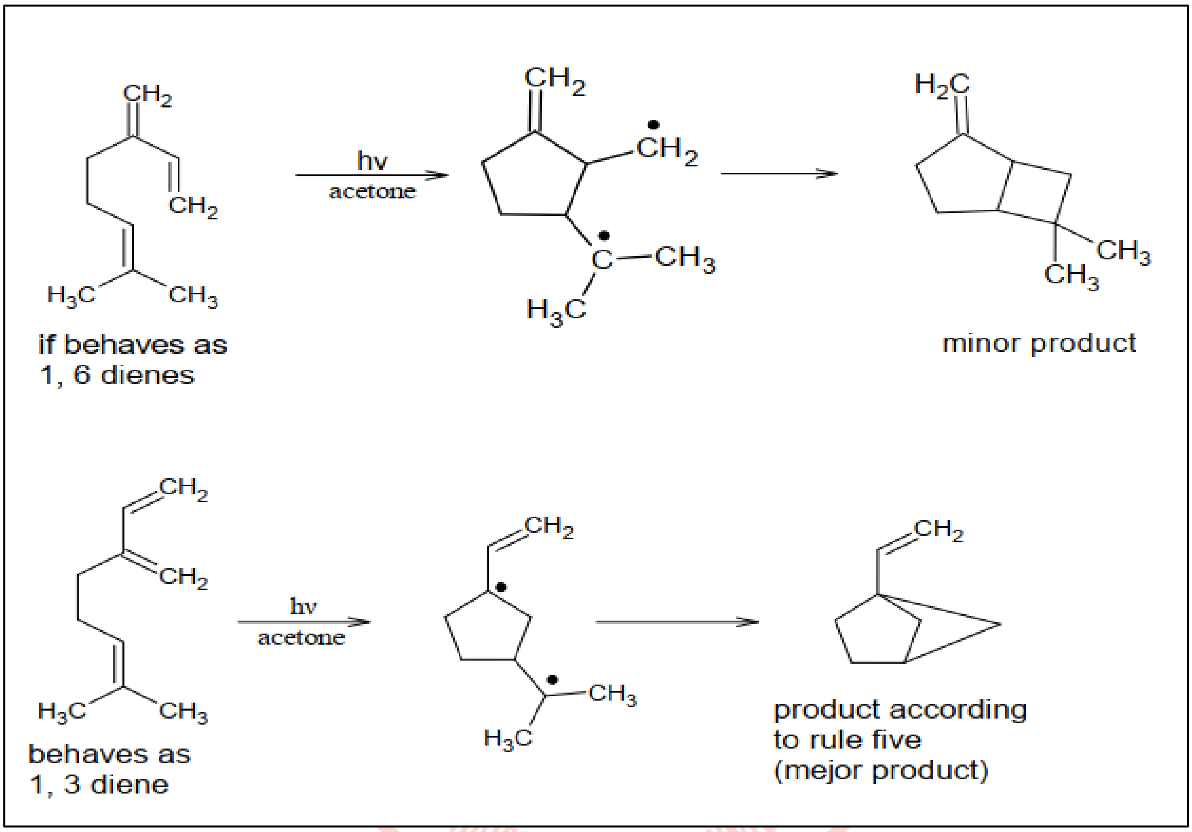
If n is even, such as 1, 5-hexadiene, the primary product is generated by a "cross," i.e., an x [2 + 2] cycloaddition that results in two crossed (sigma) bonds.



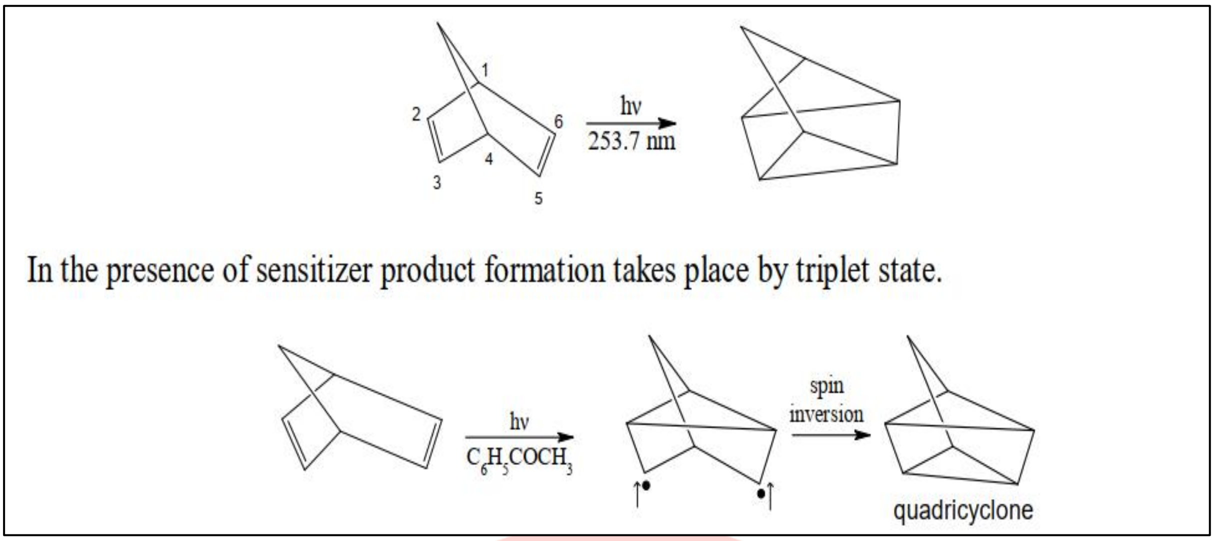
This property is much more obvious in cyclic dienes, such as n = m = 2 (1, 5-cyclooctadiene), where the lone product is the x [2 + 2] cycloadduct.



The photoreaction of 1, 5-hexadiene from the T1 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.

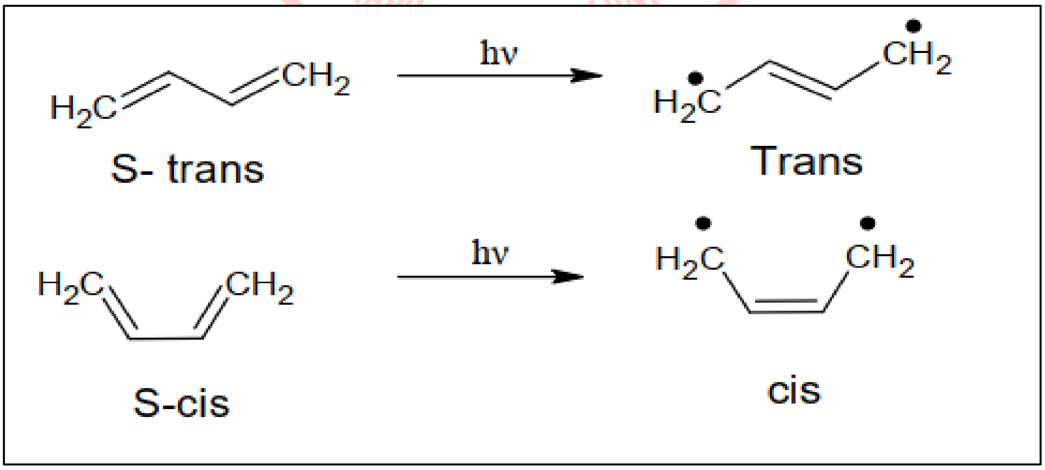


In the presence of sensitizer product formation takes place by triplet state.

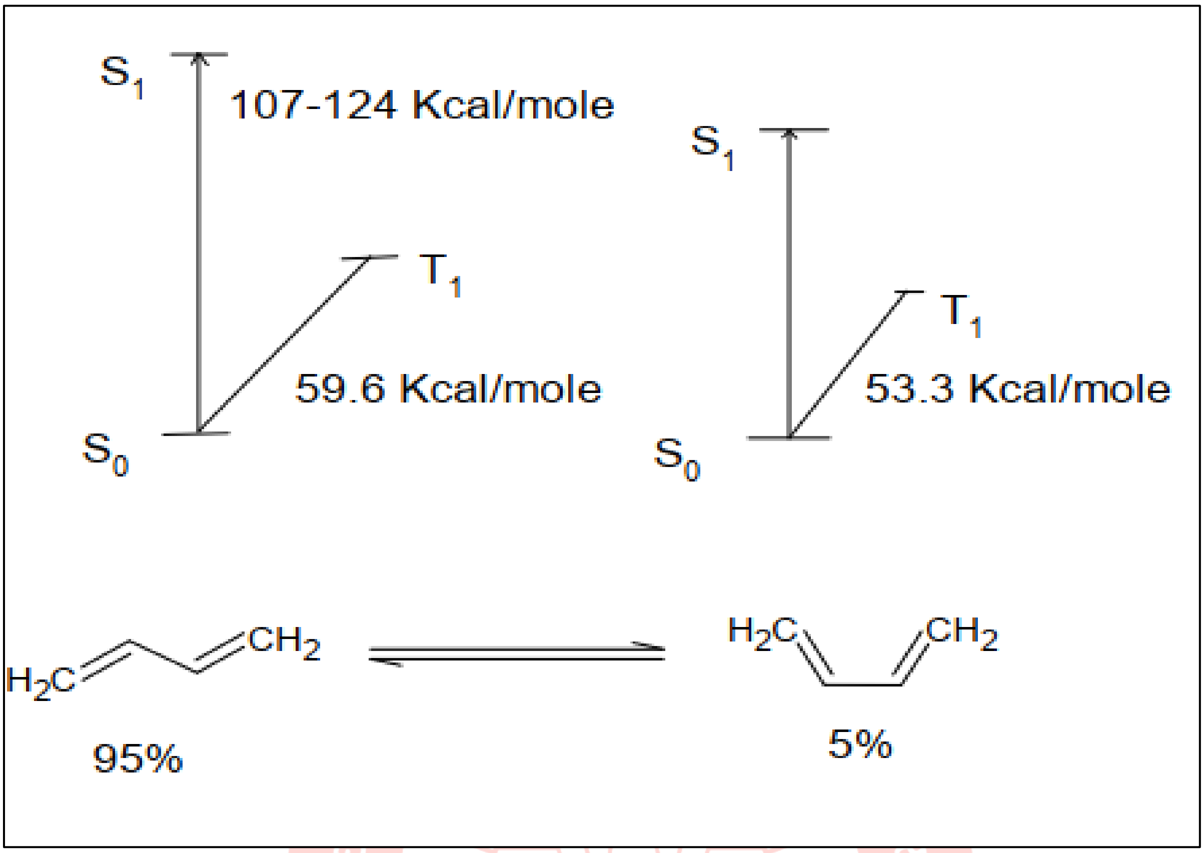
Photochemistry of conjugated dienes in solutions:

(i) 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 (ψ2 → ψ3*), 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. Butadiene's' conformational nature is thus preserved in stimulated states.



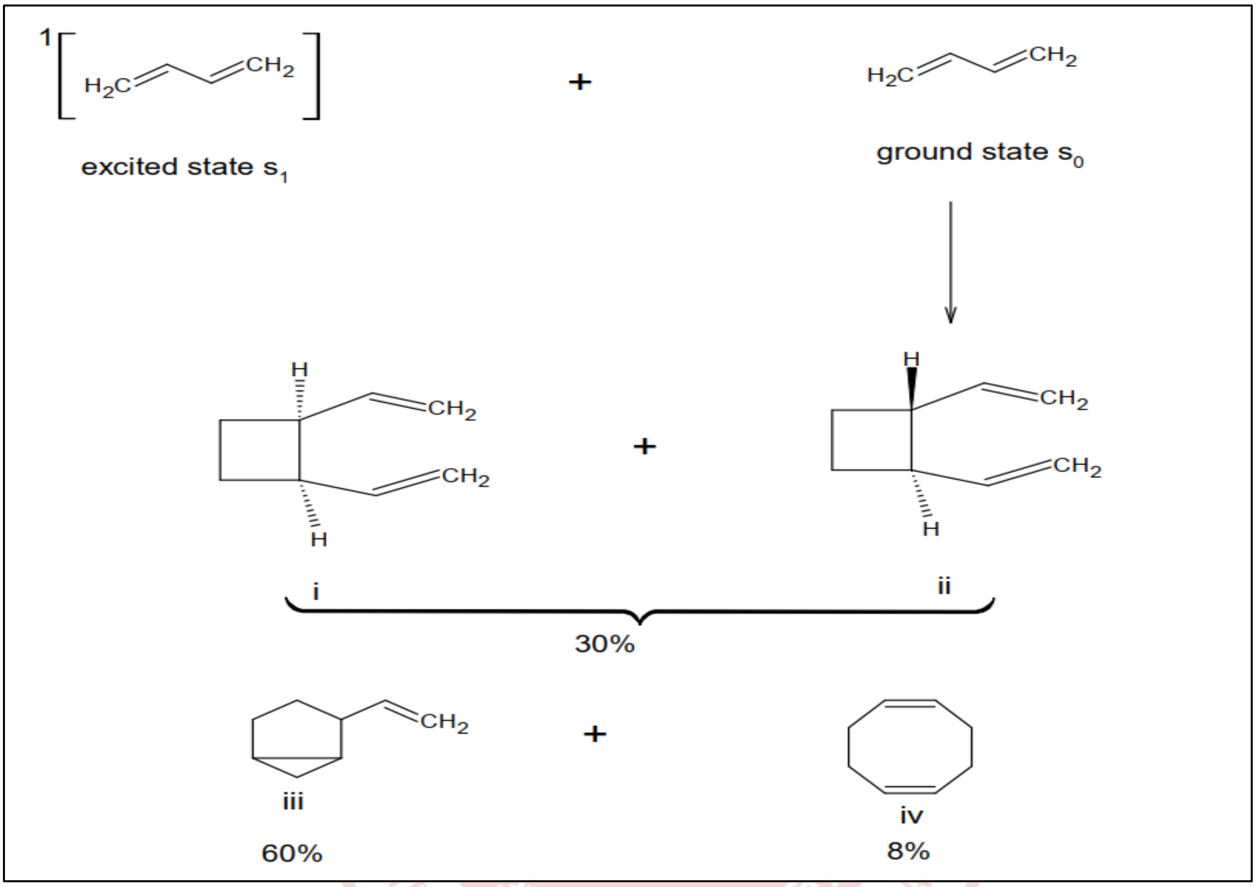
The energy of the excited states of butadiene’s are shown in the Fig



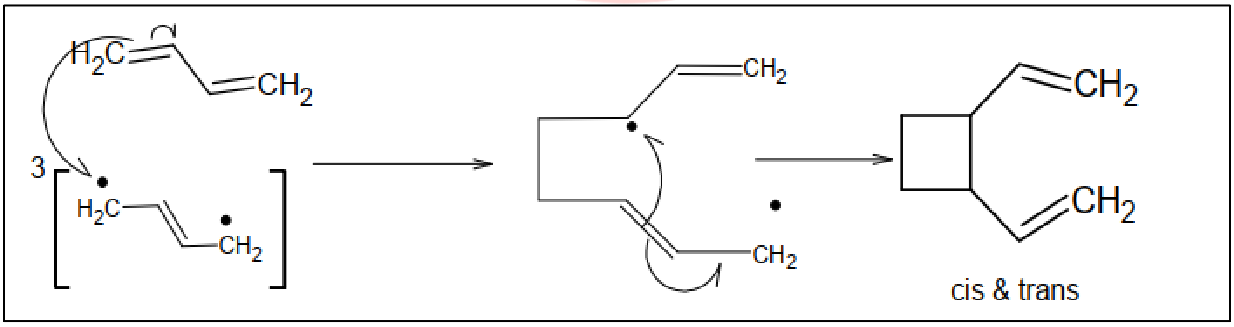
Intramolecular [2 + 2] cycloaddition reaction

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:

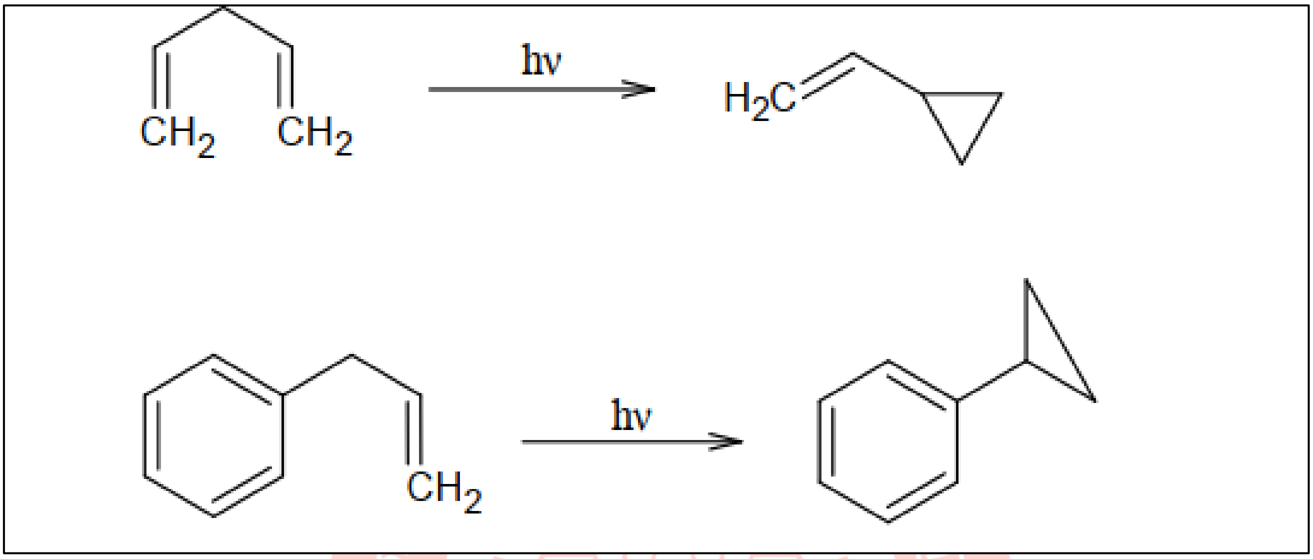


When acetophenone is used as a sensitiser, the reactive species is s-trans-T1, which reacts with the s-trans ground state to produce dimer.

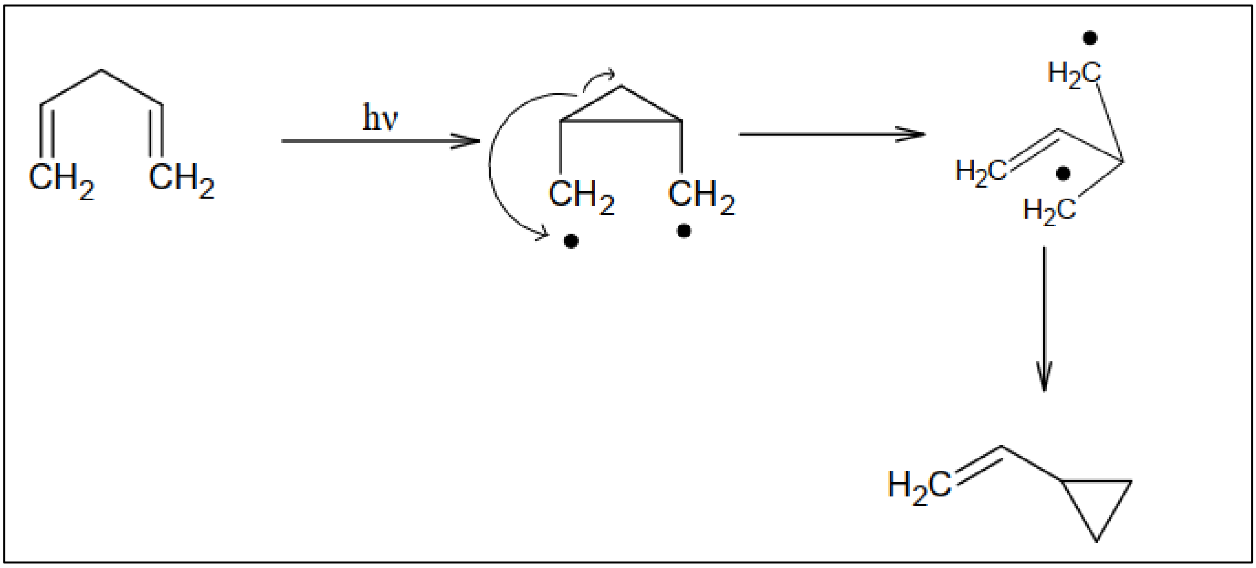


Rearrangement of 1,4- and 1,5-dienes:

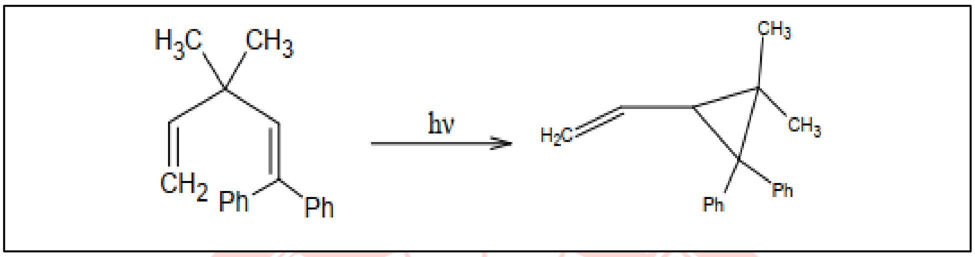
Irradiation of 1,4-diene or 3-phenyl alkenes frequently leads to vinyl cyclo propane or phenyl cyclo propane's via a 1,2-shift of the vinyl or phenyl group followed by ring closure, resulting in a photoproduct that is rarely obtained through other routes. The di-methane rearrangement, commonly known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

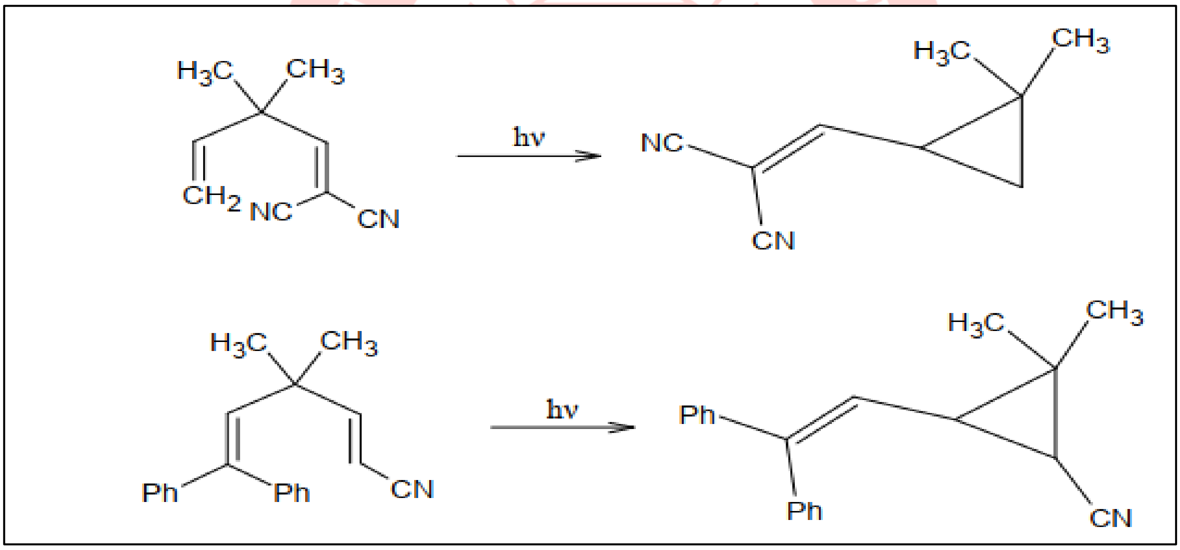


The 1,3- and 1,4-biradical intermediates, as well as the second -bond, may be linked in the suggested stepwise biradical mechanism. The procedure begins with the production of a bond between atoms 2 and 4 of the 1,4-diene unit, followed by the cleavage of the 2,3-bond and the formation of the 3,5-bond.



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 Dia stereoselectivity and regioselectivity.





Short & Long Answer Type Question-

Q. What is Photochemistry of Alkenes?(CSJMU2016,18,20)

Ans. 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.

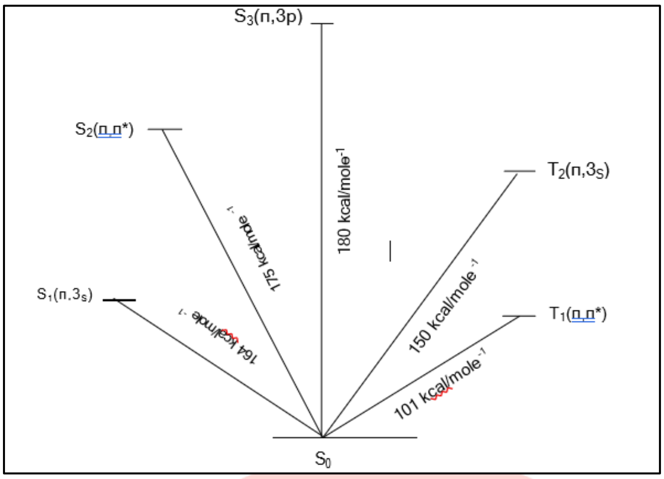


Fig. different electronic state of ethylene

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 unfavorable interactions between the carbon atoms' singly-filled orbitals.

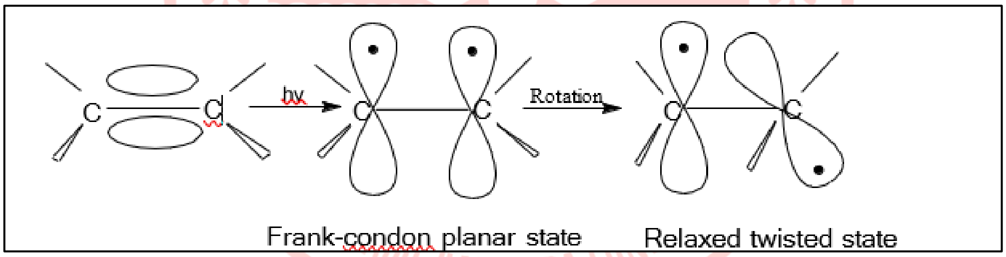


Fig. Formation of relaxed twisted state

Q. Cis-trans isomerization of alkenes. (CSJMU2017)

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

Cis-Trans isomerisation of alkenes by direct irradiation

Because of the large energy absorptions, direct irradiation of the simplest alkenes (whose λmax 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.

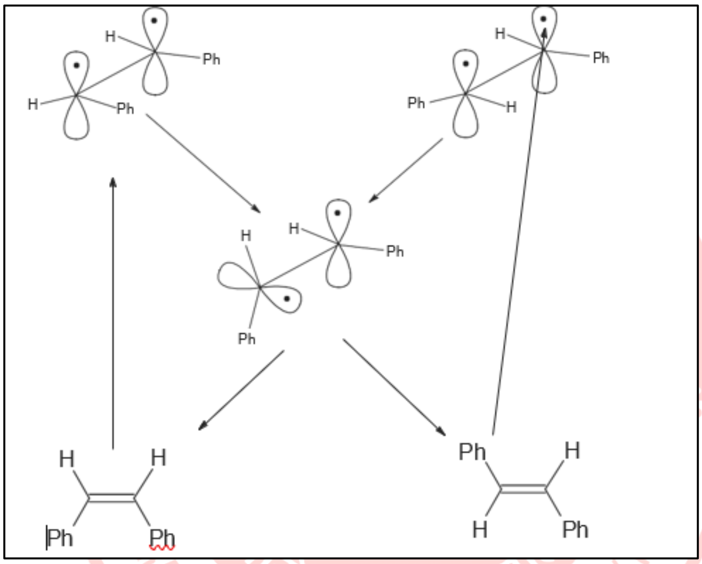
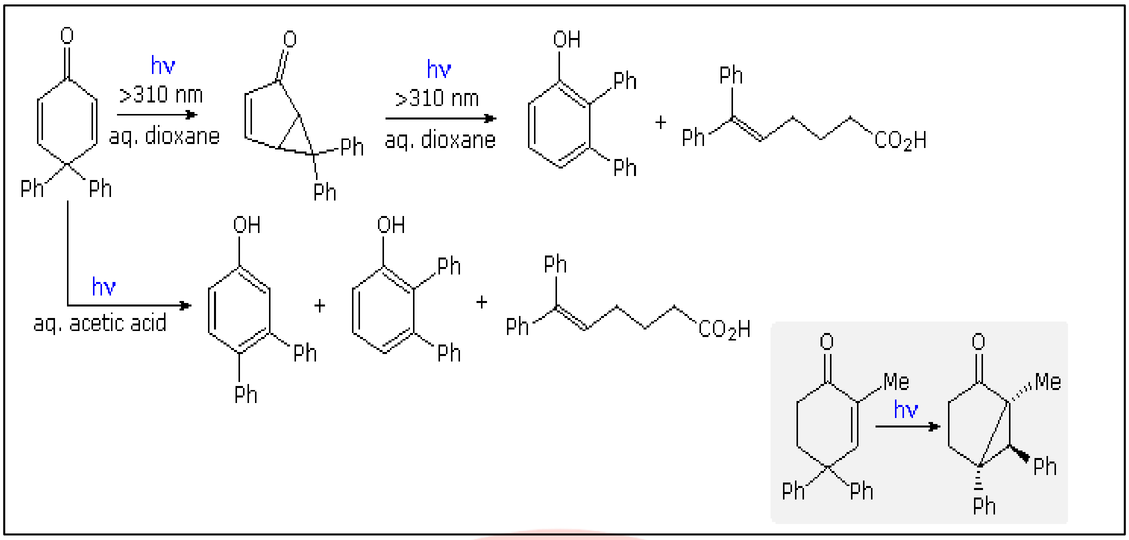


Fig. Cis-Trans isomerisation of alkenes by direct irradiation

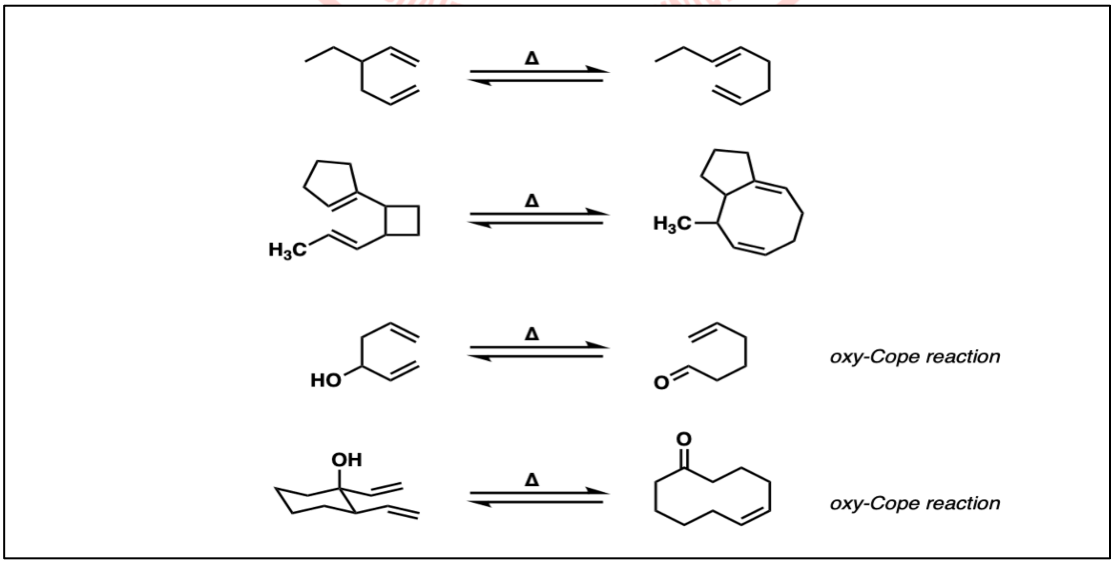
Q. Discuss rearrangement of cyclohexadienone. (CSJMU2011)

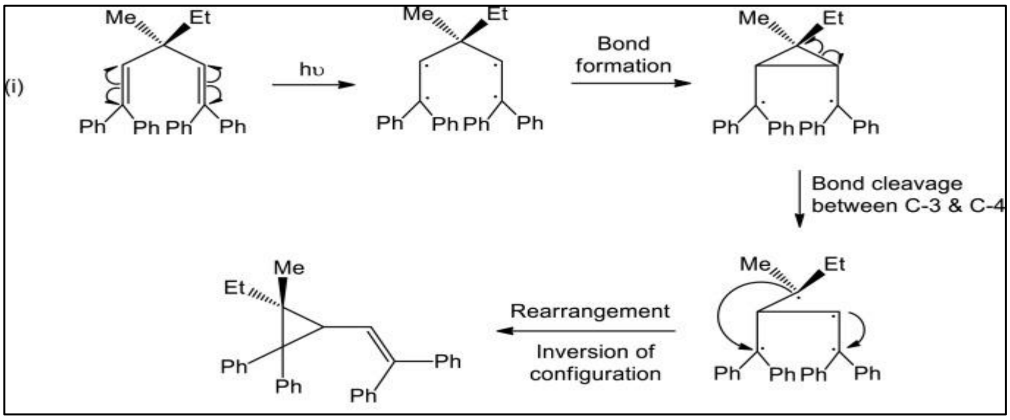
Ans. In photochemistry, cyclohexadienone undergo diverse rearrangements, including the dienone-phenol rearrangement to form phenols, spiro-ketone formation via cyclization, and 1,2-shifts to form ketenes. These reactions are driven by light-induced excitation to energetic states, leading to different intermediates like zwitterions, oxyallylcations, and cyclopropylcarbinyl cations. The outcomes depend on the specific dienone structure (e.g., cross-conjugated vs. para-conjugated), solvent, and presence of catalysts.



Q. Discuss photochemical rearrangement of 1,5-dienes. (CSJMU2012,11)

Ans. Photochemical rearrangements of 1,5-dienes are pericyclic reactions that can differ from their thermal counterparts, often involving sigmatropic shifts rather than the Cope rearrangement. These reactions can access high-energy, vibrationally excited states and involve a concerted movement of electrons, with the specific pathway (antarafacial or suprafacial) determined by the reaction conditions and the molecule's structure. Unlike thermal reactions that favor the Cope rearrangement's chair transition state, photochemistry can access different pathways or intermediates.





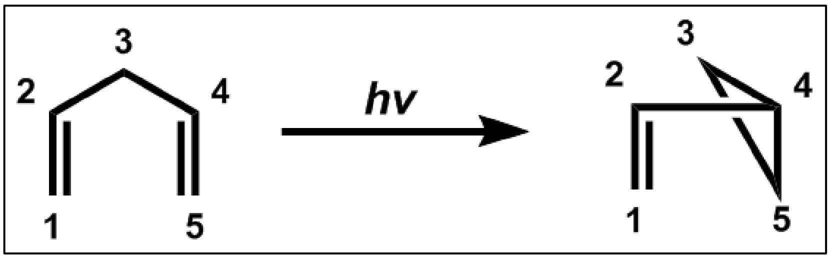
Q. Rearrangement of 1,4 di-π methane. (CSJMU2011)

Ans. The **di-π-methane rearrangement** is a light-driven reaction that happens in molecules with **two double bonds** (π-systems) that are separated by one single carbon atom.

- If the molecule is an **aliphatic compound** (a 1,4-diene), the reaction gives a **cyclopropane ring** with an extra double bond (ene-substituted cyclopropane).
- If the molecule is an **aromatic compound** (an allyl-substituted benzene), the reaction gives a **cyclopropane ring** attached to the benzene (aryl-substituted cyclopropane).

The key step is:

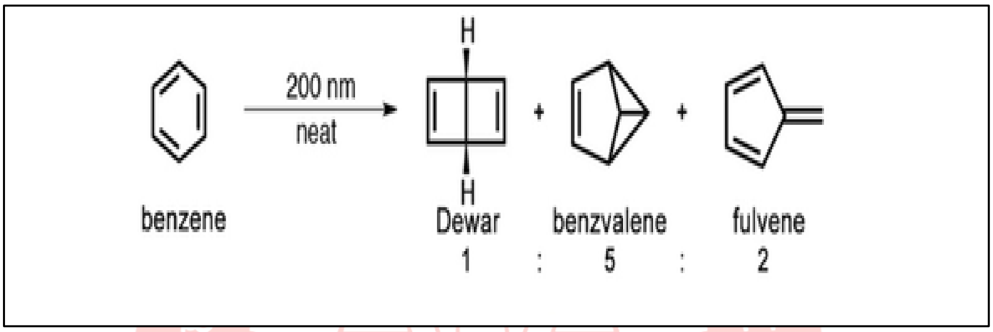
1. **One group shift** (either a double bond or the benzene ring).
2. Then, the two outer carbons of the other group join together to make the small **cyclopropane ring**.

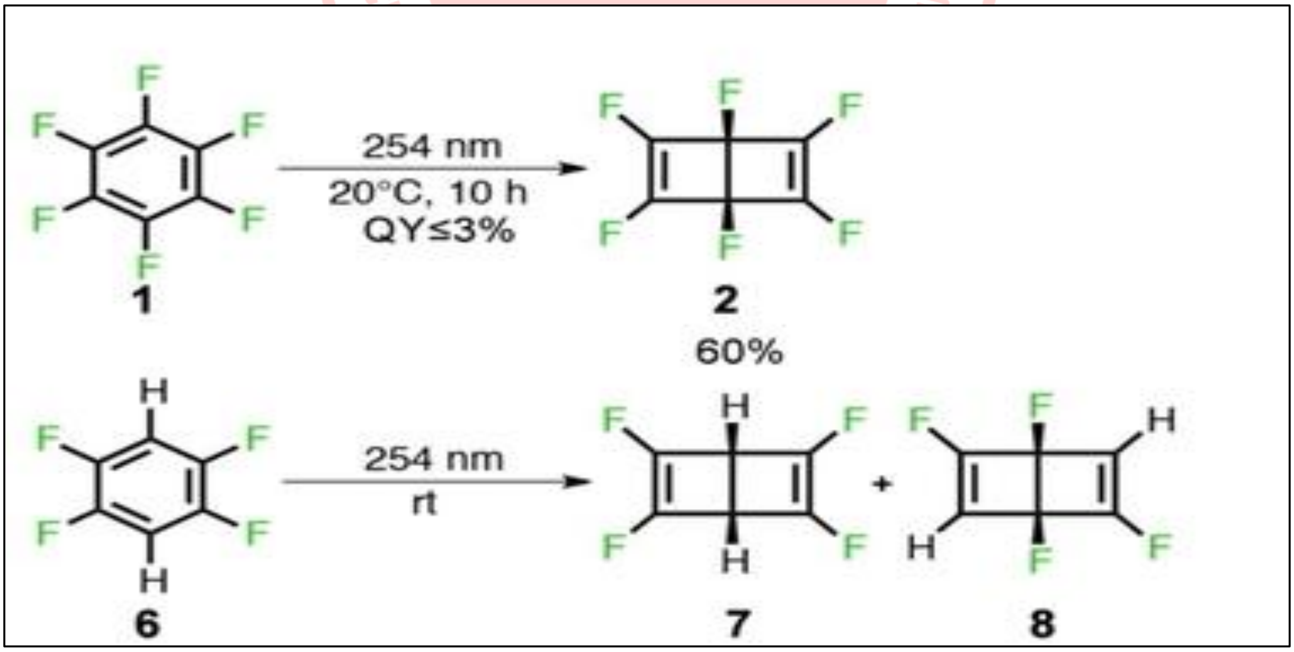


Q. Valence isomerization of benzene. (CSJMU2011,14,18)

Ans. The valence photoisomerization of benzene involves the transformation of benzene into strained, higher-energy isomers, such as Dewar benzene and benzvalene, upon absorption of light. This photochemical process is an example of how light can activate molecules to overcome high-energy barriers and form unique structures, including those with different bonding patterns and enhanced reactivity. The specific isomer formed can depend on the excitation energy, with higher energy excitations potentially leading to different product distributions.

Valence isomerization of fluorobenzene-





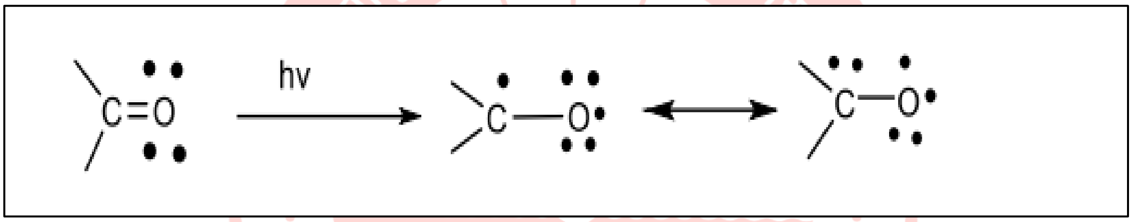
Unit-IV

Photochemistry of Carbonyl Compound:

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.

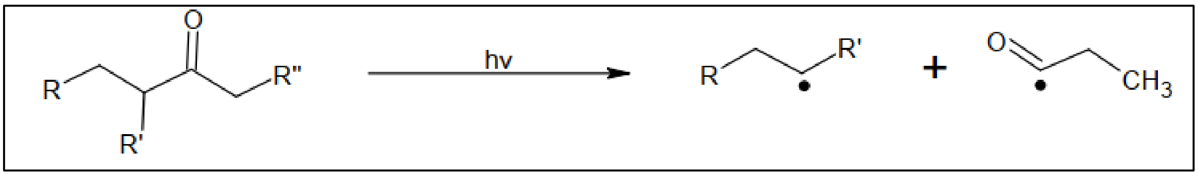
Norrish Type-I or α-Cleavage

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.



Primary Processes

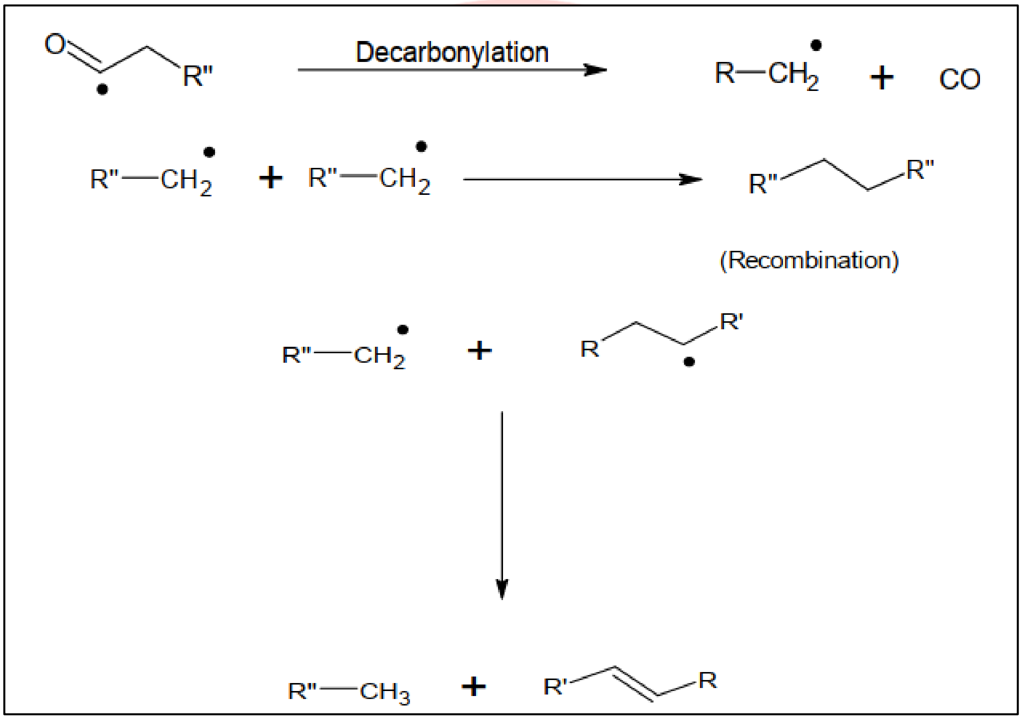
Norrish Type I process is characterized by initial cleavage of the carbonyl carbon and alpha carbon bond to give an acyl and an alkyl radical. This process is known as primary photochemical process.



Secondary Processes

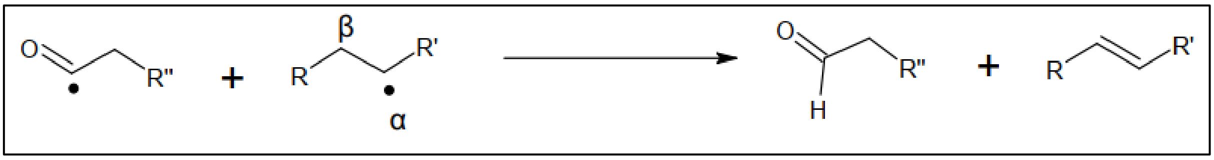
Decarbonylation of acyl radical

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.



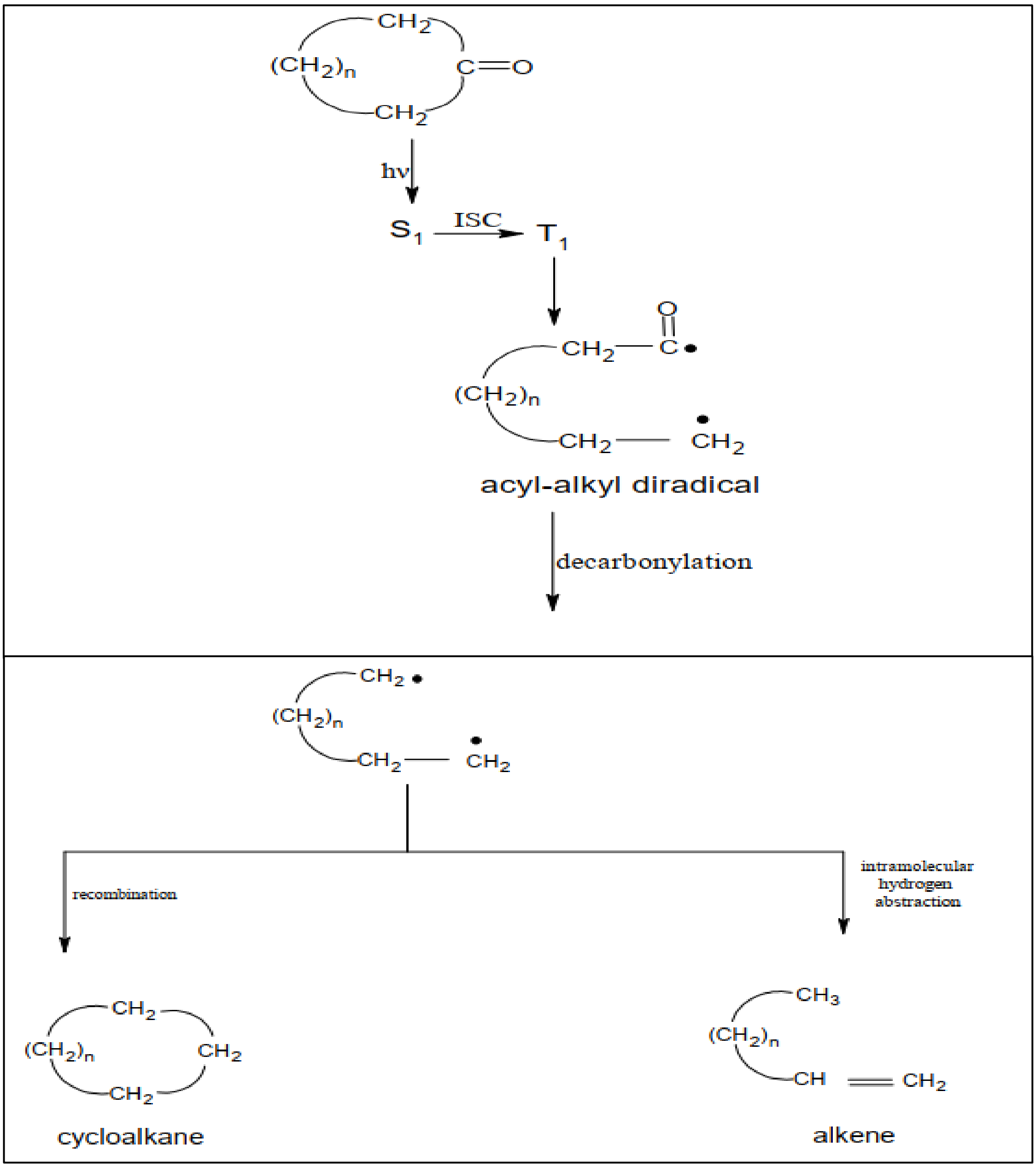
Intermolecular hydrogen abstraction

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.

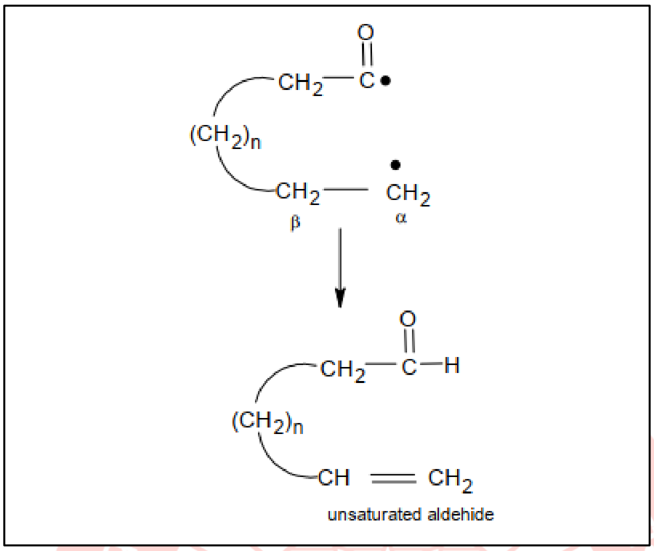


Norrish type I reaction of saturated cyclic ketones

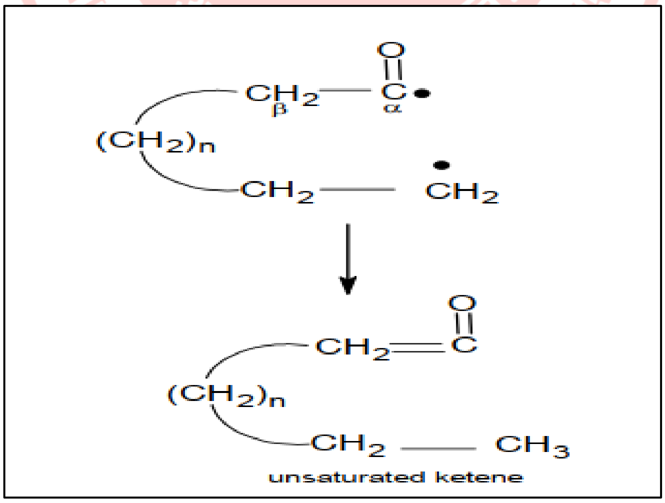
(a) Carbon monoxide and a dialkyl radical are produced by decarbonylation of an acyl-alkyl diradical. The dialkyl radical can either recombine to produce a cycloalkane or undergo intramolecular hydrogen abstraction to produce an alkene.



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

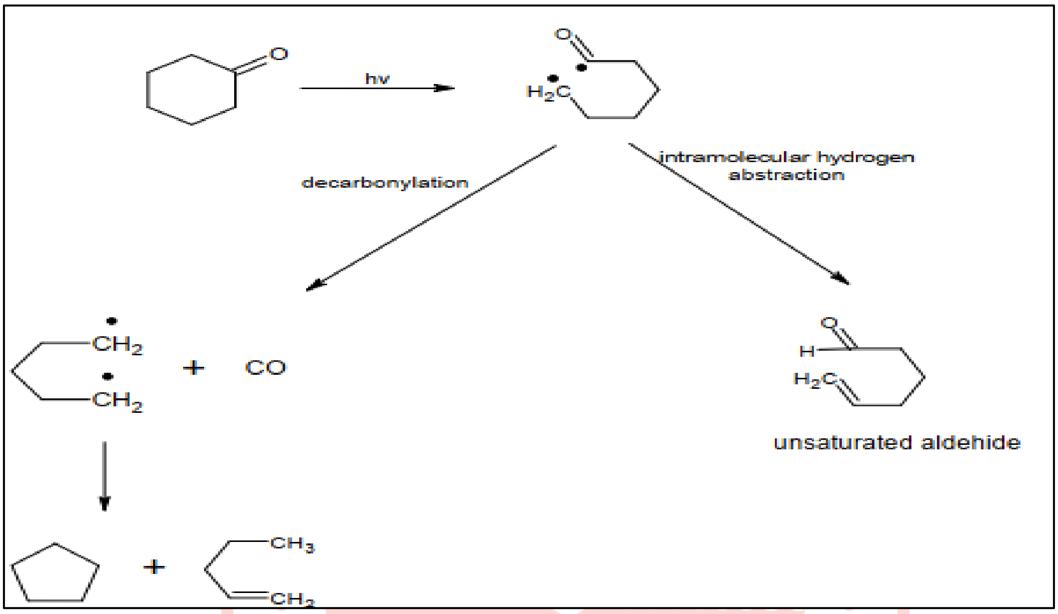


(c) Intramolecular β-hydrogen abstraction from the acyl radical by the alkyl radical, resulting in the formation of ketene.

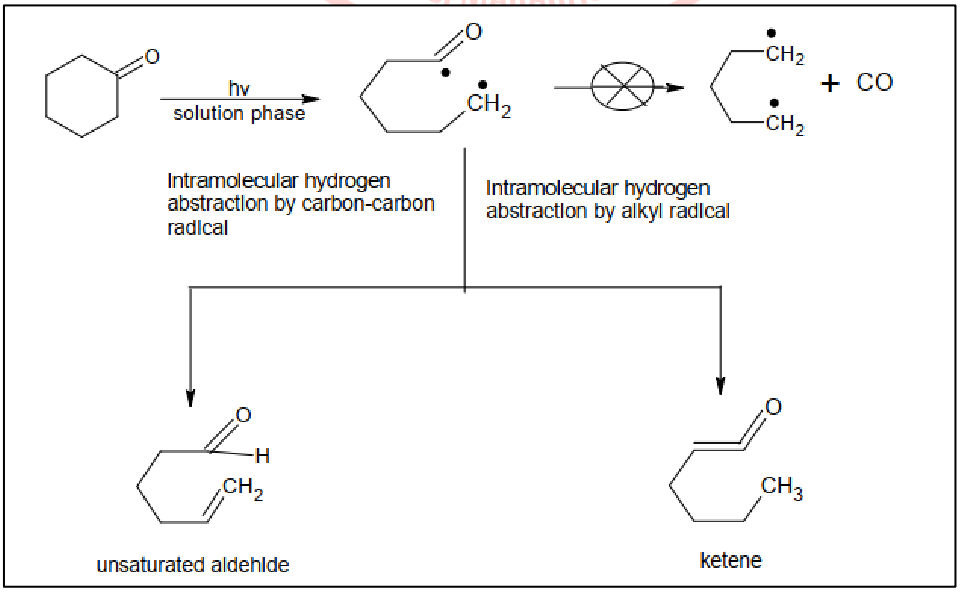


The biradical of cyclic ketones can go through one of two hydrogen transfer processes via a cyclic transition state, in which a hydrogen atom is moved from an atom near to the other radical centre to one radical centre.

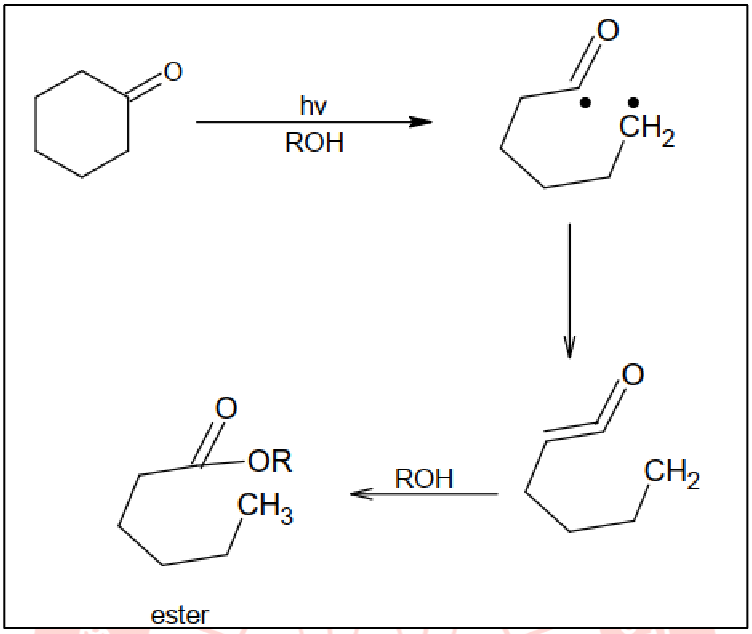
In the gas phase, photolysis of cyclic ketones results in decarbonylation and intramolecular hydrogen abstraction. The synthesis of unsaturated aldehyde is mostly achieved by intramolecular hydrogen abstraction.



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.

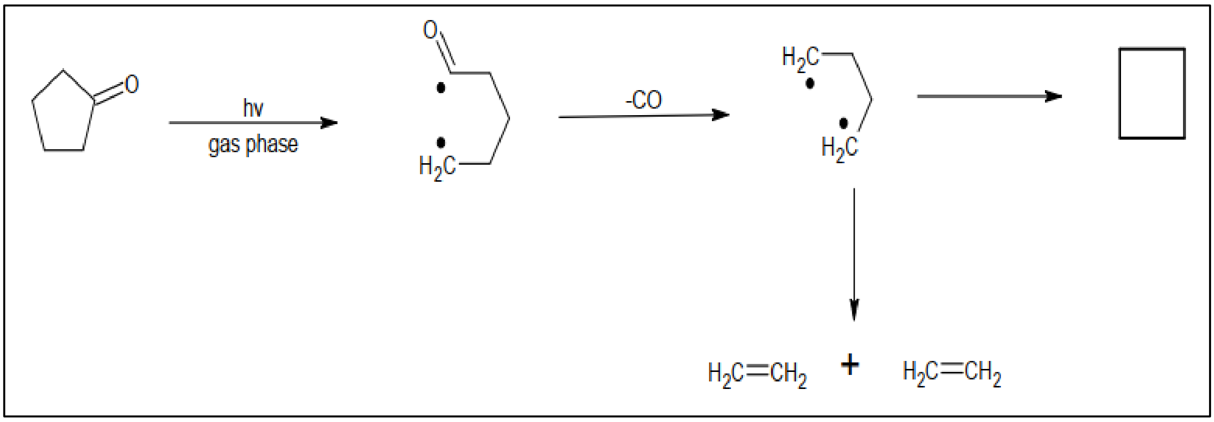


The major species produced by photolysis in the presence of a polar protic solvent is ketene. The carboxylic acid (with water) or its derivative (ester with alcohol) is the only result of solvent addition to this ketene.

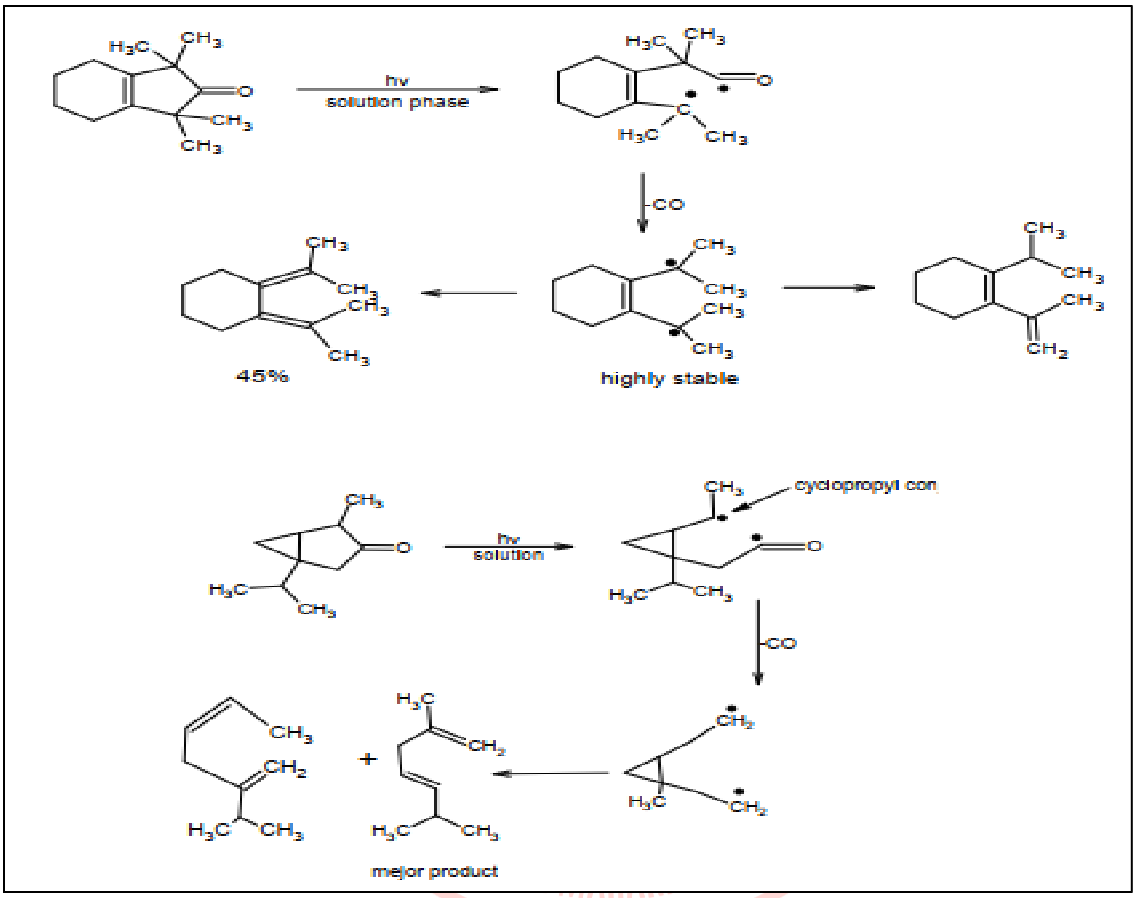


Norrish type-I in Cyclopentanone

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.

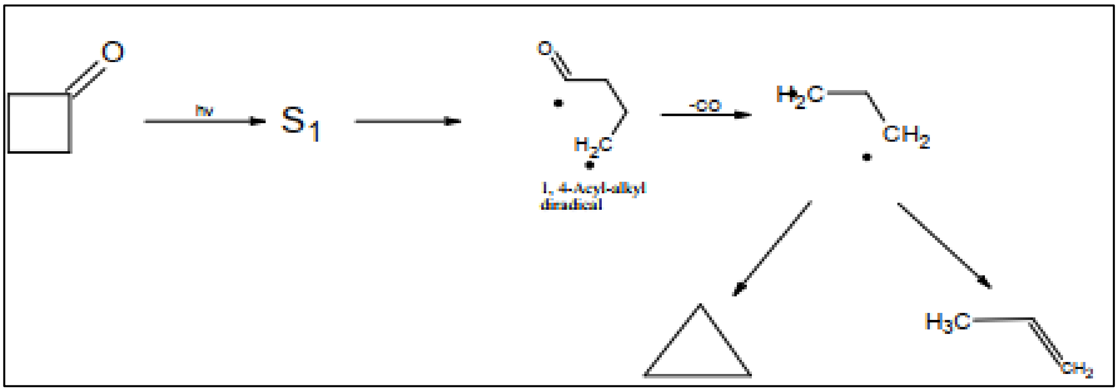


Only when the radical centres generated are stabilised by alkyl substitution, double bond, or cyclopropyl ring is the loss of carbon monoxide from a cyclopentanone a prominent path in solution.

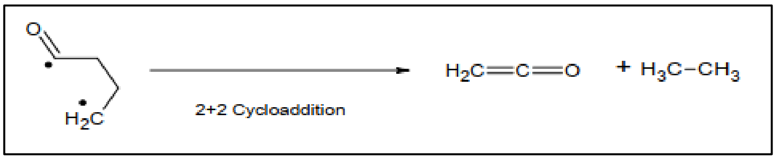


α-cleavage by Cyclobutanone

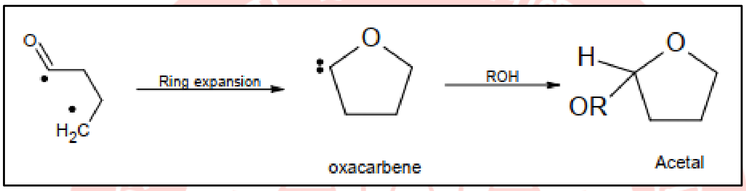
1. Carbon monoxide is lost, and 1, 3-diradical is formed, which proceeds either recombination to cyclopropane or hydrogen abstraction to generate propene.



2. By a subsequent β-cleavage and formation of ethylene and ketene.

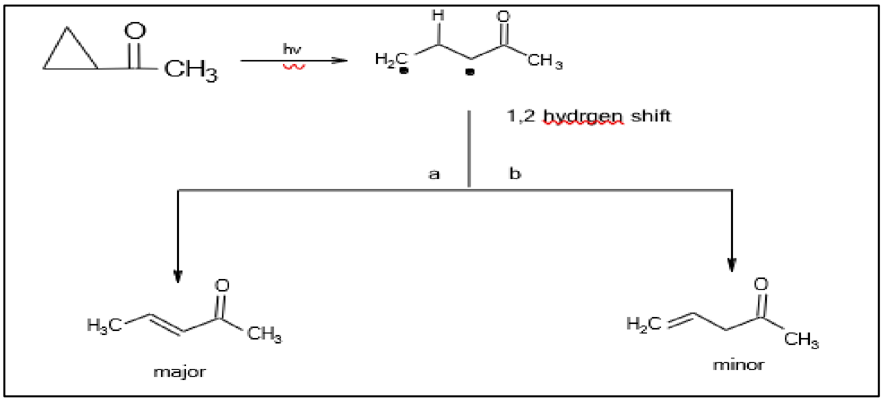


3. The 1, 4-acyl-alkyl biradical can expand its ring by rebonding to oxygen, resulting in oxacarbene. Polar protic nucleophile solvents can trap this carbene. A ring expansion is the overall reaction.

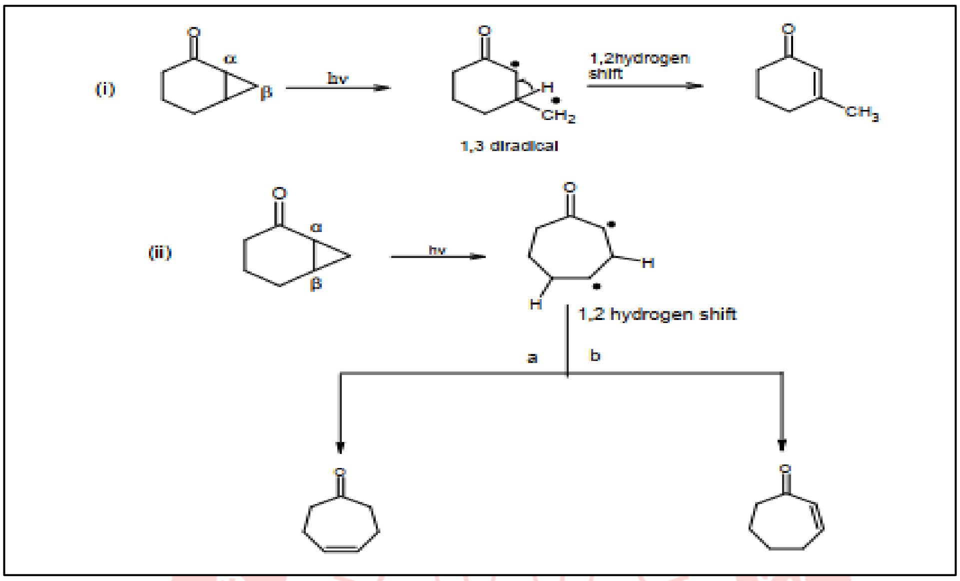


B –CLEAVAGE OR NORRISH TYPE II REACTION

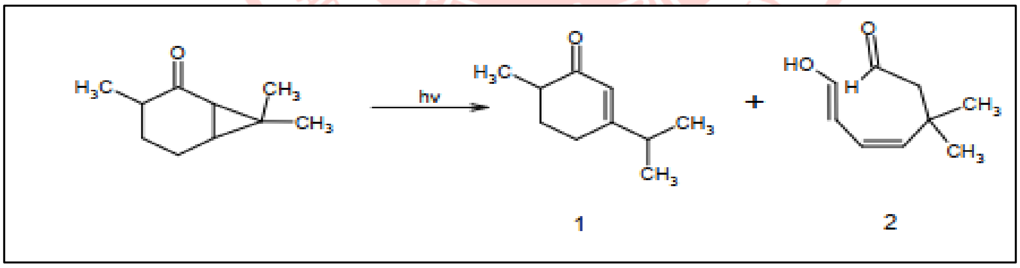
Some compounds have relatively weak Cα-Cβ bonds that can be cleaved as a result of the carbonyl group's electronic excitation. The UV spectrum shows evidence for coupling between the carbonyl and cyclopropyl groups, which provides a mechanism for energy transfer from the carbonyl group to the broken 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*-Carbo* .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.

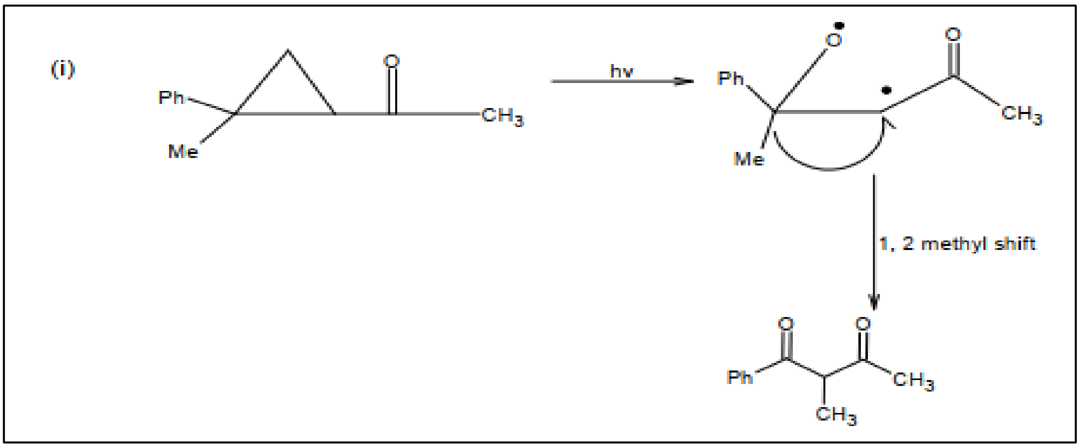


In some cases, the α-cleavage and β-cleavage are often in competition as shown below



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—Cβ 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:

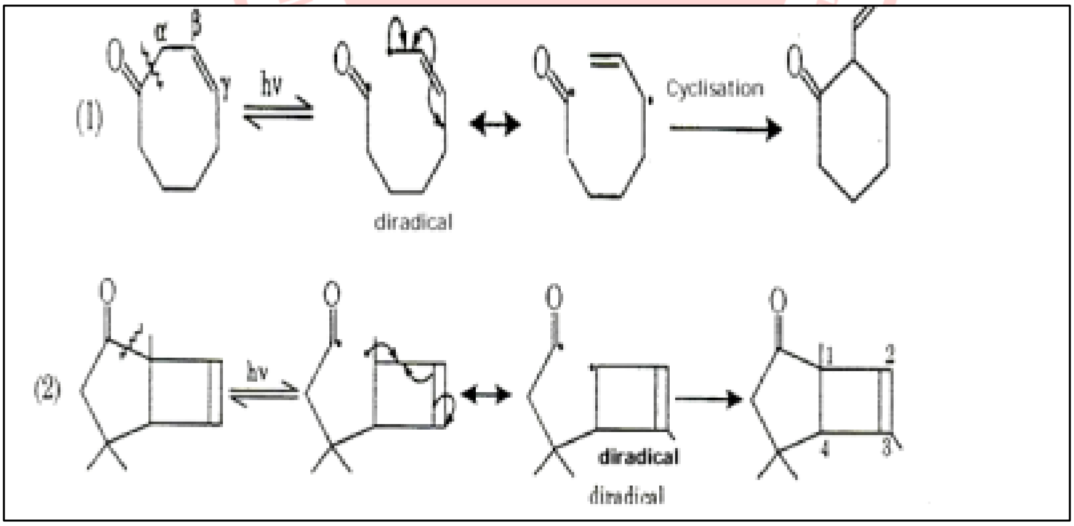


Intramolecular Reaction In β,γ Unsaturated Carbonyl Compund:

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

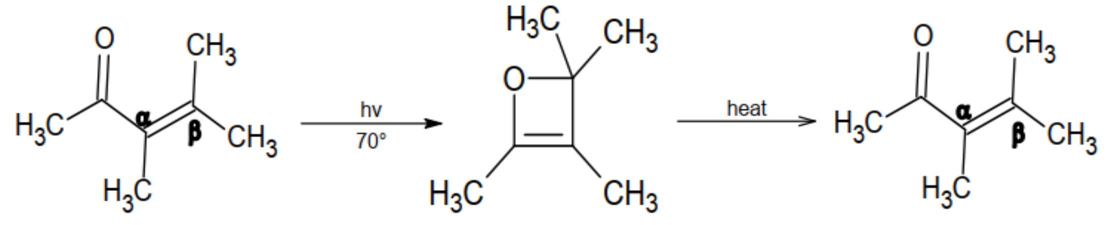
case I - 1,3-acyl shifts is involved, which form an isomeric β, γ- Unsaturated ketones.

Case II- Ring closure process takes place.



Intramolecular Reaction Of α-β- Unsaturated Carbonyl Compounds

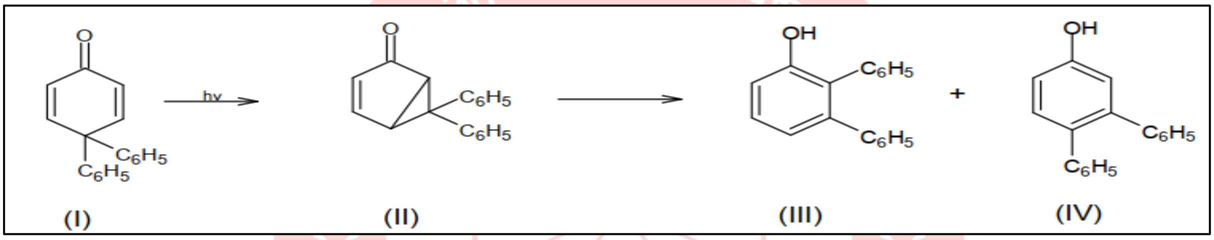
At 70o C, an intramolecular reaction of α-β - unsaturated carbonyl molecule produces oxetene. This product can be turned into reactant by heating it.



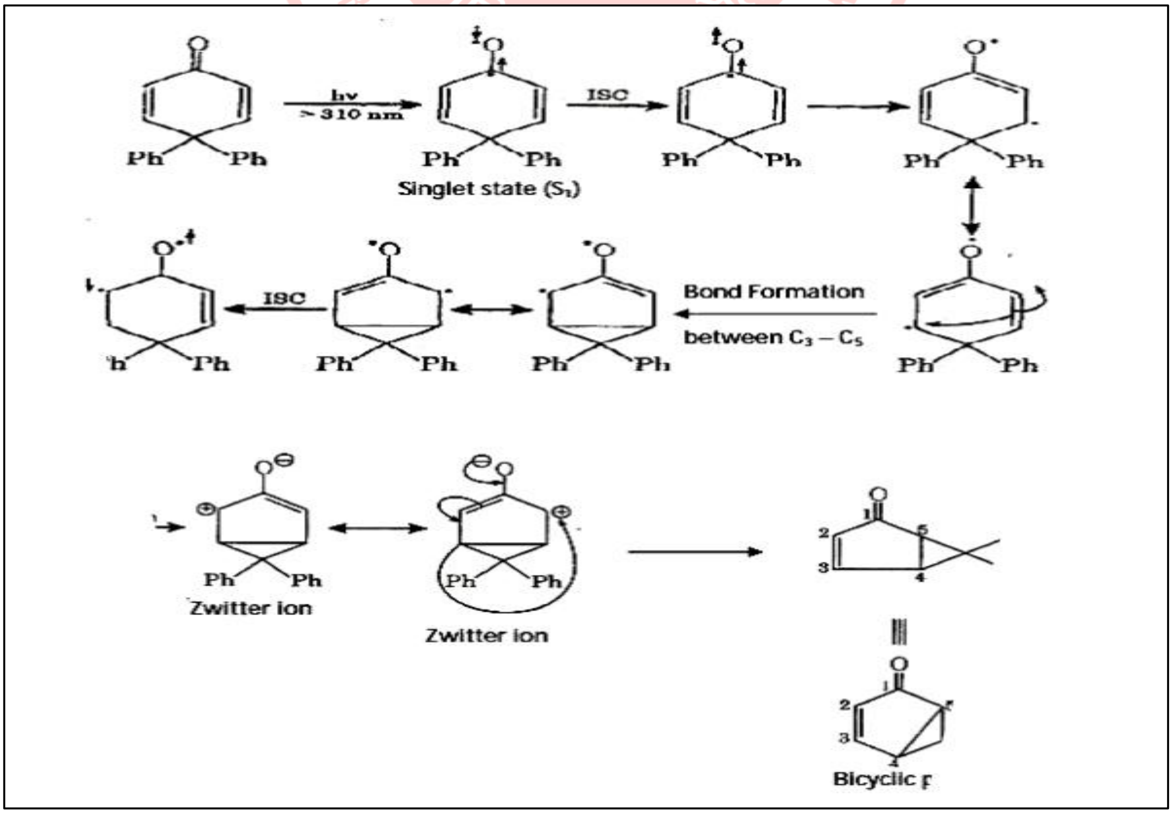
α-β- Unsaturated ketone oxeteneα-β- Unsaturated ketone

Intramolecular Photoreaction of Cyclo Hexadienone:

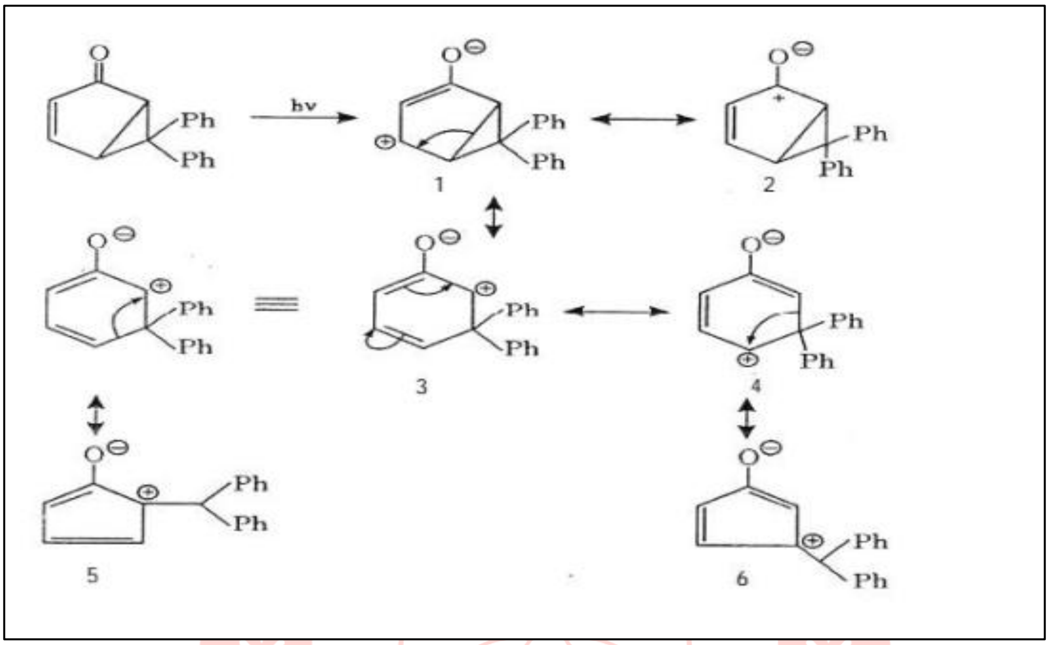
The photochemical rearrangement of compounds containing the cyclohexadienone chromophore is an example of this type of reaction. Irradiation converts 4,4 diphenylcyclohexadinenone (I) to a ketone (II) and two phenols (III) and (IV).



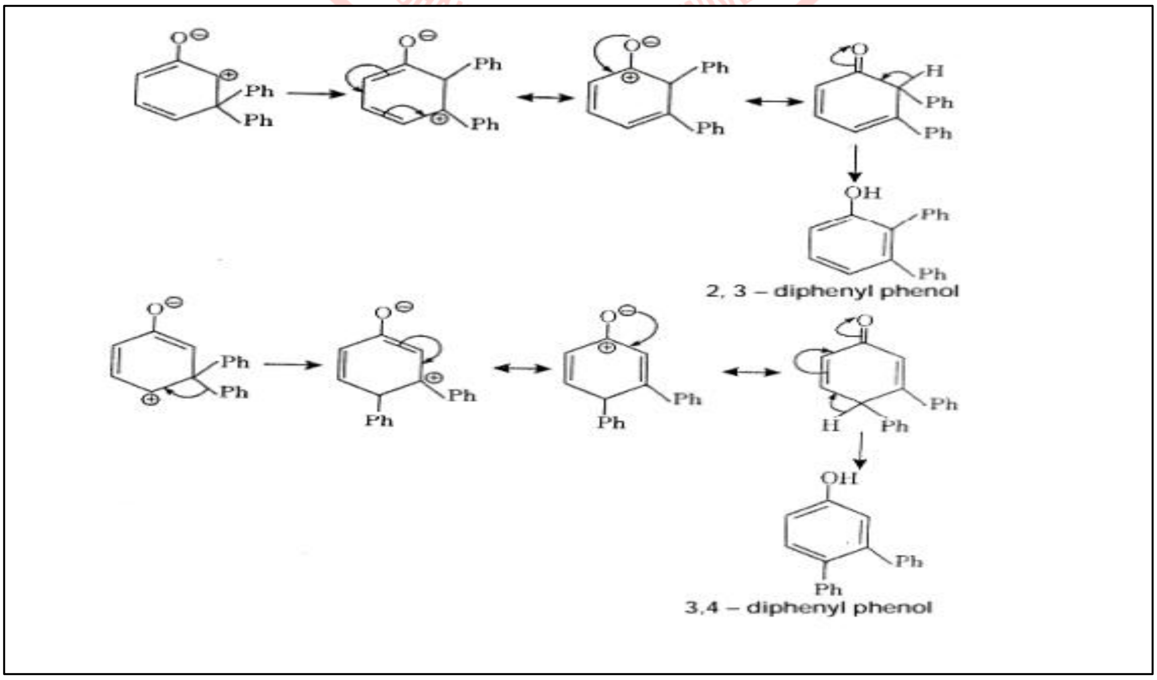
Mechanism -



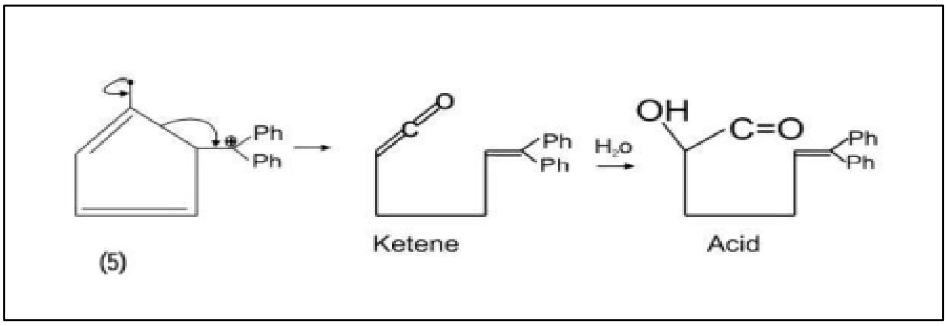
Because it is still a bicyclic product, it can be rearranged again consists of one or more enone systems capable of undergoing n-Л*excitement.



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.

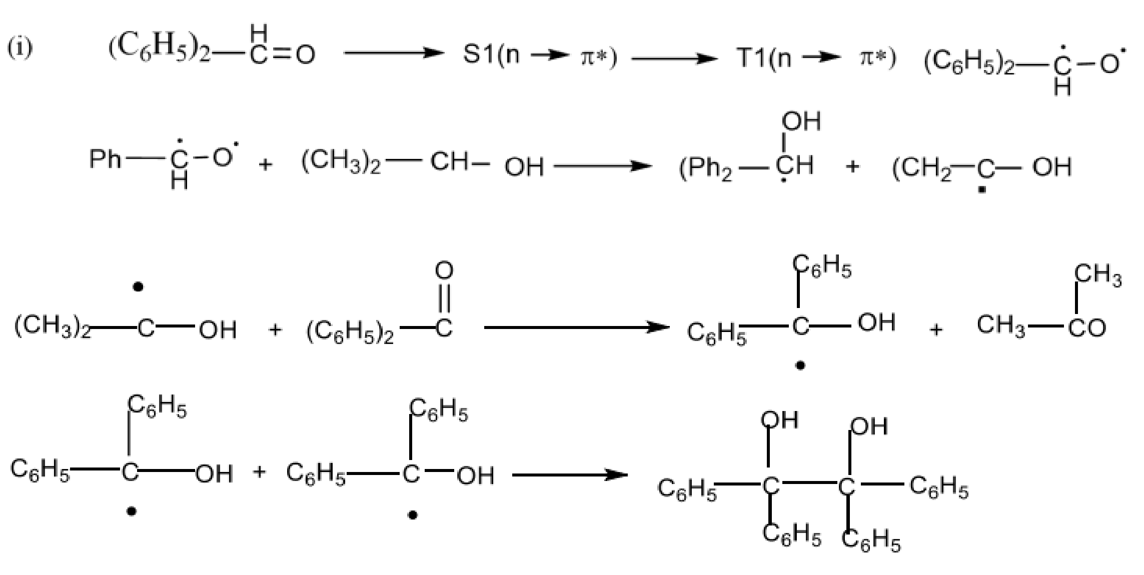


If medium is aqueous, then the structure no (5) can rearrange and gives a ketene and then form an acid.



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.



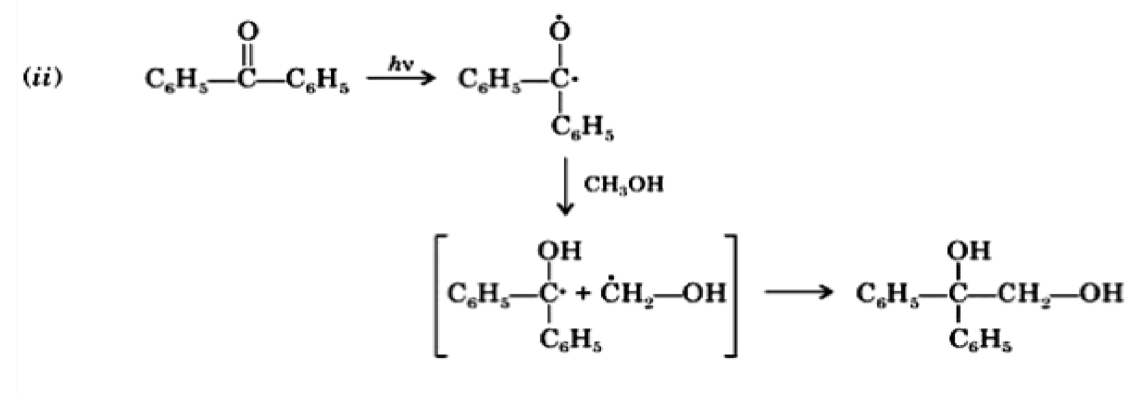
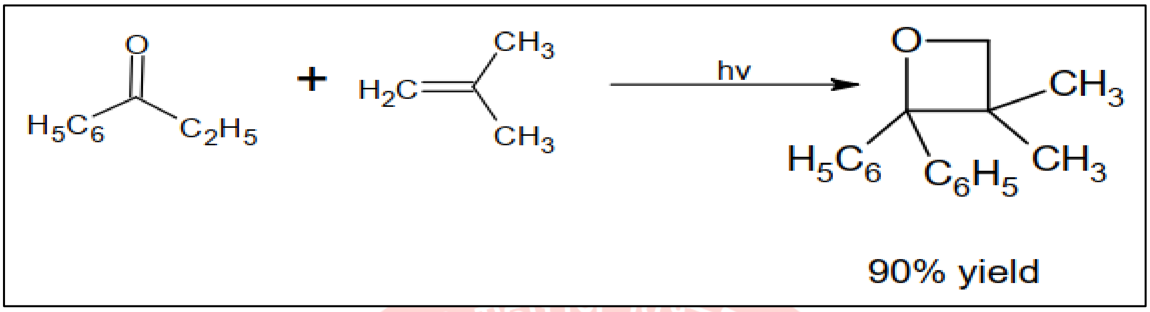


Photo Cycloaddition Reaction (Paterno-Buchi Reaction)

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.

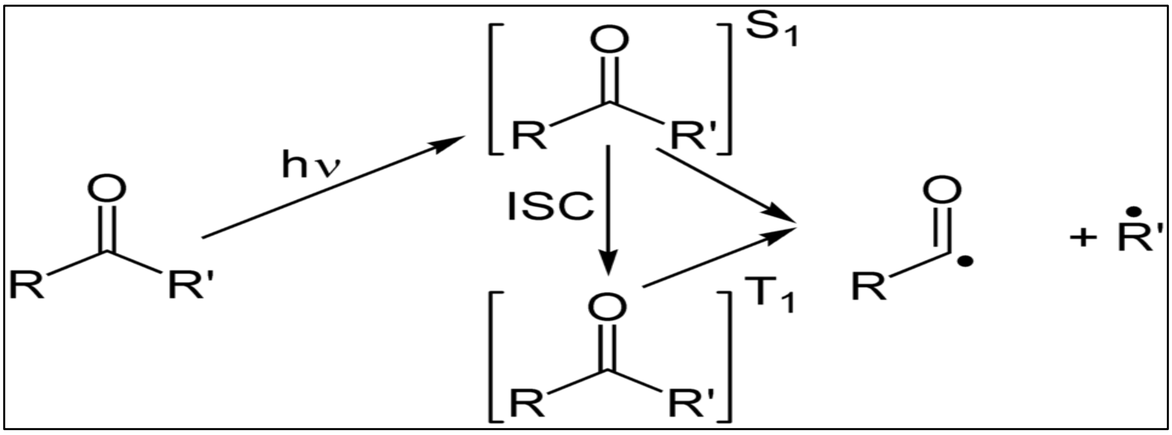


The Paterno-Buchi reaction can be classified into two types, depending on the nature of the alkenes.

Short & Long answer type Questions

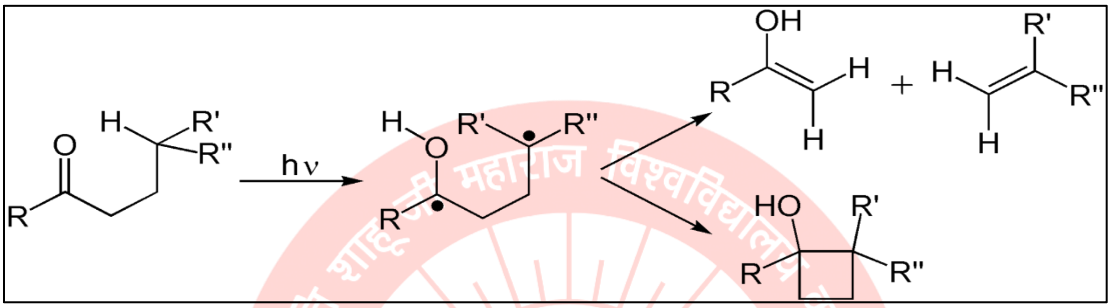
Q. Write a note on Norrish type-I and Norrish type-II reactions. (CSJMU2020)

Ans- The Norrish type I reaction is the photochemical cleavage or homolysis of aldehydes and ketones into two free radical 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; for instance, the cleavage of 2-butanone largely yields ethyl radicals in favor of less stable methyl radicals.



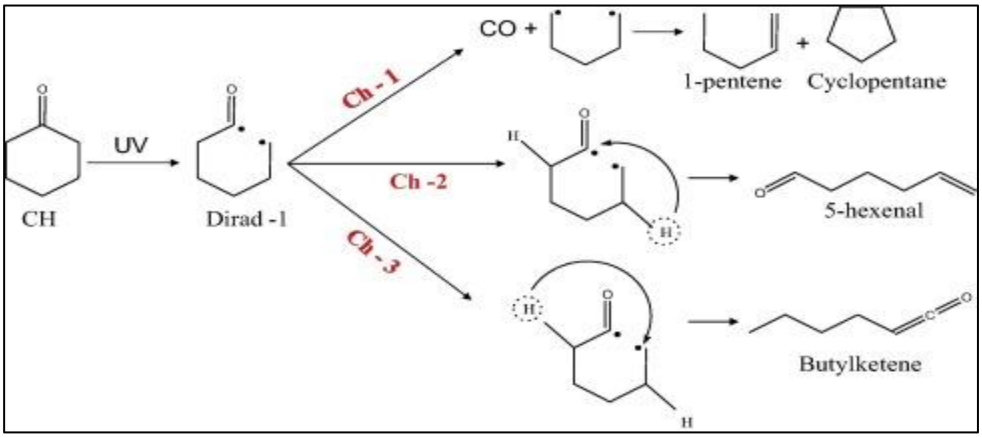
A Norrish type II reaction is the photochemical intramolecular abstraction of a γ-hydrogen (a hydrogen atom three carbon positions removed from the carbonyl group) by the excited carbonyl compound to produce a 1,4-biradical as a primary photoproduct.

Secondary reactions that occur are fragmentation (β-scission) to form an alkene and an enol (which will rapidly tautomerise to a carbonyl), or intramolecular recombination of the two radicals to a substituted cyclobutane (the Norrish–Yang reaction).



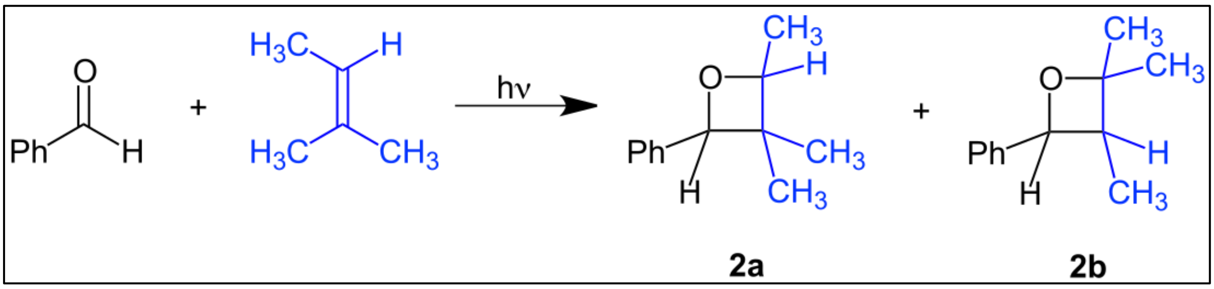
Q. Photochemistry of cyclic ketones. (CSJMU2016)

Ans. The photochemistry of cyclic ketones is characterized by Norrish Type I alpha-cleavage to form diradicals, which can then undergo reactions like decarbonylation or hydrogen abstraction to form other products, and Norrish Type II hydrogen abstraction. The dominant pathway depends on the ketone's ring size, structural features, solvent, and excited-state (singlet or triplet) involvement, with smaller rings (< 6 members) more prone to alpha-cleavage and larger rings favouring hydrogen abstraction.



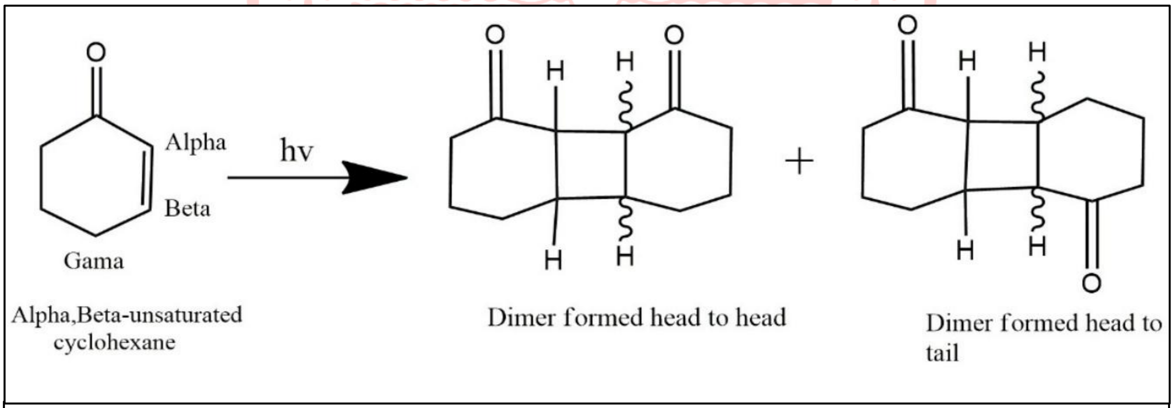
Q. Explain Paterno-Buchi reaction. (CSJMU2015,13)

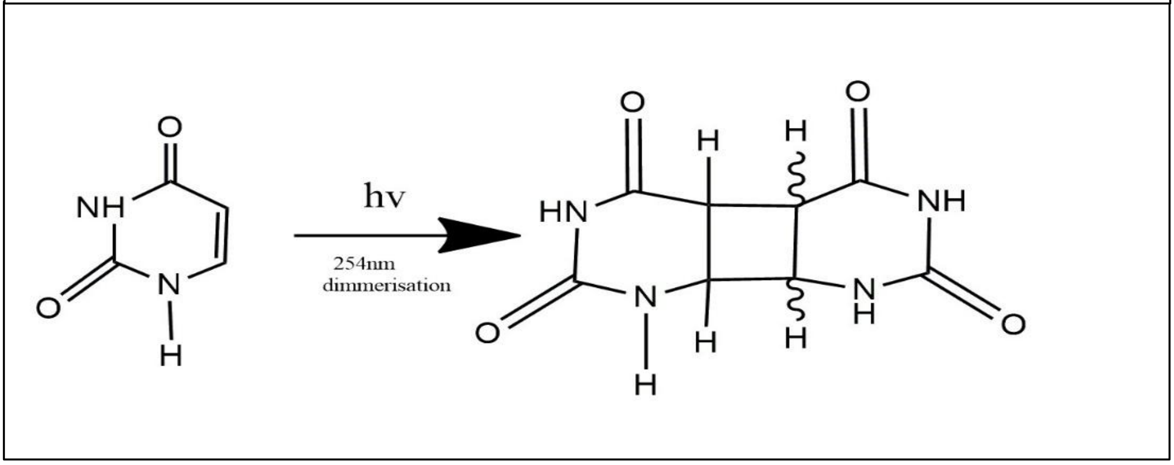
Ans. The Paternò–Büchi reaction, named after Emanuele Paternò and George Büchi, who established its basic utility and form,[1][2] is a photochemical reaction, specifically a 2+2 photocycloaddition, which forms four-membered oxetane rings from an excited carbonyl and reacting with an alkene.



Q. Dimerization of α, β- unsaturated ketones. (CSJMU2014,16,18,21)

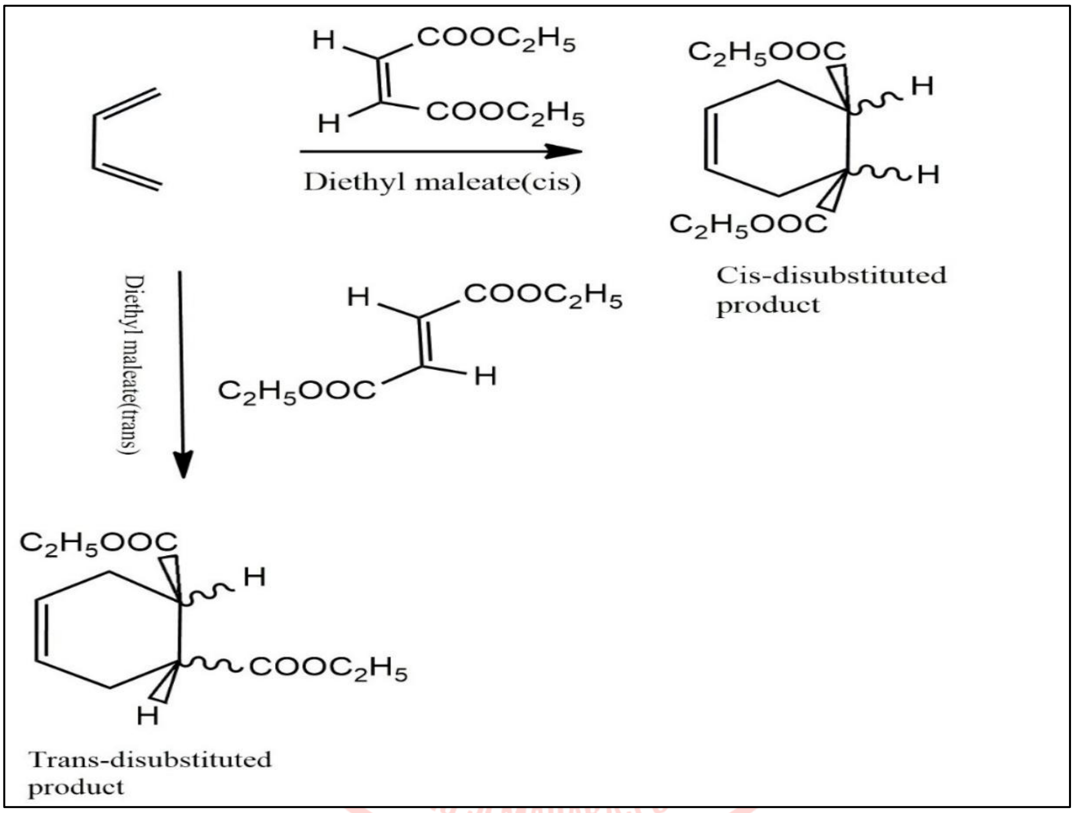
Ans. Dimerization of α, β-unsaturated ketones refer to the reaction where two molecules of an α, β-unsaturated ketone combine to form a larger molecule, often a diketone, and can be promoted by various methods including base catalysis, photocatalysis, and metal catalysts like samarium (II) iodide or ytterbium metal. The specific product and regiochemistry (e.g., "head-to-head" or "head-to-tail") depend on the catalyst and reaction conditions used.





Q. Intermolecular cycloaddition reaction. (CSJMU2012)

Ans. An intermolecular cycloaddition is a chemical reaction between two separate molecules that join to form a cyclic product. In this process, two pi bonds are converted into two sigma bonds, creating a ring structure. Well-known examples include the Diels-Alder reaction, where a diene and dienophile react, and 1,3-dipolar cycloadditions, which involve a 1,3-dipole and a dipolarophile.



Unit-V

Photochemical Addition Reactions of Aromatic Compounds:

When benzene and its derivatives absorb light, they get excited to the S1 (singlet excited) state. In this state, they can undergo cycloaddition reactions with π-systems such as alkenes, alkynes, and dienes.

However, in the T1 (triplet) state, benzene doesn't undergo these reactions because its energy is transferred to the alkene instead of reacting. In some special cases, the reverse can happen — where an excited alkene (S1) reacts with a ground-state arene (S0).

Cycloaddition reactions with benzene can happen in three ways:

- 1,2 (ortho) addition
- 1,3 (meta) addition
- 1,4 (para) addition

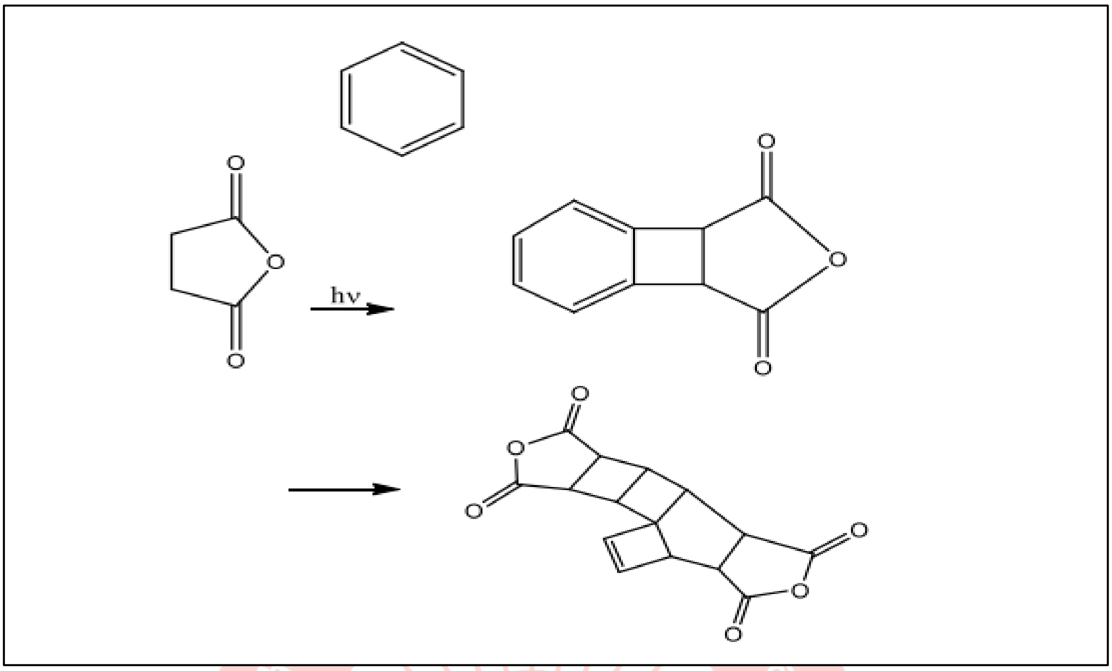
Out of these, the 1,4-addition is the least efficient.

These reactions may occur either between two different molecules (bimolecular) or within the same molecule (intramolecular). Interestingly, they are often reversible — meaning the cyclic product can break back into the original components. Since the products are ring compounds, these are called cycloaddition reactions.

If a mixture of olefins is irradiated with light of the right wavelength, a wide variety of products form due to additions at different positions (1,2; 1,3; or 1,4) on the benzene ring.

Scientists have proposed four possible mechanisms for how these reactions happen:

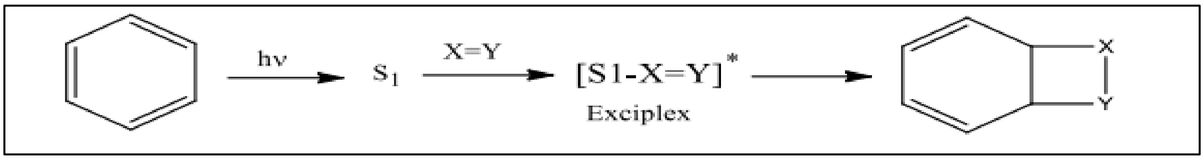
1. An excited aromatic compound reacts with a ground-state alkene.
2. An excited alkene reacts with a ground-state aromatic compound.
3. The excited aromatic compound first converts into a biradical, which then reacts with an alkene.
4. The reaction occurs through charge-transfer complexes or electron transfer between polar species.



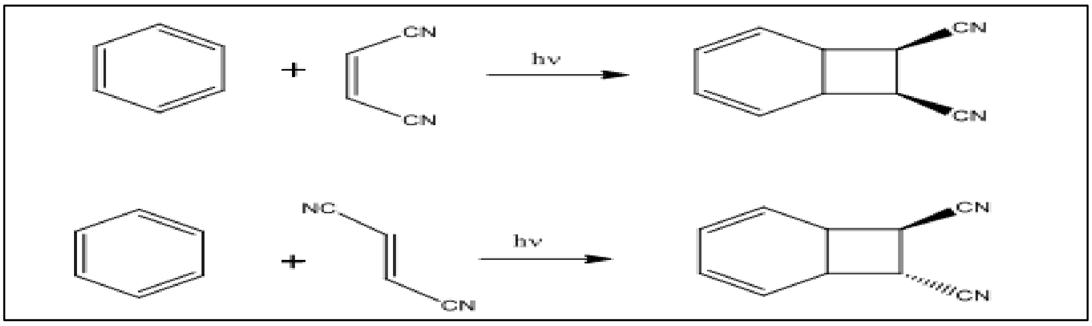
With mono and disubstituted benzenes, a similar reaction is observed to proceed via a charge transfer complex involving benzene and the maleic anhydride, but with a delayed kinetics due to steric hindrance by the substituent (S) present on the benzene ring. However, no reaction occurs with substantially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

[1, 2]-Photochemical Addition Reactions of Aromatic Compounds

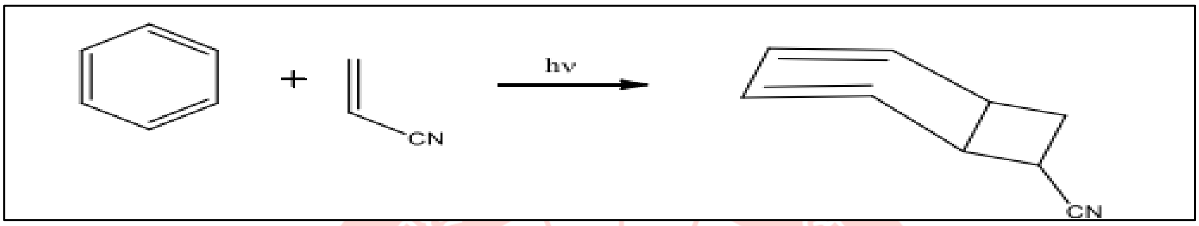
In addition to some 1, 4 products, electron poor alkenes (alkenes with electron withdrawing groups) give a 1, 2-addition reaction with arenes. The secondary product is the para product. Donor-acceptor contact is often beneficial to the creation of the ortho product. The longer the fraction of ortho and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



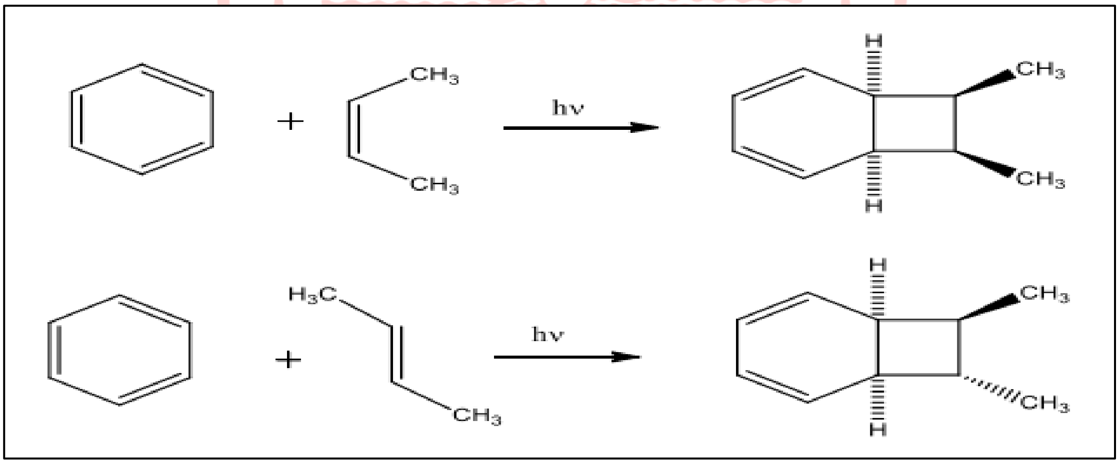
The reactions of 1, 2-cycloaddition are coordinated reactions. In the liquid phase, photocycloaddition of cis and trans-2-butene to benzene produces the 1, 2-adduct stereo specifically, indicating that the reaction is concerted. This also proved that the product is formed by the creation of exciplex.



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.

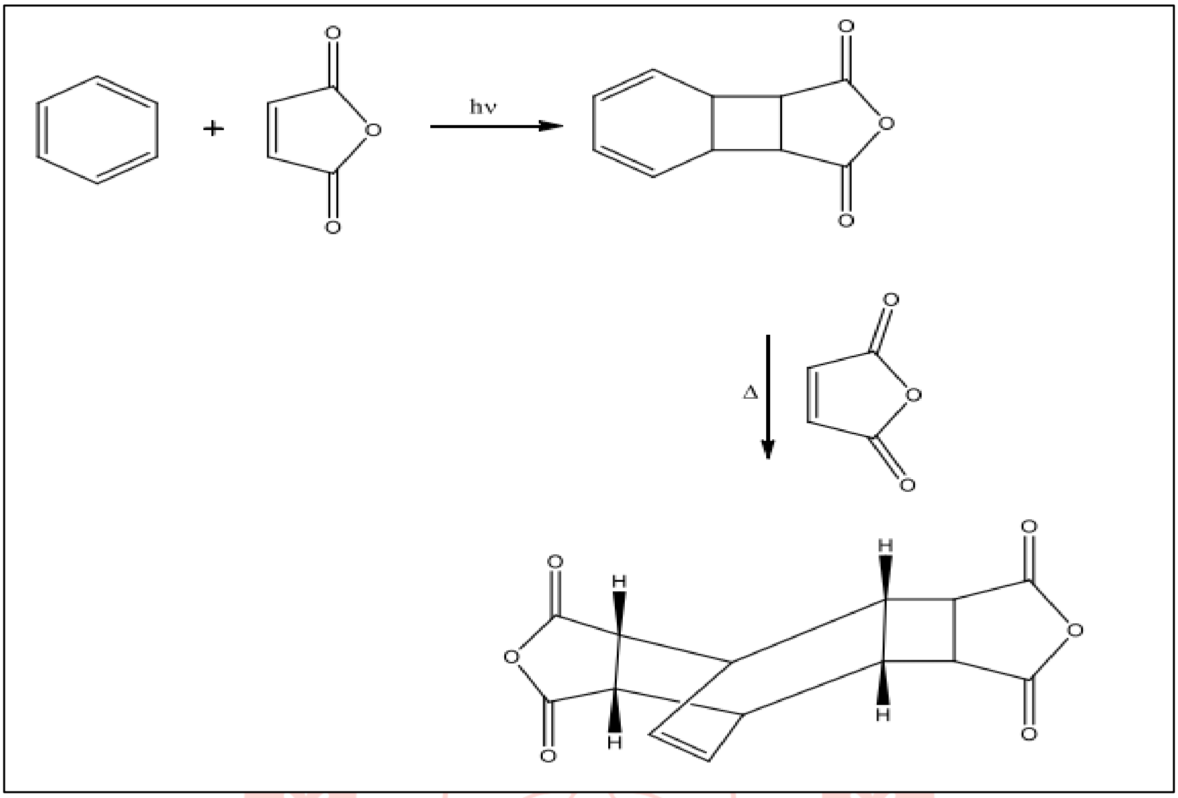


When light is shone on benzene (liquid) and 2-butane (Cis or Trans), 1,2 photoaddition occurs. It's worth noting that the stereochemistry of 2-butene is preserved in this reaction. This demonstrates that the reaction is stereotypical and coordinated.



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.

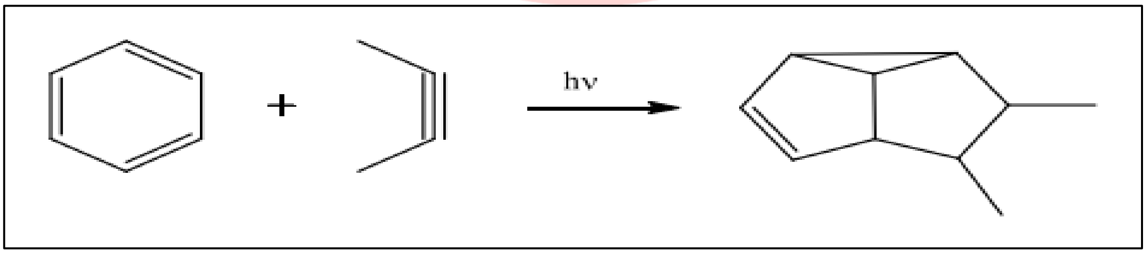
When benzene is irradiated in the presence of maleic anhydride, an exo 1, 2-cycloadduct is formed. The production of the product occurs in the S1 state of a charge transfer complex. A photochemical | 2 + 2 | ortho-cycloaddition reaction is followed by a thermal | 4 + 2 | cycloaddition to produce the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



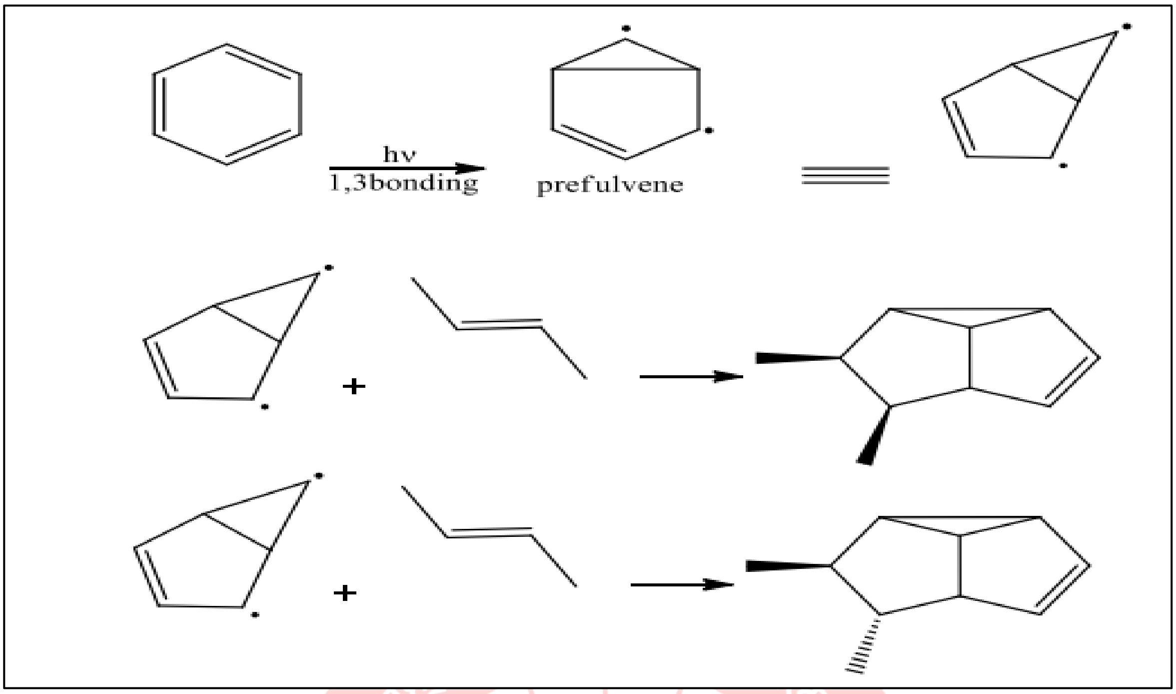
The ortho cycloaddition products are the principal products of irradiating alkynes, especially those having electron-withdrawing groups, with benzene. At room temperature, these adducts are frequently unstable.

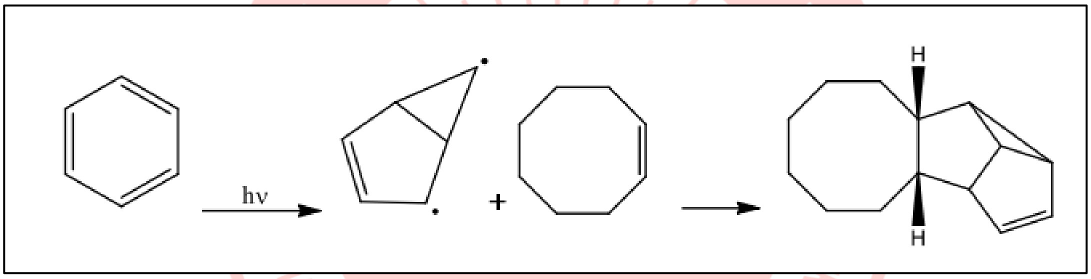
[1, 3]-Photochemical Addition Reactions of Aromatic compounds:

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 additions.



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.





When a **double bond (olefinic side chain)** is attached to a benzene ring, the molecule can sometimes react with itself (**intramolecular cycloaddition**).

For example, when **6-phenylhex-2-ene** is exposed to UV light, the double bond reacts with the **meta-positions of the benzene ring**, forming a **tricyclic system** (a structure with three connected rings).

This type of reaction usually happens when the side chain contains certain types of double bonds, such as in **2-butene, norbornene, allene, or cyclobutene**.

The reaction:

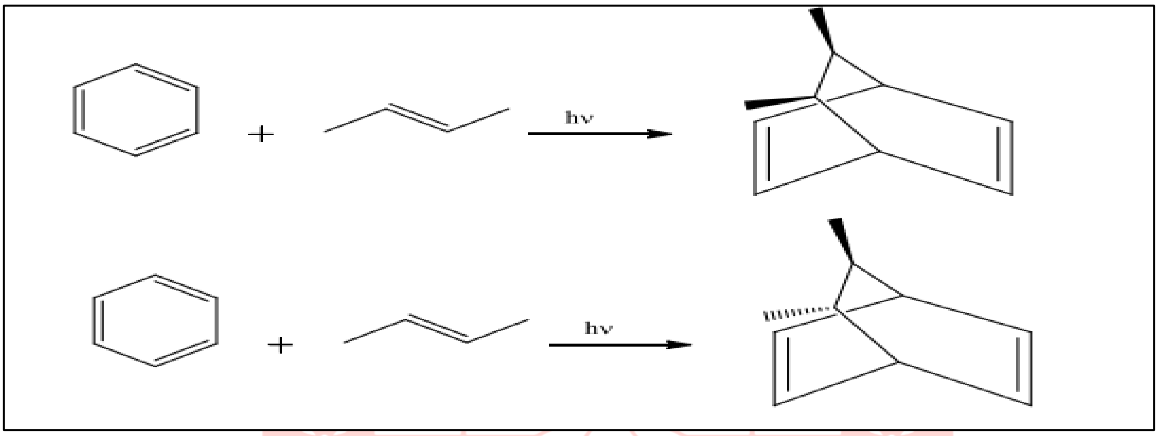
- Takes place in both **gas** and **liquid** phases.
- Requires **254 nm UV light**.
- Involves **singlet excited benzene** (not the triplet).
- Is **stereospecific** (the product keeps the original spatial arrangement).

The mechanism does **not** involve **fulvene** or **benzvalene** intermediates. Instead, the reaction goes through a **prefulvene biradical**, which then leads to the product.

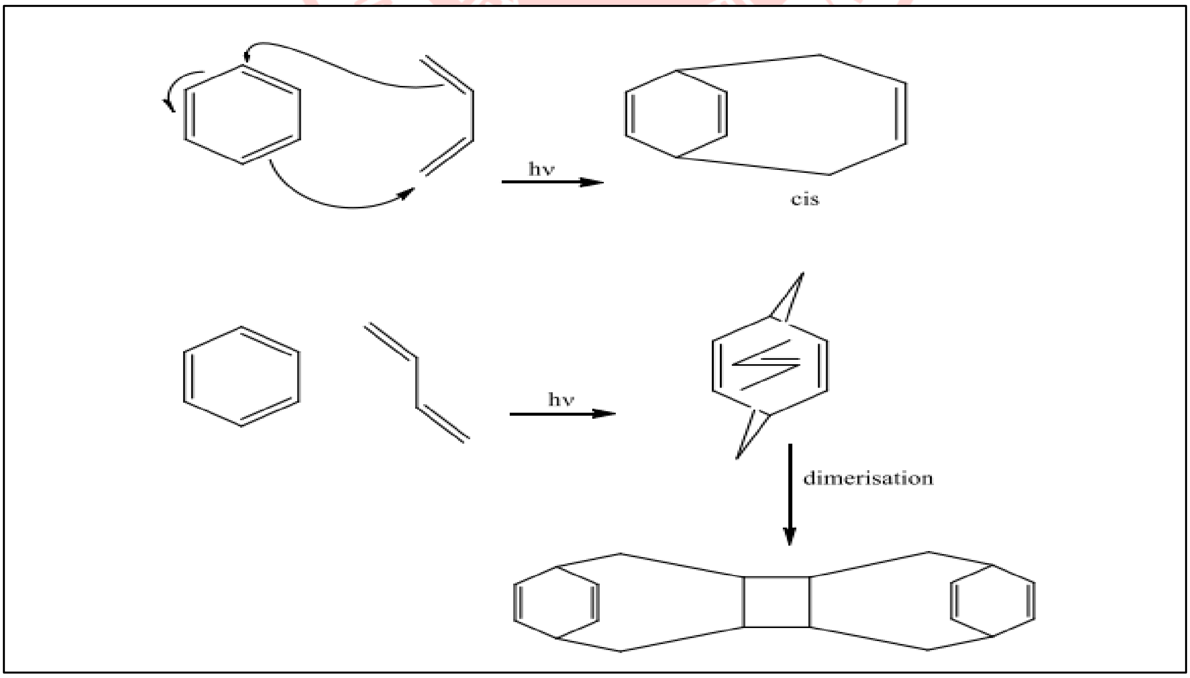
In **1,3-cycloaddition**, the main product formed is the **endo product** (where substituents are oriented inside the new ring system).

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

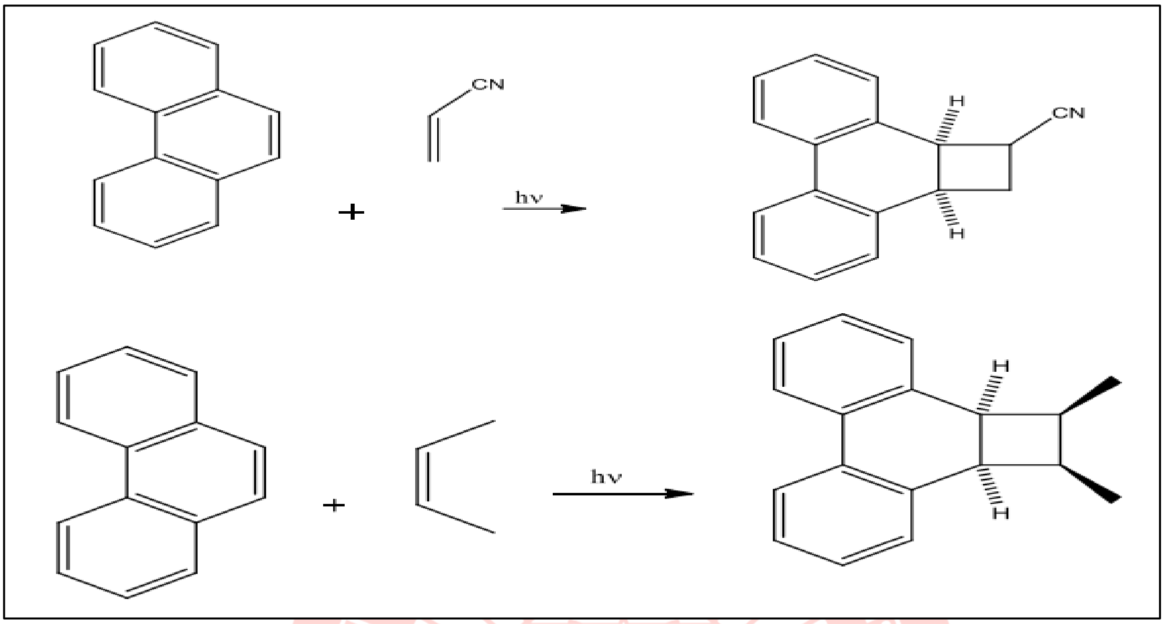
The olefin is added at the para position of benzene in these types of photochemical reactions. The reaction takes place in benzene's singlet excited state and is stereospecific, meaning the olefin's stereochemistry is preserved. Because benzene acts as a diene in these reactions, they are similar to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



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

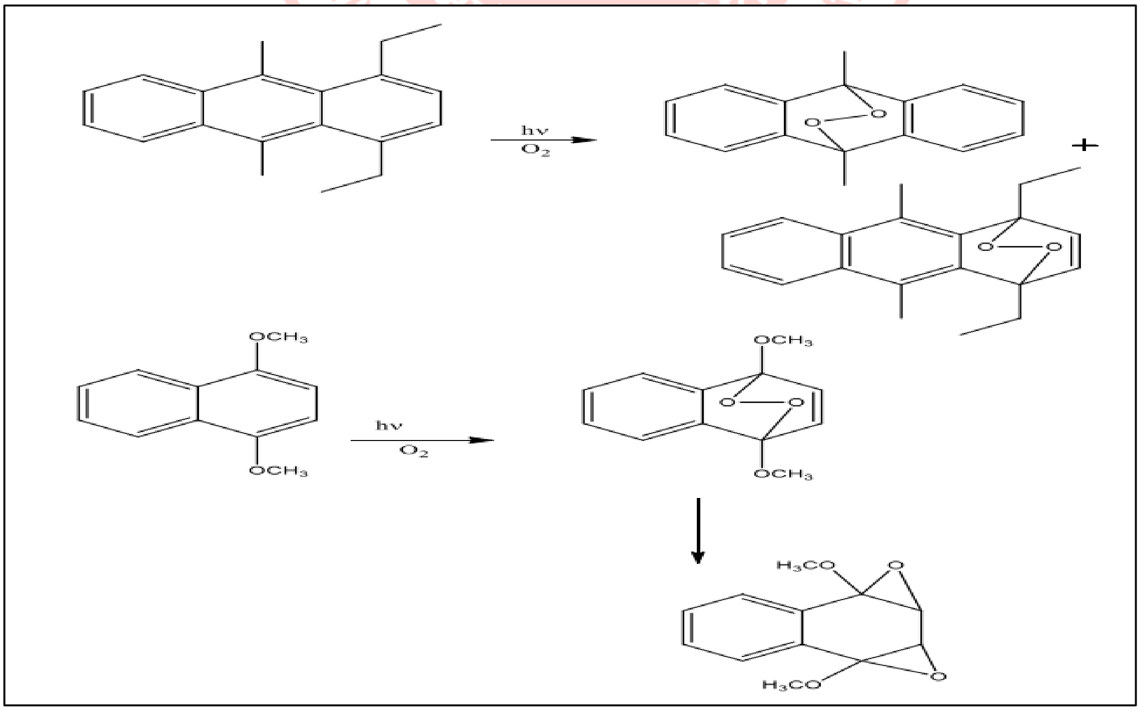


Benzene and its simple homologues are not the only olefinic systems that can be photoaddition. Condensed aromatics like naphthalene, phenanthrene, and anthracene go through a similar process. The cycloaddition of anthracene is [4 + 2], while that of phenanthrene and naphthalene is [2 + 2].



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.



Studies of this photochemical reaction show that when an aromatic hydrocarbon is excited to its triplet state, it can transfer energy to an oxygen molecule. This excites oxygen and converts it into singlet oxygen.

The singlet oxygen then reacts with the ground-state aromatic hydrocarbon in a [4+2] cycloaddition reaction (similar to a Diels–Alder reaction).

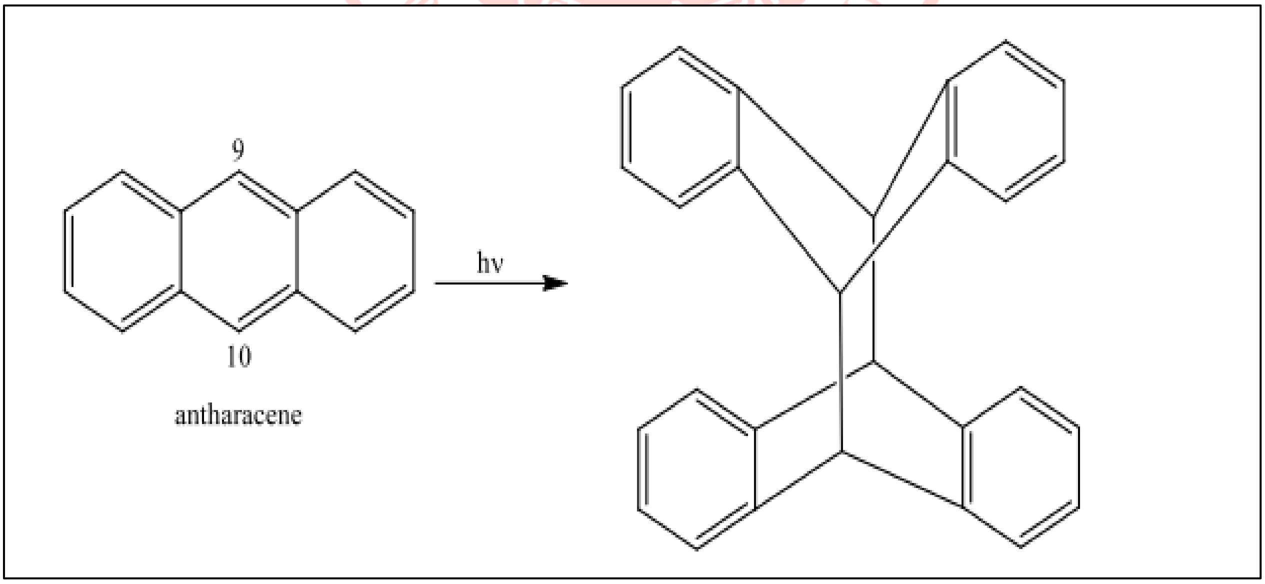
When transannular peroxides are exposed to light in the presence of oxygen, polynuclear aromatic hydrocarbons (like naphthalene and anthracene) are formed. The exact place where the oxygen attacks depends on the substituents on the aromatic ring.

Mechanistic studies confirm that:

1. The triplet excited hydrocarbon transfers energy to oxygen, converting it into singlet oxygen ($^1O_2$).
2. This singlet oxygen then reacts thermally with the ground-state hydrocarbon.
3. The overall process is a [4+2] cycloaddition reaction.

Photochemical dimerization 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 naphthalene and anthracene, as well as the reaction of anthracene.



At the 9,10-positions, two anthracene molecules can join together to form a dimer.

- If there is a substituent at the 9-position, the dimer forms in a head-to-tail fashion.

The wavelength of light used in the photochemical reaction strongly affects this dimerisation:

- Shorter wavelength light (higher energy) → breaks the dimer back apart (photochemical cleavage).
- Longer wavelength light (lower energy) → promotes dimerisation or other reactions.

For example:

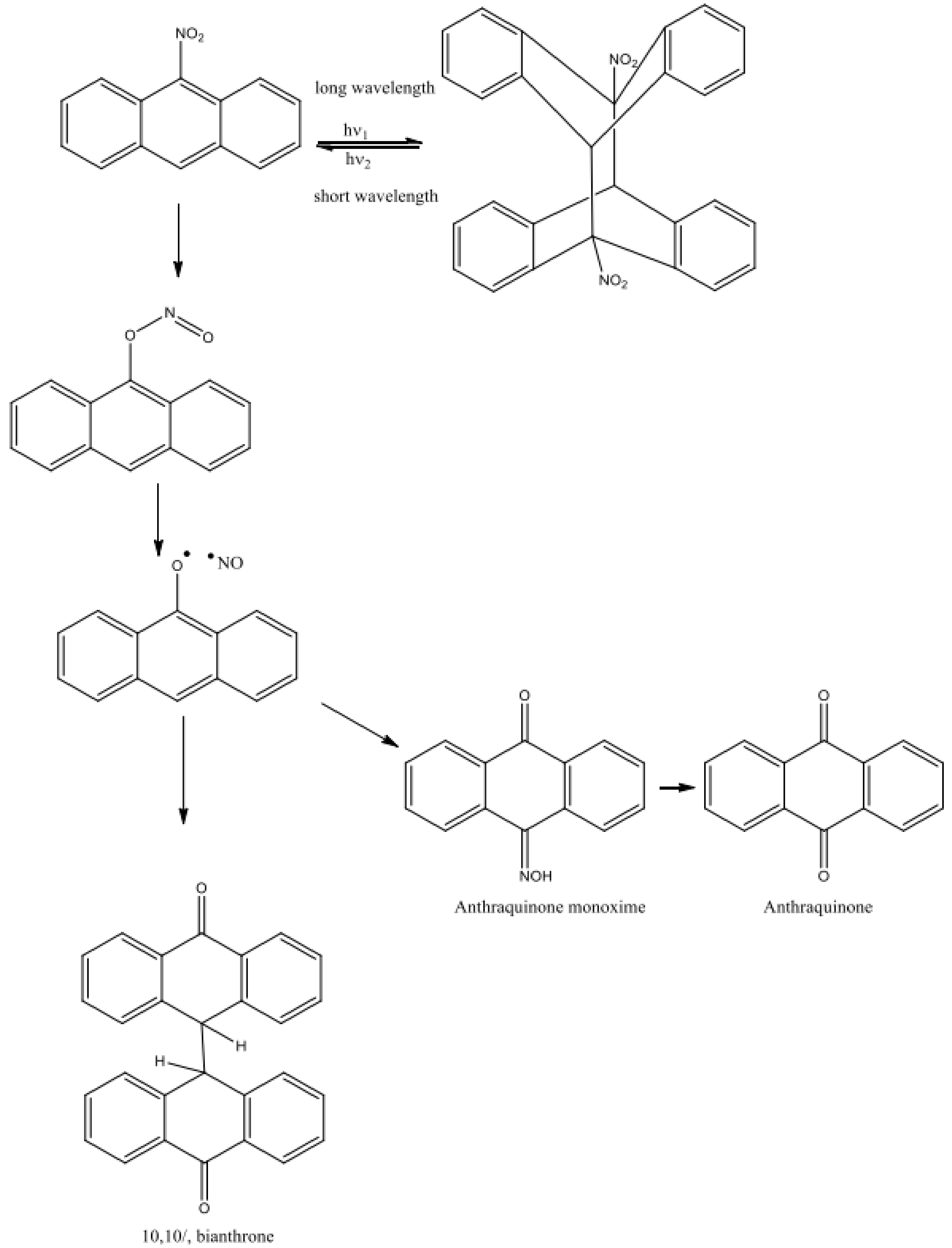
- When 9-nitroanthracene is irradiated with long-wavelength light, a dimer is formed.
- When it is irradiated with short-wavelength light, different products appear, such as:
  - Nitric oxide (NO)
  - Anthraquinone
  - Anthraquinone monoxime
  - 10,10′-bianthrone

These products are believed to come from a 9-anthryl nitrile intermediate.

It’s also important to note that the electron distribution in an aromatic molecule changes a lot between the ground state (S0) and the excited state (S1).

This can be seen by comparing acid–base properties (pKa values):

- For example, 2-naphthol and 2-naphthylamine show very different pKa values in the ground state and the excited state.
- This difference clearly shows how electron density shifts when the molecule is excited by light.


NO2
long wavelength
hν1
hν2
short wavelength
NO2
NO2
O
N
O
O•
•NO
O
NOH
Anthraquinone monoxime
O
O
Anthraquinone
O
H
H
O
10,10/, bianthrone

Photochemical Substitution Reaction of Aromatic Compounds:

When aromatic compounds absorb light, they can undergo substitution reactions. The substitution may happen:

- On the aromatic ring carbon, or
- On an atom in a substituent group attached to the ring.

These reactions can follow two main pathways:

- Radical mechanism (bond breaks evenly → free radicals).
- Heterolytic mechanism (bond breaks unevenly → ions form).

Most photochemical substitutions occur by the heterolytic pathway. They are grouped into two types:

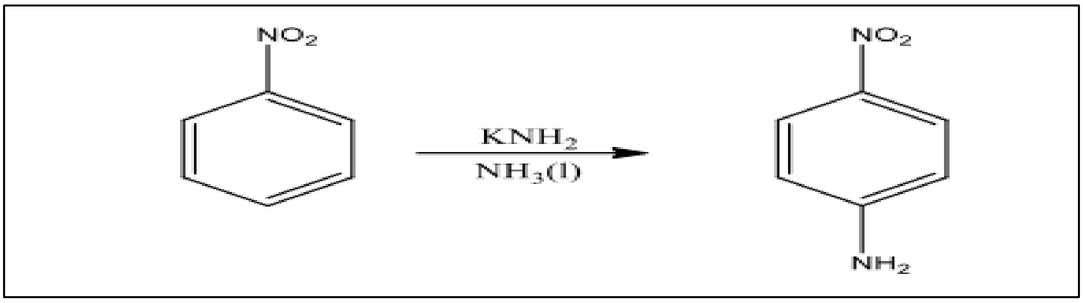
- Type A: The product orientation is different from what is normally seen in the ground state.
- Type B: The product orientation is the same as in the ground state, but the reaction is much faster because light provides extra energy.

Key points:

- These reactions mostly involve the lowest singlet excited state (S1) of the aromatic compound.
- They often give products with high efficiency (high quantum yield).
- Substitution can happen either on the ring itself or on the side chain.
- In both cases, the chemical bond can break either homolytically (radicals) or heterolytically (ions).

Nucleophilic 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.



However, it has been discovered that the -NO2 group acts as a Meta directing group during photochemical reactions involving excited states.

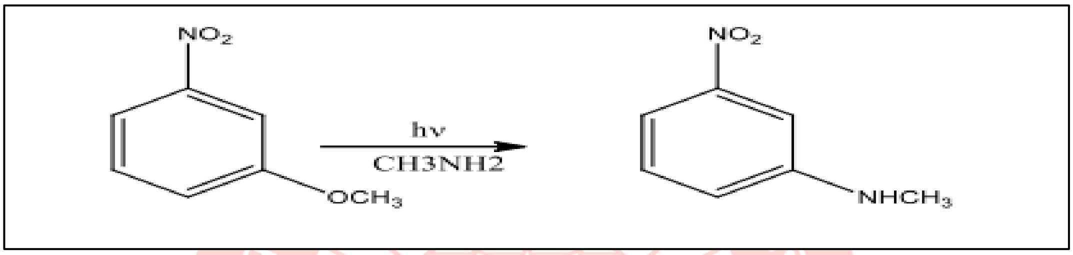
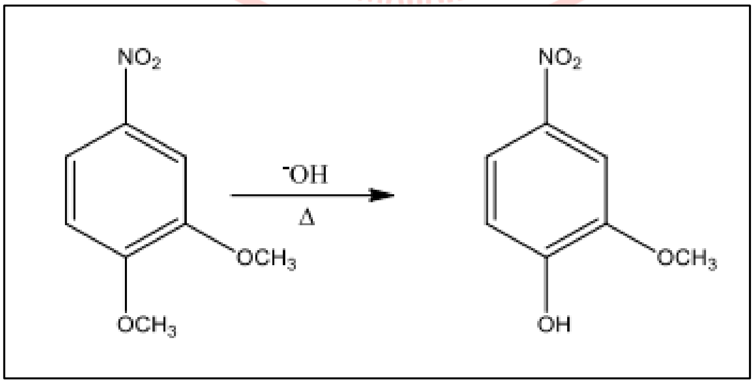
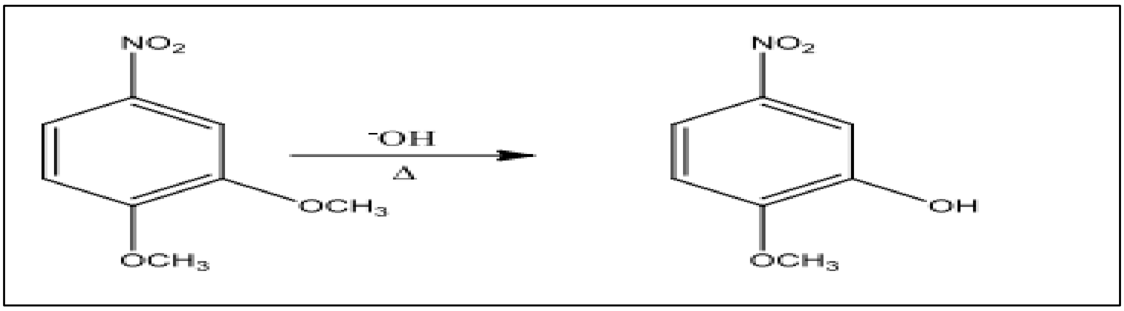


Fig. Nucleophilic substitution m-position

When heated with -OH ions, the molecule 3,4-dimethoxynitrobenzene becomes 4-hydroxy-3- methoxy nitrobenzene, in which the -OCH3 group at position 4 is replaced by the -OH group.



When the same reaction is carried out photochemically, that is, by irradiating with UV



light, the -OCH3 group in the 3-position is replaced by the OH group.

The reason for this behaviour is linked to how substituents affect electron distribution in the aromatic ring.

- Under thermal (heat) conditions, a $–NO_2$ group withdraws electrons through both –I (inductive) and –M (mesmeric/resonance) effects. This makes the ortho and para positions of the ring electron-poor (positively charged), so substitution avoids those sites.
- Under photochemical (light) conditions, the situation changes. Now the ortho and meta positions become electron-poor (positively charged) compared to the para position, leading to a different substitution pattern.

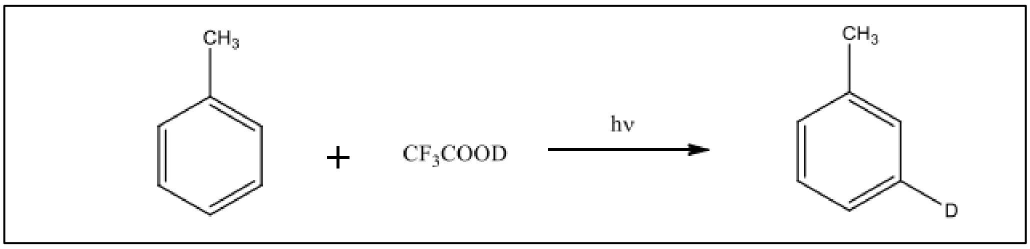
A similar effect is seen when a –CN (cyano) group is present on naphthalene or substituted naphthalene — the substitution positions depend on whether the reaction is driven by heat or by light.

Electrophilic Substitutions:

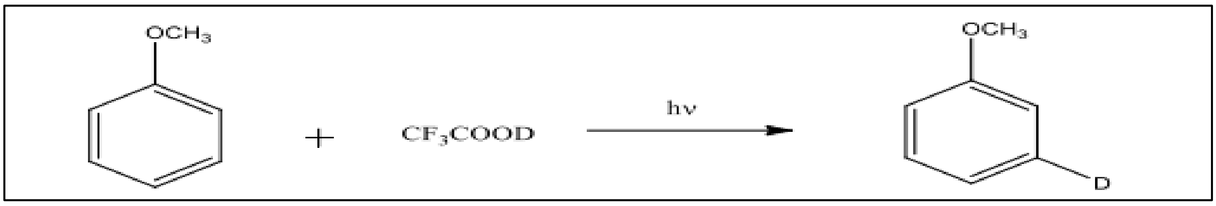
Photochemical substitution in benzene derivatives can sometimes give **unexpected products**.

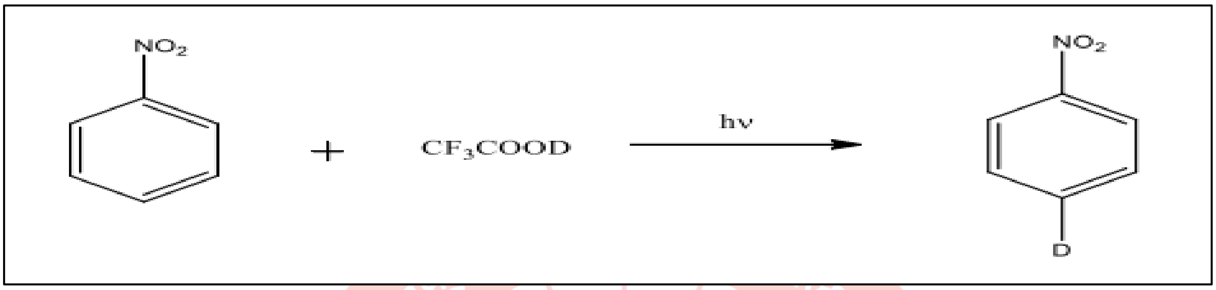
For example:

- Normally, in thermal (heat-driven) reactions, a **$–CH_3$ group** directs substitution to the **ortho** and **para** positions.
- But when **toluene** is exposed to **light** in the presence of **CF_3COOD**, the main product formed is **meta-deuterated toluene** (substitution happens at the **meta position**, not ortho or para).



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





In photochemical reactions, the normal directing effects of substituents can change.

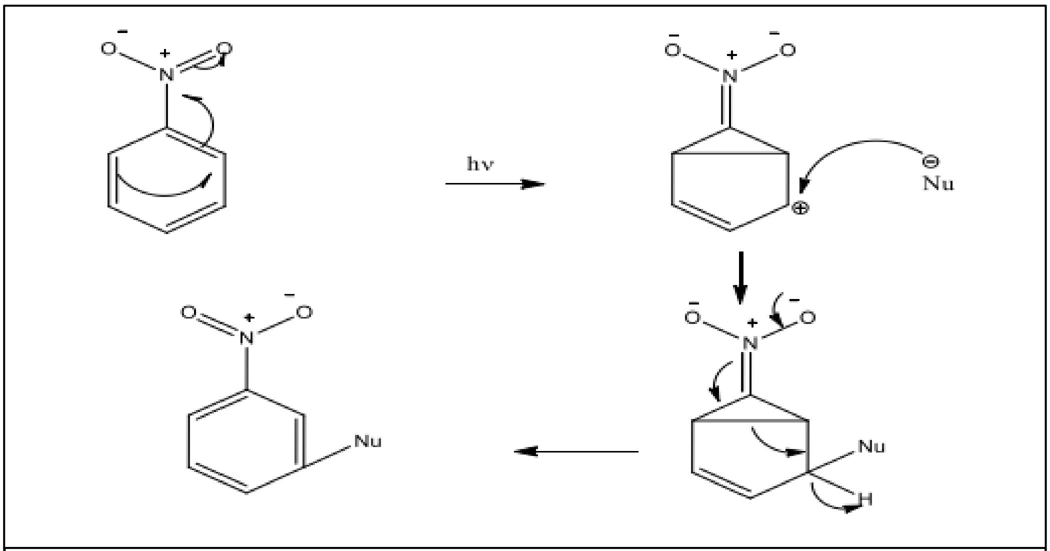
- For example, a $-NO_2$ group (normally meta-directing in thermal conditions) can instead make the para position more reactive under light.
- A $-OCH_3$ group (normally ortho/para-directing) may instead make the meta position more reactive under photochemical conditions.

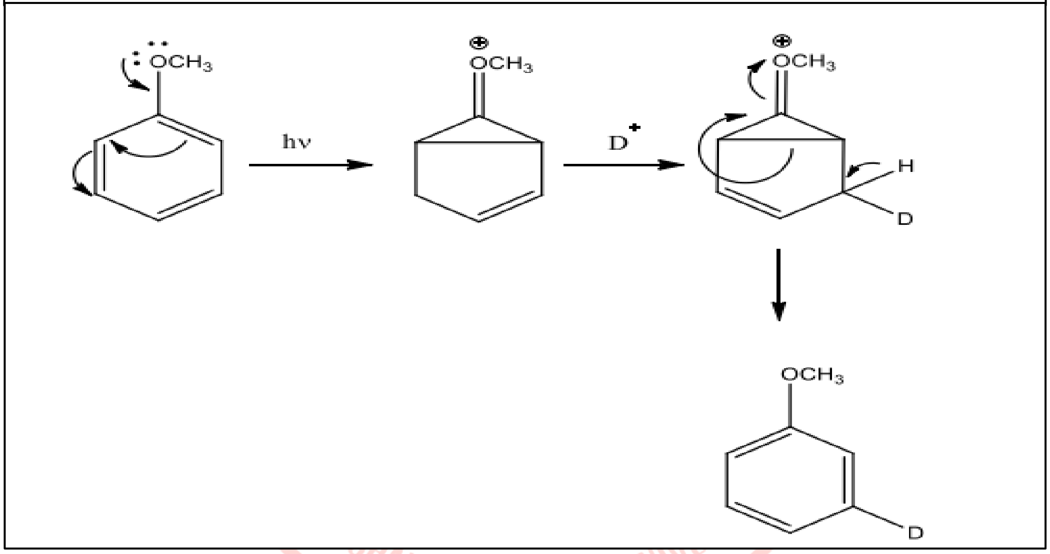
This happens because the electron distribution in the aromatic ring is different in the ground state (S_0) compared to the excited state (S_1).

By considering how the electron density shifts in the excited state, the orientation rules for electrophilic and nucleophilic substitution can be reorganized.

For example:

- An electron-withdrawing group reduces the electron density at the meta position, which makes it act as a meta-directing group for incoming nucleophiles in photochemical substitution.





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.

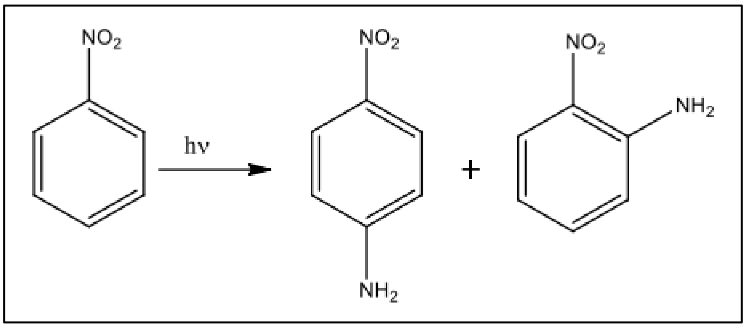
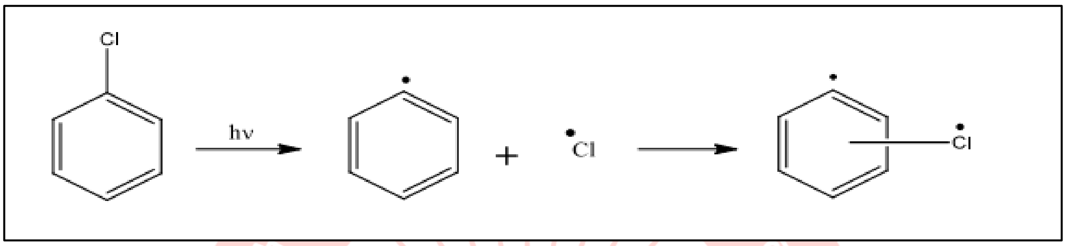


Fig. 5.28 Ortho para substitution

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 that 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-.



Phenyl-substituted aromatic compounds can be made through **photochemical homolytic cleavage** of the bond between a **halogen atom** and the **carbon of an aromatic ring**.

These reactions usually give a **very high yield** of products. In addition, they can also produce a **large amount of polynuclear (multi-ring) compounds**.

Photochemistry Of Diazo Compounds:

Diazoalkanes absorb light weakly in the visible region (400–500 nm) because of an n → π* transition.

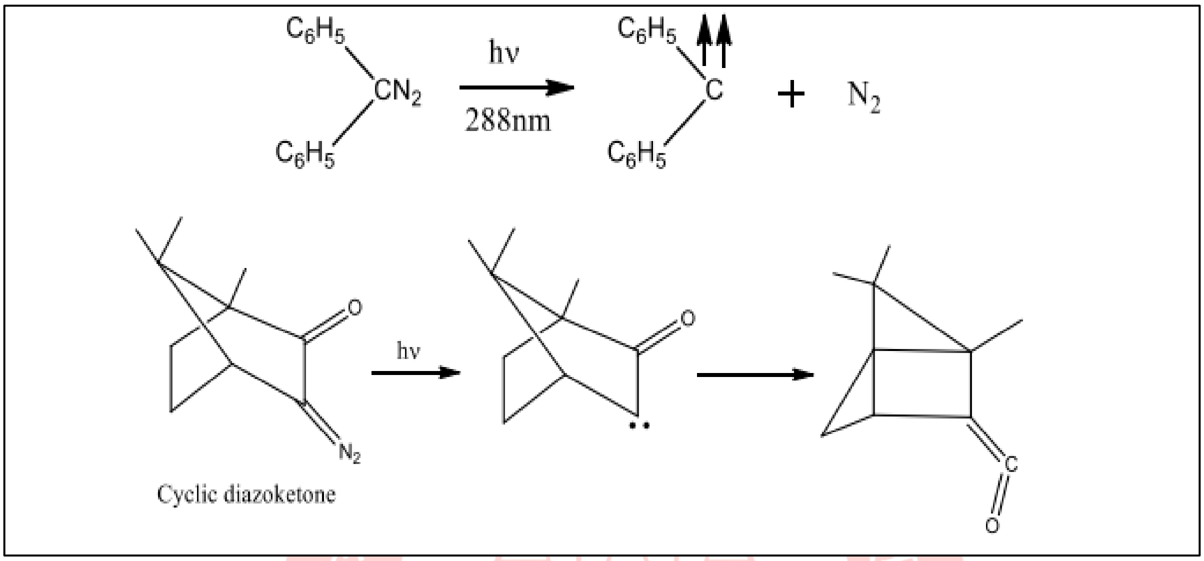
When excited, they easily break apart to give nitrogen gas (N_2) and a carbene. This is a common way to produce divalent carbon species (carbenes).

- If diazoalkanes are irradiated directly with light, they first form a singlet excited state, which produces a singlet carbene.
- However, collisions between molecules often convert this singlet carbene into a triplet carbene, especially at high pressure in vapour or in solution.
- If a triplet sensitiser is used, the reaction goes through the triplet excited state and directly gives a triplet carbene.

These processes are very useful in organic synthesis. For example:

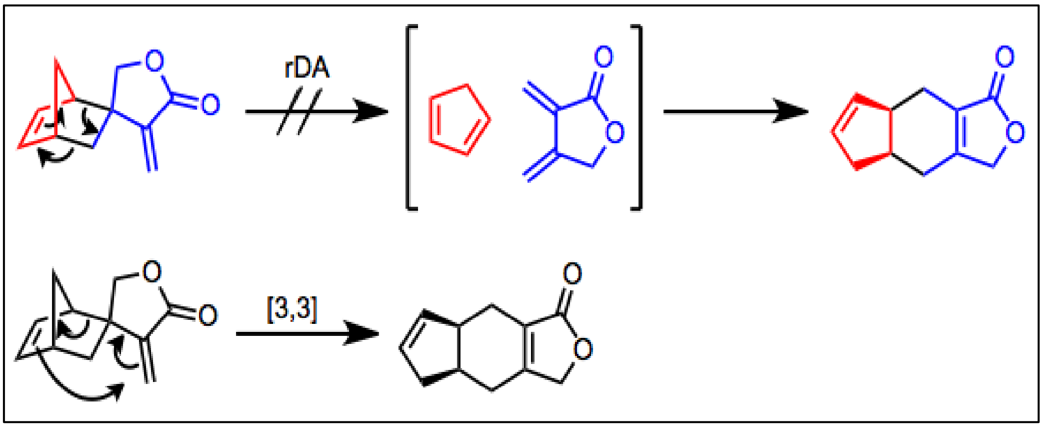
- Cyclic diazoketones undergo ring contraction.
- α-Diazoamides can form β-lactams.

Thus, photochemical breakdown of diazoalkanes is a valuable method for generating carbenes.



Q. Write short note on retro-Diels Alder reaction. (CSJMU2011,14)

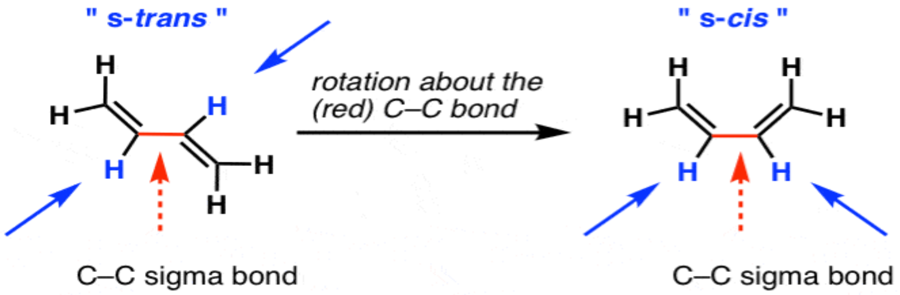
Ans. The retro-Diels-Alder reaction is the reverse of the Diels-Alder reaction, where a cyclic adduct (cyclohexene derivative) breaks apart into its original conjugated diene and dienophile. This electrocyclic process is typically initiated by high temperatures, although catalysts like acids, bases, or Lewis acids can also facilitate the reaction. The reaction is entropically favored as it produces more molecules from one, which becomes more influential at elevated temperatures, and can be used in organic synthesis and material science.



Q. Give the photochemical intra molecular cis, trans isomerization of butadiene. (CSJMU2011,16,19)

Ans. Photochemical intramolecular cis,trans isomerization in butadiene involves the molecule absorbing light (typically ultraviolet) and entering an excited state, leading to rotation around a double bond to interconvert between cis and trans isomers. This process is often studied using substituted butadienes, such as diphenylbutadiene (DPB), where transient absorption spectroscopy reveals the formation of a perpendicular "P" state followed by relaxation and isomerization to different isomers. The efficiency and products of this photoisomerization depend on factors like solvent polarity and the specific butadiene structure.

" s-*trans* " and "s-*cis*" conformations of a diene



Notice that the two hydrogens are on the **opposite side ("trans")** of the (red) C–C sigma bond

Notice that the two hydrogens are on the **same side ("cis")** of the (red) C–C sigma bond

Unit-VI

Miscellaneous photochemical Reactions:

Photochemical smog Formation-

Photochemical smog is a type of air pollution due to the reaction of solar radiation with airborne pollutant mixtures of nitrogen oxides (NOx) and volatile organic compounds (hydrocarbons). Smog is a byproduct of modern industrialization. Due to industry and the number of motor vehicles, this is more of a problem in large cities that have a warm, sunny and dry climate.

- **Oxidation**: Photochemical smog is also referred to as oxidizing smog. Oxidation reactions have been defined several ways. In terms of oxygen transfer, oxidation is a gain of oxygen. Oxidation can also be defined as a loss of hydrogen. The most important use of oxidation is described in terms of electron transfer. Oxidation can be described as an increase in oxidation number or loss of electrons. Oxidation numbers represents a distribution of charge. In other words, oxidation numbers represent the charge of the atom if the compound was composed of ions. (Oxidation Numbers – Rules and Practice Problems).
- **Reduction**: Reduction can involve the gain of hydrogen or loss of oxygen. Reduction can refer to the gain of electrons, which results in a decrease in oxidation number.

Formation of Photochemical Smog

Step 1: People begin driving in the morning, nitrogen is burned or oxidized

$N2+O2 \rightarrow 2NO$ (1)

- Oxidation number of N_2 is 0. The nitrogen in NO has acquired an oxidation number of +2.

Step 2: After a few hours, NO combines with O_2, in another oxidation reaction

$2NO+O2 \rightarrow 2NO2$ (2)

- The nitrogen in NO has an oxidation number of +2. The nitrogen in NO_2 has an oxidation number of +4.

Step 3: Nitrogen dioxide absorbs light energy, resulting in a reduction reaction

$NO_2 \rightarrow NO+O$ (3)

- The nitrogen in NO_2 has an oxidation number of +4 and the nitrogen in NO is +2.

Step 4: In sunlight, atomic oxygen combines with oxygen gas to form ozone

$$O+O_2 \rightarrow O_3 \quad (4)$$

Step 5: Reaction is temperature and sunlight dependent

$$O_3+NO \rightleftharpoons NO2+O_2 \quad (5)$$

Barton Reaction-

The Barton reaction commences with a photochemically induced cleavage of the nitrite O-N bond, typically using a high-pressure mercury lamp. This produces an alkoxyl radical which immediately abstracts a hydrogen atom from the δ-carbon. In the absence of other radical sources or other proximal reactive groups, the alkyl radical recombines with the nitrosyl radical. The resultant nitroso compounds undergo tautomerization to the isolated oxime product.

The carbon centred radical can be intercepted by other radical sources such as iodine or acrylonitrile. The first instance results in the δ-hydrogen being replaced with iodine, then subsequent cyclization to a tetrahydrofuran by an SN2 reaction. The second example results in a chain elongation product with the oxime formed 2 carbon units further from the oxygen than normal.

This mechanistic hypothesis is supported by kinetic isotope effect experiments. Isotopic labelling of the nitrite with 15N has shown the mechanism non- ‘caged’ and that the nitrosyl radical formed from a given nitrite recombines randomly with other alkyl radicals. However, recombination of the nitrosyl radical with the alkoxyl radical (a reversal of the homolytic cleavage) has been shown to proceed without scrambling of isotope labels. This lack of tight radical pairing is also supported by the observation that alkyl radicals generated by Barton conditions can undergo radical cyclization while analogous intermediates generated by lead tetraacetate oxidation do not.

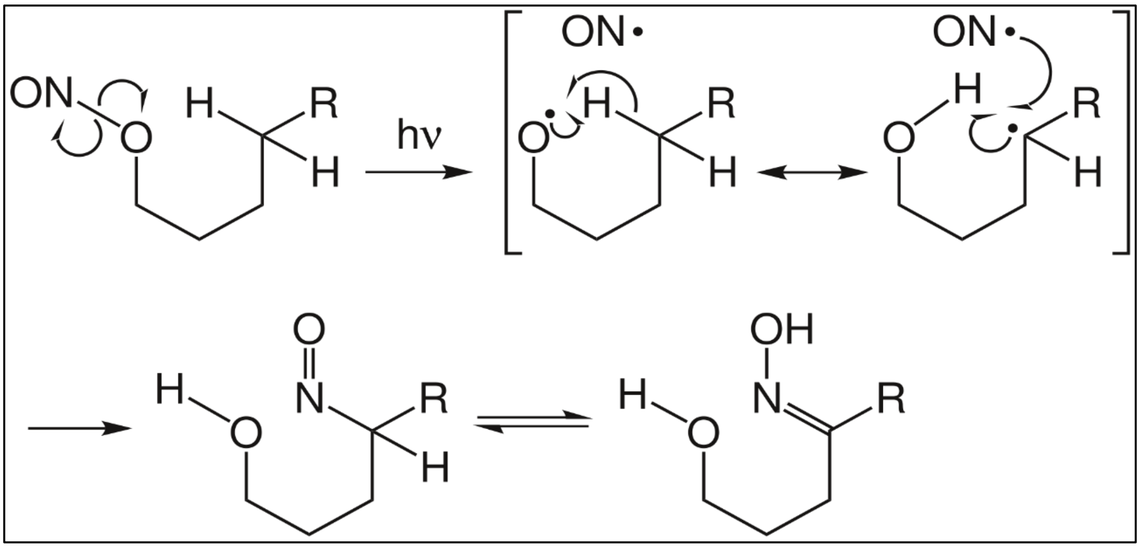
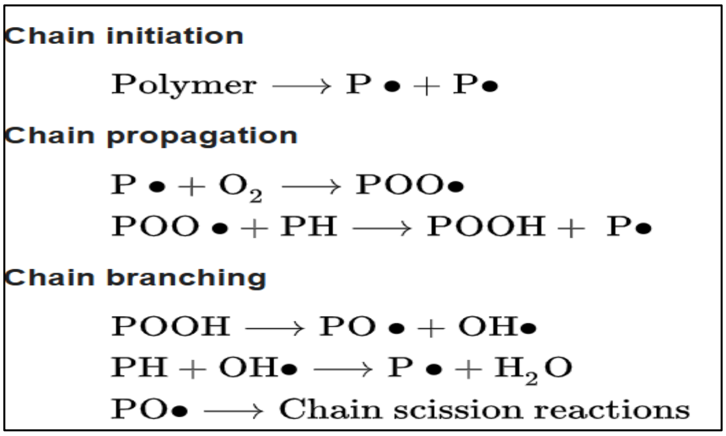


Photo-oxidation of polymers-

Polyolefins such as polyethylene and polypropylene are susceptible to photo-oxidation and around 70% of light stabilizers produced world-wide are used in their protection, despite them representing only around 50% of global plastic production. Aliphatic hydrocarbons can only adsorb high energy UV-rays with a wavelength below ~250 nm, however the Earth's atmosphere and ozone layer screen out such rays, with the normal minimum wavelength being 280–290 nm. The bulk of the polymer is therefore photo-inert and degradation is instead attributed to the presence of various impurities, which are introduced during the manufacturing or processing stages. These include hydroperoxide and carbonyl groups, as well as metal salts such as catalyst residues.

All of these species' act as photoinitiators. The organic hydroperoxide and carbonyl groups are able to absorb UV light above 290 nm whereupon they undergo photolysis to generate radicals. Metal impurities act as photocatalysts, although such reactions can be complex. It has also been suggested that polymer-O_2 charge-transfer complexes are involved. Initiation generates radical-carbons on the polymer chain, sometimes called macroradicals (P•).


Chain initiation

$$\text{Polymer} \longrightarrow \text{P}\bullet + \text{P}\bullet$$

Chain propagation

$$\text{P}\bullet + \text{O}_2 \longrightarrow \text{POO}\bullet$$
$$\text{POO}\bullet + \text{PH} \longrightarrow \text{POOH} + \text{P}\bullet$$

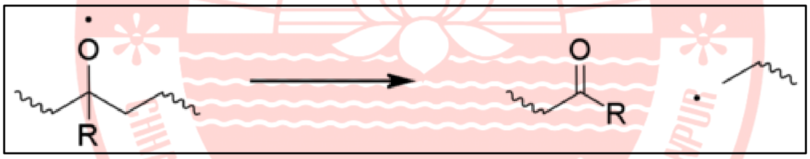
Chain branching

$$\text{POOH} \longrightarrow \text{PO}\bullet + \text{OH}\bullet$$
$$\text{PH} + \text{OH}\bullet \longrightarrow \text{P}\bullet + \text{H}_2\text{O}$$
$$\text{PO}\bullet \longrightarrow \text{Chain scission reactions}$$

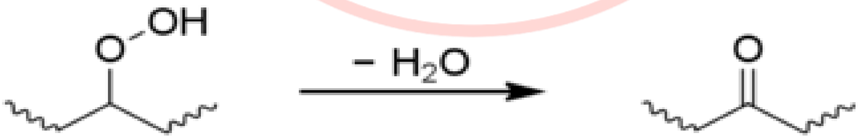
Termination

$$\begin{aligned}
&\mathrm{POO\bullet + POO\bullet} \longrightarrow \text{cross linking reaction to non}-\text{radical product}\\
&\mathrm{POO\bullet + P\bullet} \longrightarrow \text{cross linking reaction to non}-\text{radical product}\\
&\mathrm{P\bullet + P\bullet} \longrightarrow \text{cross linking reaction to non}-\text{radical product}
\end{aligned}$$

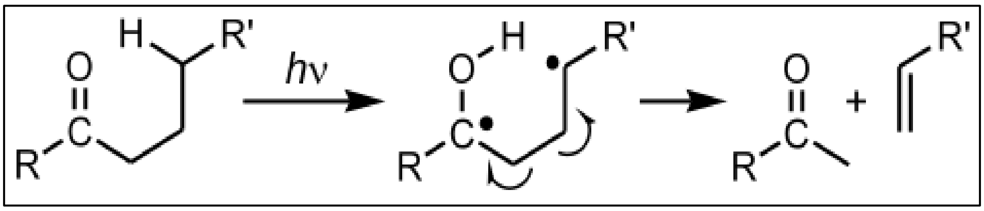
Classically the carbon-centred macroradicals (P•) rapidly react with oxygen to form hydroperoxyl radicals (POO•), which in turn abstract an H atom from the polymer chain to give a hydroperoxide (POOH) and a fresh macroradical. Hydroperoxides readily undergo photolysis to give an alkoxyl macroradical radical (PO•) and a hydroxyl radical (HO•), both of which may go on to form new polymer radicals via hydrogen abstraction. Non-classical alternatives to these steps have been proposed. The alkoxyl radical may also undergo beta scission, generating an acyl-ketone and macroradical. This is considered to be the main cause of chain breaking in polypropylene.

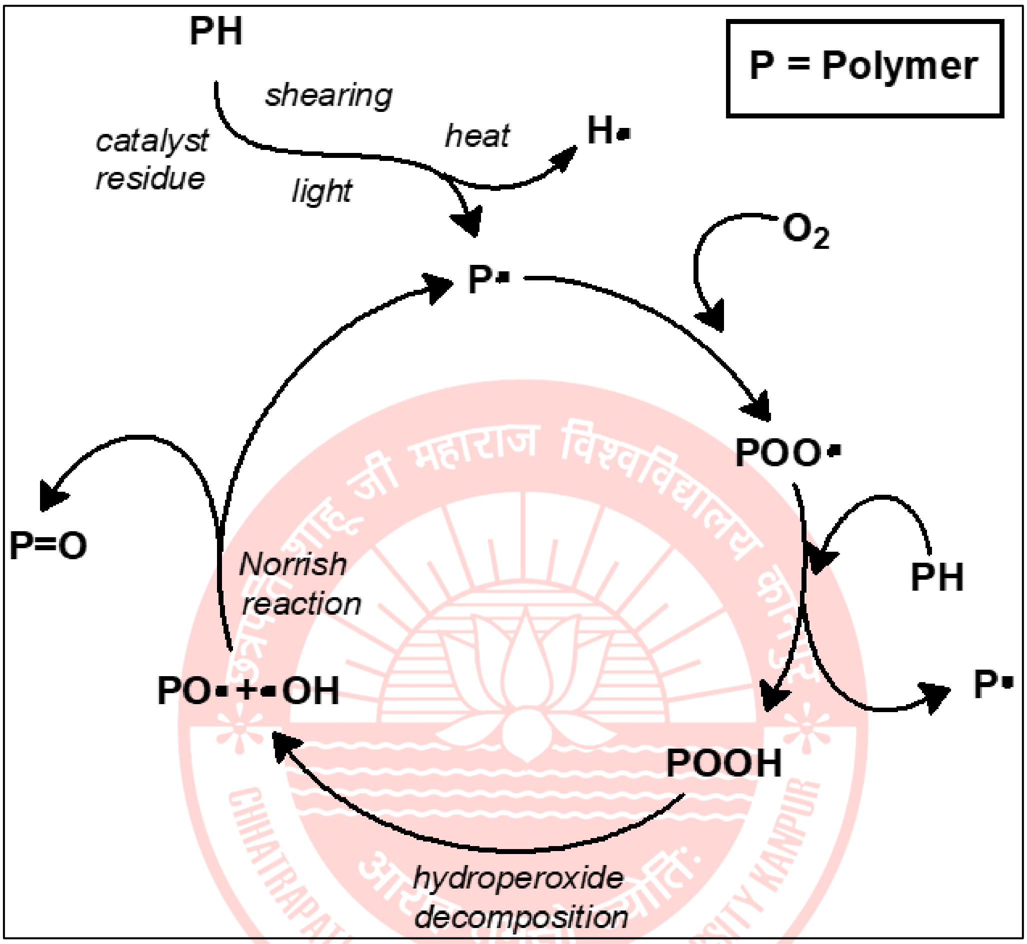


Secondary hydroperoxides can also undergo an intramolecular reaction to give a ketone group, although this is limited to polyethylene.



The ketones generated by these processes are themselves photo-active, although much weeklies. At ambient temperatures they undergo Type II Norrish reactions with chain scission. They may also absorb UV-energy, which they can then transfer to O_2, causing it to enter its highly reactive singlet state. Singlet oxygen is a potent oxidising agent and can go on to cause further degradation.



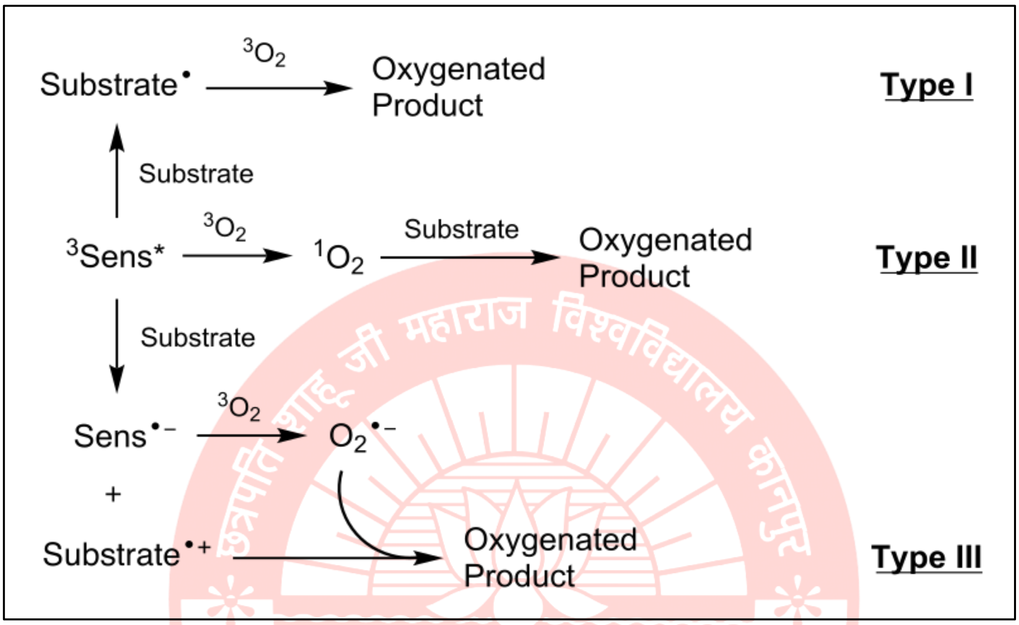


Photooxygenation-

A **photooxygenation** is a light-induced oxidation reaction in which molecular oxygen is incorporated into the product(s).

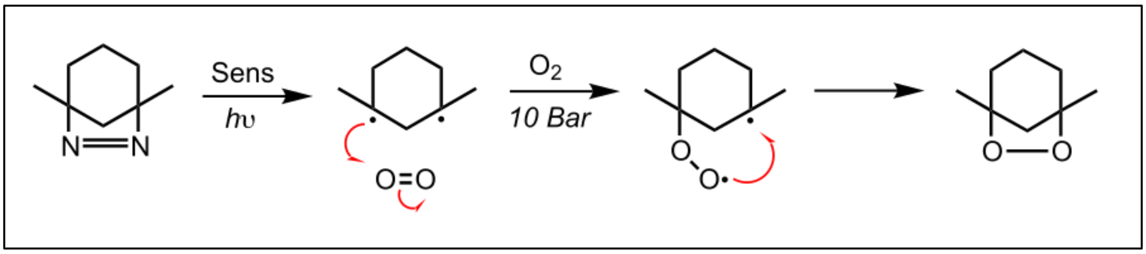
Types of photooxygenation

he three types of photooxygenation reactions are distinguished by the mechanisms that they proceed through, as they are capable of yielding different or similar products depending on environmental conditions. Type I and II reactions proceed through neutral intermediates, while type III reactions proceed through charged species. The absence or presence of $^1O_2$ is what distinguishes type I and type II reactions, respectively.



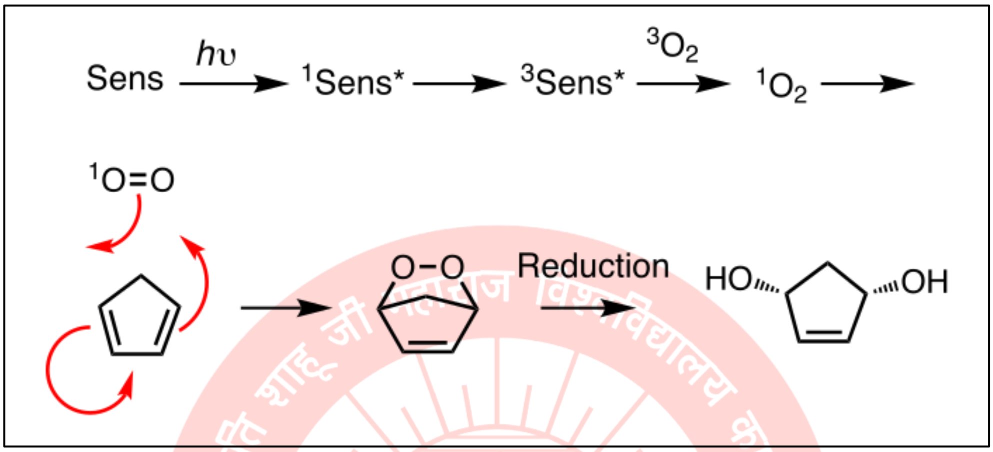
Type I

In type I reactions, the photoactivated ^{3}Sens* interacts with the substrate to yield a radical substrate, usually through the homolytic bond breaking of a hydrogen bond on the substrate. This substrate radical then interacts with $^3O_2$ (ground state) to yield a substrate-O_2 radical. Such a radical is generally quenched by abstracting a hydrogen from another substrate molecule or from the solvent. This process allows for chain propagation of the reaction.



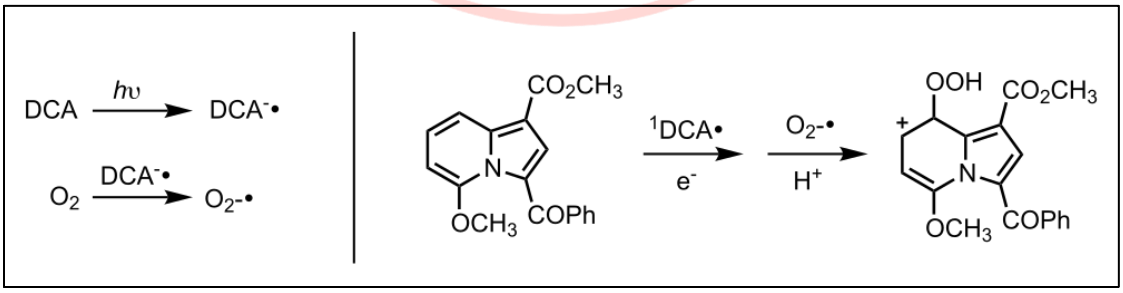
Type II

In type II reactions, the ^{3}Sens* transfers its energy directly with $^3O_2$ via a radiation-less transition to create $^1O_2$. $^1O_2$ then adds to the substrate in a variety of ways including: cycloadditions (most commonly [4+2]), addition to double bonds to yield 1,2-dioxetanes, and ene reactions with olefins (the Schenck ene reaction).



Type III

In type III reactions, there is an electron transfer that occurs between the ^{3}Sens* and the substrate resulting in an anionic Sens and a cationic substrate. Another electron transfer then occurs where the anionic Sens transfers an electron to $^3O_2$ to form the superoxide anion, O_2^-. This transfer returns the Sens to its ground state. The superoxide anion and cationic substrate then interact to form the oxygenated product.



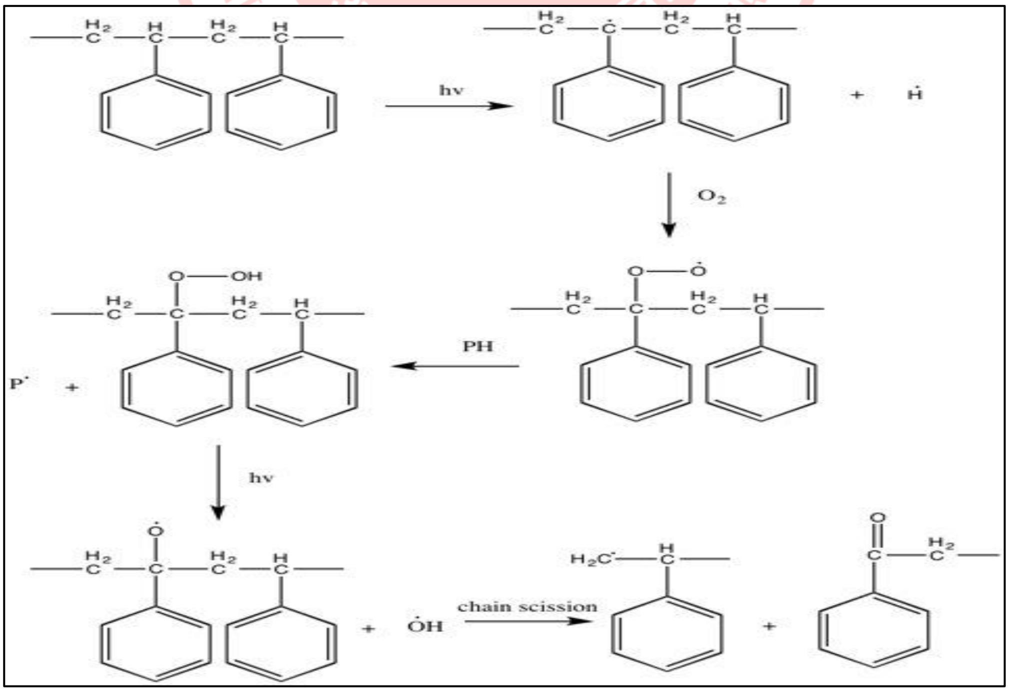
Short & Long Answer Type Question-

Q. Write a note of photodegradation of polymers. (CSJMU2020,18,17,15,12)

Ans. For polystyrene the complete mechanism of photo-oxidation is still a matter of debate, as different pathways may operate concurrently and vary according to the wavelength of the incident light. Regardless, there is agreement on the major steps.

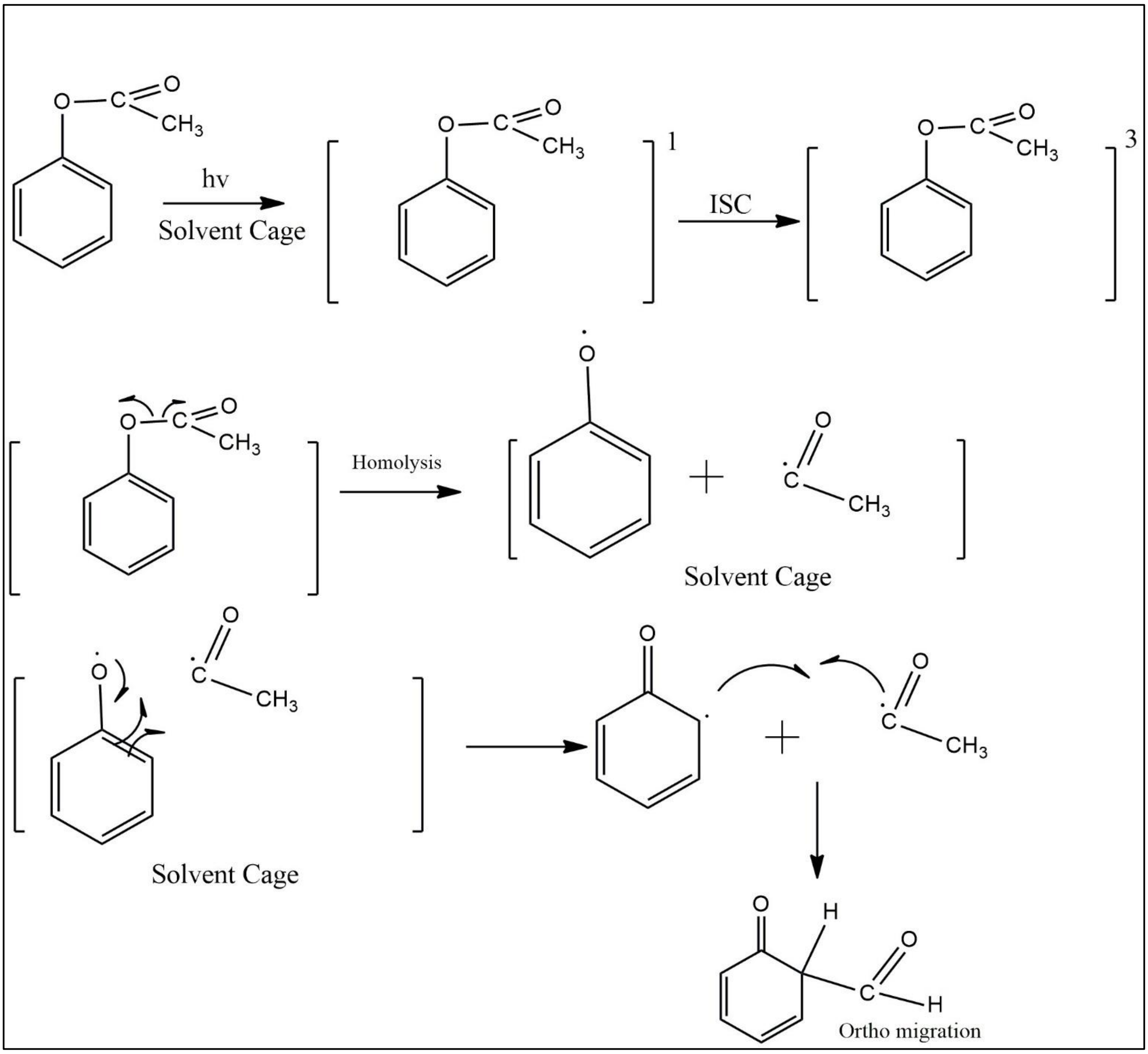
Pure polystyrene should not be able to absorb light with a wavelength below ~280 nm and initiation is explained though photo-labile impurities (hydroperoxides) and charge transfer complexes,[23] all of which are able to absorb normal sunlight. Charge-transfer complexes of oxygen and polystyrene phenyl groups absorb light to form singlet oxygen, which acts as a radical initiator. Carbonyl impurities in the polymer (cf. acetophenone) also absorb light in the near ultraviolet range (300 to 400 nm), forming excited ketones able to abstract hydrogen atoms directly from the polymer. Hydroperoxide undergoes photolysis to form hydroxyl and alkoxyl radicals.

These initiation steps generate macroradicals at tertiary sites, as these are more stabilised. The propagation steps are essentially identical to those seen for polyolefins; with oxidation, hydrogen abstraction and photolysis leading to beta scission reactions and increasing numbers of radicals. These steps account for the majority of chain-breaking, however in a minor pathway the hydroperoxide reacts directly with polymer to form a ketone group (acetophenone) and a terminal alkene without the formation of additional radicals.

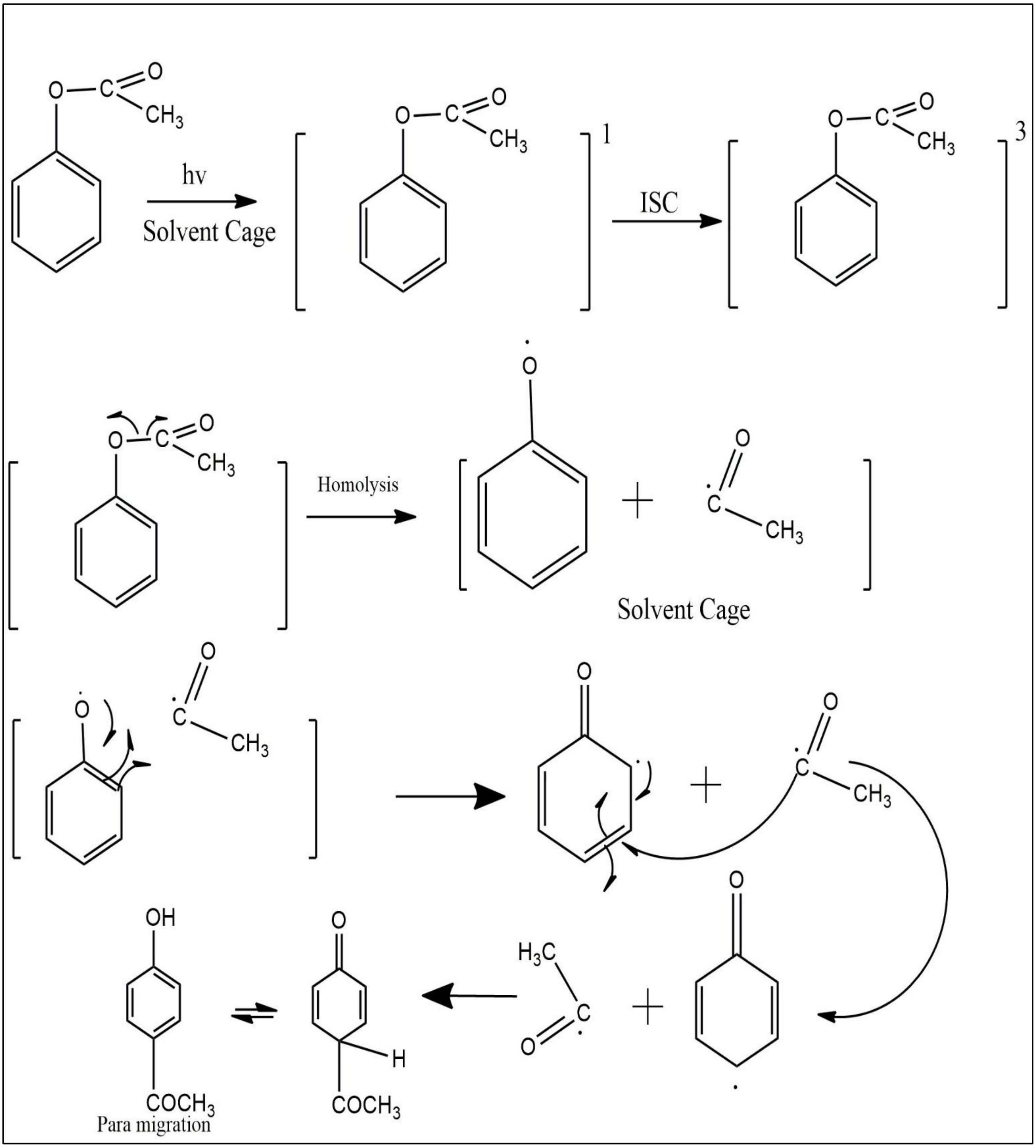


Q. Explain photo Fries rearrangements. (CSJMU2019,18,17,16,12)

Ans. The photo-Fries rearrangement is the photochemical version of the Fries rearrangement, where a phenolic ester rearranges to hydroxy aryl ketones upon exposure to UV light. Unlike the thermally activated Fries rearrangement, it doesn't require a Lewis acid catalyst. Instead, it proceeds via a free radical mechanism where the ester undergoes homolytic bond cleavage to form radicals, which then recombine within the solvent cage. Although yields are generally low and not used for commercial production, the photo-Fries rearrangement can be important in understanding plastic photodegradation and is used in certain organic syntheses.



Para Migration-



Q. Barton reaction. (CSJMU2016,14)

Ans. The Barton reaction is a photochemical process discovered by Sir Derek Barton in 1960, where an alkyl nitrite undergoes photolysis to generate a nitroso alcohol through a free radical mechanism, typically involving homolytic cleavage of the O-NO bond, abstraction of a delta (δ) hydrogen atom to form a six-membered radical intermediate, and subsequent radical recombination and tautomerization into an oxime. This reaction allows for the regio- and stereo-selective functionalization of complex molecules by introducing a nitroso group, and it has been used in the synthesis of various natural products and steroid analogues.

Mechanism

The Barton reaction proceeds through the following key steps:

1. **Photolysis:**

Light initiates the reaction by causing the homolytic cleavage of the O-NO bond in the alkyl nitrite, forming an alkoxy radical (RO•) and a nitrosyl radical (•NO).

2. **Hydrogen Abstraction:**

The alkoxy radical then abstracts a hydrogen atom at the δ-position from the alkyl chain, creating a new carbon radical.

3. **Radical Recombination:**

The carbon radical and the nitrosyl radical recombine.

4. **Tautomerization:**

The resulting nitroso alcohol undergoes tautomerization to form a more stable oxime.

Key Features

- **Photochemical Initiation:**

The reaction requires light energy to initiate the bond cleavage.

- **Free Radical Pathway:**

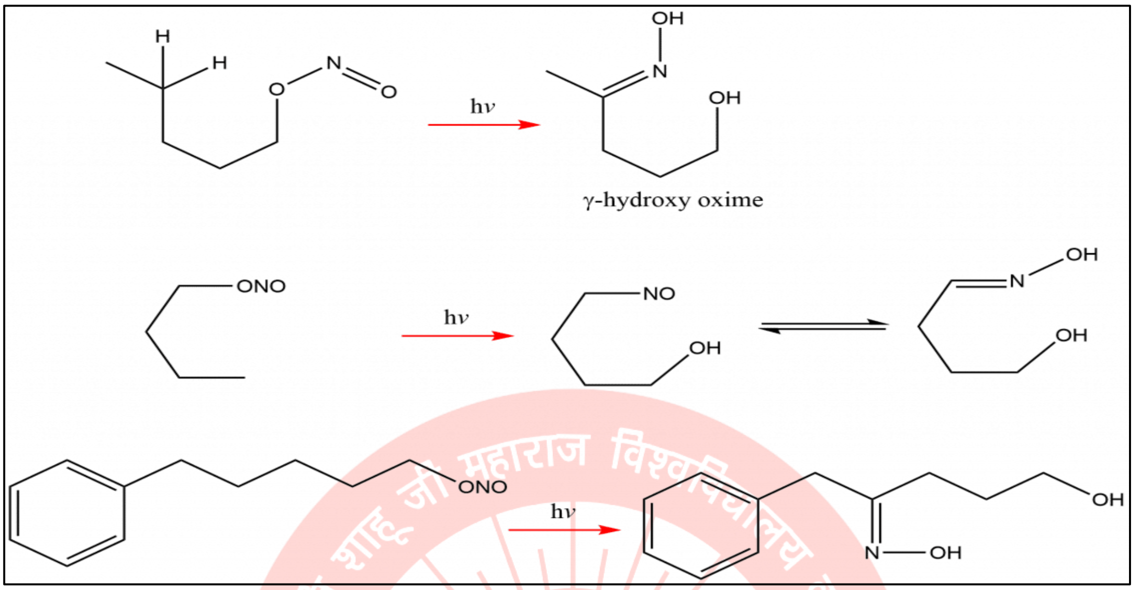
The entire process involves a free radical chain mechanism, which allows for unique chemical transformations.

- **δ-Hydrogen Selectivity:**

The reaction exhibits high selectivity for abstraction of the δ-hydrogen due to the favourable conformation of the six-membered radical intermediate.

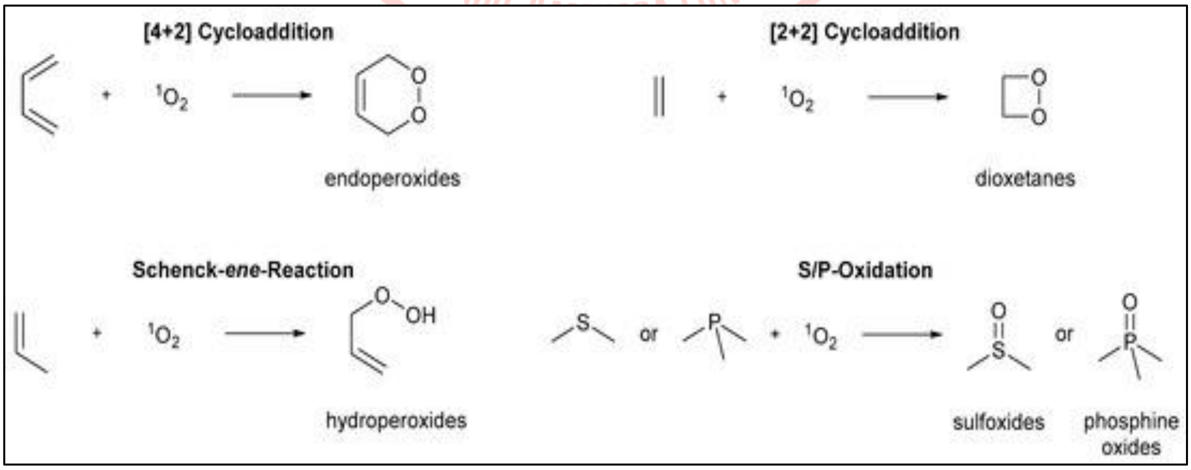
- **Regio- and Stereoselective Functionalization:**

The Barton reaction allows for the precise and controlled introduction of functionality into complex organic molecules.



Q. What are photo-oxygenation reaction? (CSJMU2015,14,13,12)

Ans. Photooxygenation is a light-induced chemical reaction in which molecular oxygen is incorporated into a substrate, typically with the aid of a photosensitizer. It is a powerful and sustainable method for synthesizing a wide range of oxygenated organic compounds.



Q. What is photochemical smog formation? (CSJMU2015,14,13)

Ans. Photochemical smog forms when sunlight interacts with nitrogen oxides (NOx) and volatile organic compounds (VOCs), which are released by vehicle exhaust and industrial processes. Sunlight breaks down NO2, creating oxygen atoms that form ozone (O3). This ozone then reacts with VOCs, leading to secondary pollutants like peroxyacetyl nitrate (PAN) and further contributing to the brownish, hazy appearance of smog.

Here are the key steps in photochemical smog formation:

1. Emission of primary pollutants:

Nitrogen oxides (NOx) and volatile organic compounds (VOCs) are released into the atmosphere, mainly from cars and industrial activities.

2. Sunlight-driven reactions:

Nitrogen dioxide (NO2) breaks down: Sunlight (photons) causes NO2 to split into nitric oxide (NO) and a highly reactive oxygen atom (O).

Reaction: NO_2 + sunlight → NO + O

Ozone formation: The free oxygen atoms quickly combine with oxygen molecules (O2) in the air to create ozone (O3).

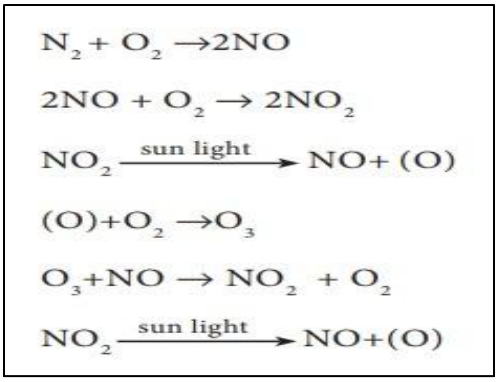
Reaction: $O + O_2 \rightarrow O_3$

Ozone and VOCs react: The ozone then reacts with VOCs (hydrocarbons), leading to more complex reactions that form harmful compounds like peroxyacetyl nitrate (PAN) and various aldehydes.

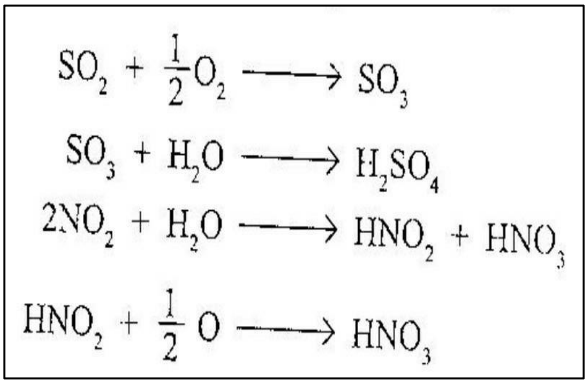
- Reactions: VOCs + other pollutants → aldehydes + ketones
- Reactions: Aldehydes + other pollutants → secondary pollutants like PAN

3. Resulting smog:

The accumulation of these secondary pollutants, particularly ground-level ozone and PAN, creates the visible brownish-grey haze of photochemical smog.



$$N_2 + O_2 \rightarrow 2NO$$
$$2NO + O_2 \rightarrow 2NO_2$$
$$NO_2 \xrightarrow{\text{sun light}} NO + (O)$$
$$(O) + O_2 \rightarrow O_3$$
$$O_3 + NO \rightarrow NO_2 + O_2$$
$$NO_2 \xrightarrow{\text{sun light}} NO + (O)$$



$$SO_2 + \frac{1}{2}O_2 \longrightarrow SO_3$$
$$SO_3 + H_2O \longrightarrow H_2SO_4$$
$$2NO_2 + H_2O \longrightarrow HNO_2 + HNO_3$$
$$HNO_2 + \frac{1}{2}O \longrightarrow HNO_3$$

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