Introduction of Photochemistry and Jablonski diagram

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- Study of physical processes and chemical change which occurs in molecules on absorption of suitable radiations

- radiation of absorptions ranging from radiowaves to γ rays

- for practical purposes, visible (400nm-800nm) & UV (200-400nm) brings about photochemical reactions

- IR absorption (≈ 1000nm / 120kJ) does not lead to chemical reactions but affects the vibrational and rotational energy levels of a molecule.

- photochemical reactions are initiated by electronically excited molecules.

- Helps in understanding photosynthesis, phototaxis, photoperiodism, photodynamic action vision and mutagenic effect of light.

- Study of effects of ionizing radiations comes in the field known as radiation chemistry.

Importance of photochemistry

- prebiotic formation of organic compounds such as proteins and nucleic acid by radiation with methane, ammonia, water and carbon dioxide as raw materials

- photochromic materials

- optical whitners

- synthesis of antioxidants by photosulphonation, vitamin D_2, antiviral agents such as cubanes, caprolactam, cleansing agents, insecticides and halogenated aromatics

- flourescence and phosphorescence

Interaction of electromagnetic radiation UV-visible with matter / organic compounds

- transition from ground state to excited state

- Changes electronic distribution, geometry and uncoupling of electronic spin

- electron moves from ground state energy level of a molecular to a higher level i.e. an unoccupied orbital of higher energy

- energy level of a molecule are quantized

- The amount of energy required to raise an electron in a given molecule from one level to a higher energy one is a fixed quantity i.e. $\Delta E = h\nu$ for one molecule and for n number of molecules it is $\Delta E = n h\nu$

- only light of different energy or frequency i.e. too low or too high is given, it will pass through the sample without change in intensity.

- with appropriate light the electron get excited and the intensity of the light will decrease or light will be gone

- electronic transitions are done by visible, UV and far UV regions

- Most of the organic compounds contain paired electrons opposite spin in ground state

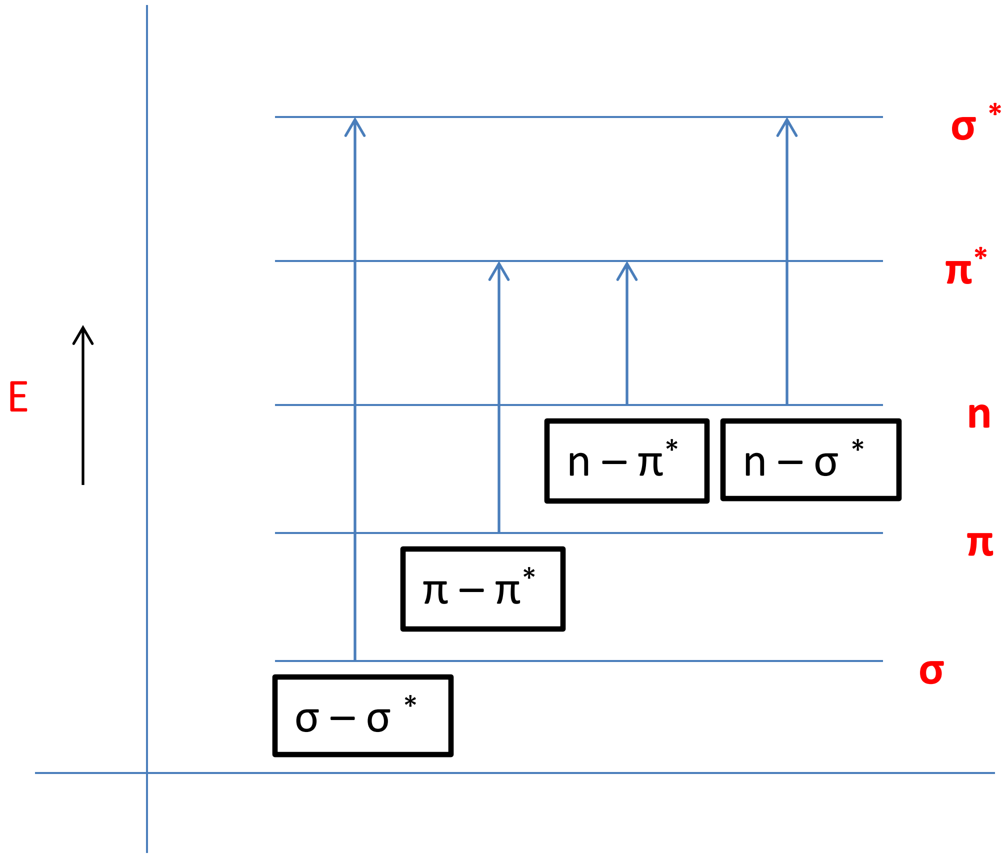
- When one electron of a pair get promoted without change in spin or with change in spin. Former is called singlet and the latter triplet excited state

- The names are according to their spin multiplicity

- For every singlet excited state, there is a triplet excited state

- triplet state has lower energy than its respective singlet state

Types of excitations



1. $\sigma - \sigma^*$ → alkanes (no n or pi electrons)
2. $n - \sigma^*$ → alcohols, amines , ethers etc
3. $\pi - \pi^*$ → aldehydes, carboxylic esters, alkenes etc.
4. $n - \pi^*$ → aldehydes, ketones,carboxylic esters(can undergo above three transitions also)

$$\sigma - \sigma^* > n - \sigma^* > \pi - \pi^* > n - \pi^*$$

$$\longrightarrow$$

Decreasing energy

- However, the order may sometimes be altered in some solvents.

- More conjugation in a molecule, the more the absorption is displaced towards higher wavelengths

Jablonski Diagram

- maximum transitions takes place from ground singlet state. (S_0 to $S_{1,}$ S_2 ....S_n)

- singlet excited states contain a number of energy levels with different vibrational energies

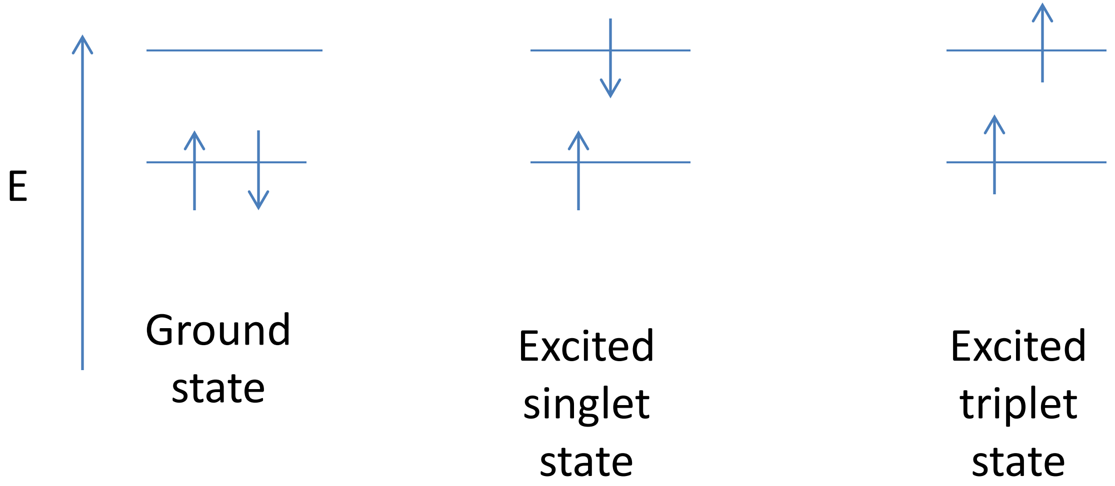
- transition to S_2 and higher excited singlet state also take place but in liquid and solids these higher excited states drops to S_1 state rapidly (10$_{-}^{-10}$ to 10 $^{-\ 11}$ sec). The energy is dissipated to surrounding by colliding with nearby molecules.

- initial excitation and decay from higher singlet states initially populates many of the vibrational levels of S_1 but these also decay to lowest vibrational level of $S_{1.}$ Hence, in most cases, lowest potential energy vibrational level of the S_1 state is the only important excited singlet state.

- S_1 state with lowest vibrational energy level undergoes further decomposition to different states or decay to S_0 state. Beside this, different states such as S_1 and T_1 may undergo chemical reactions which are shown by Jablonski diagram.

- Internal Conversion (IC)– S_n to S_1 & S_1 from higher vibrational level to ground state

- intersystem crossing (ISC) : transition from S_1 in ground vibrational level to T_1 state
- IC = 10^{-14} - 10^{-10} s, ISC= 10^{-10} - 10^{-8} s
- transitions



- radiative transitions : excited molecules emit light and return to ground state.

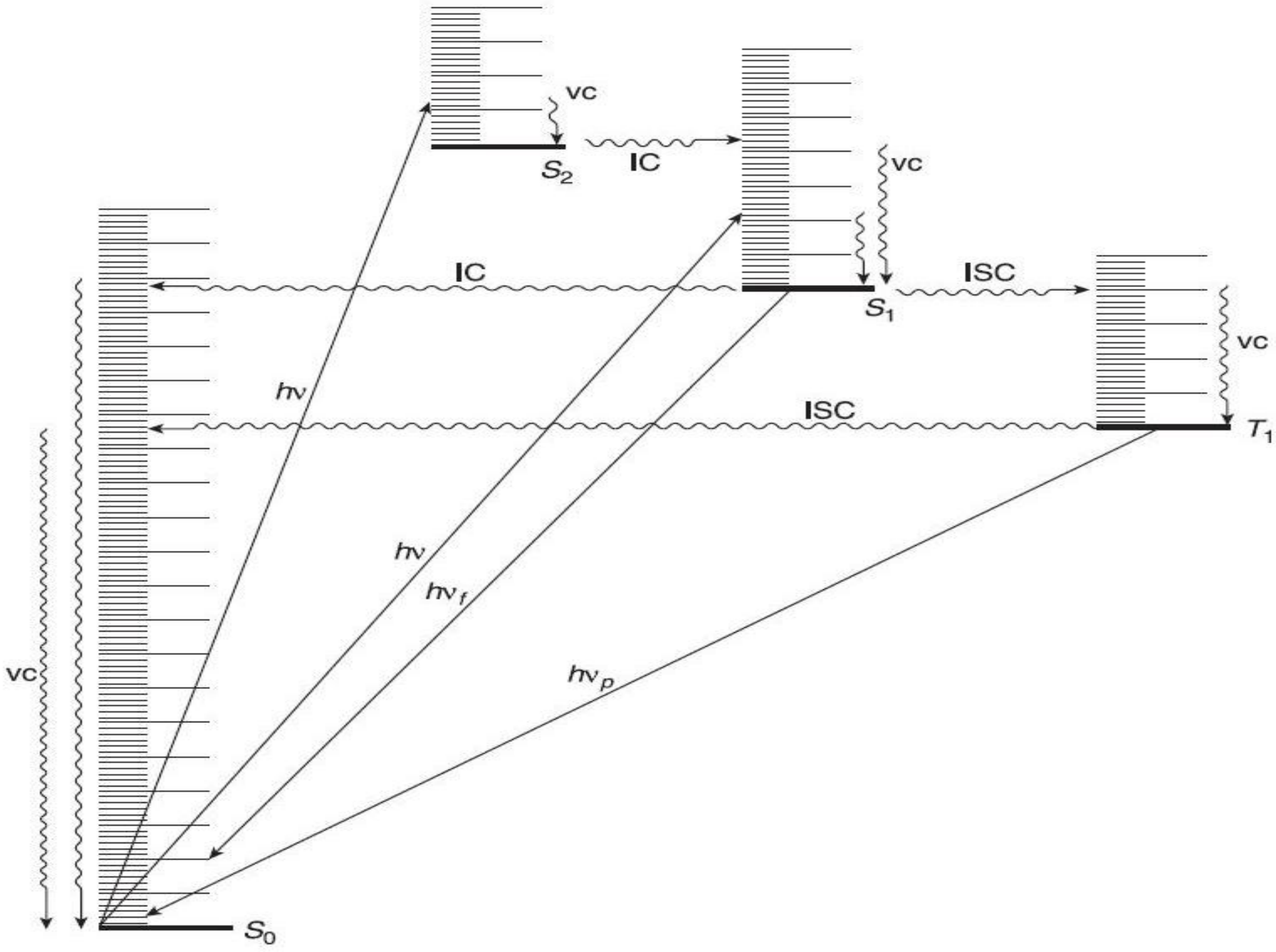
- non radiative transitions: some or alll of the energy of the absorbed photon is ultimately converted to heat by collisions

- spin multiplicity of singlet state = 2S + 1 = 1

- spin multiplicity of triplet state = 2S + 1 = 3

- in figure :
  $h\nu_f$ = flourescence (10^{-9} - 10^{-6} s)
  $h\nu_p$ = phosphorescence(10^{-3} - 10^{3} s)

- both singlet and triplet give different products.


vc
IC
S_2
vc
IC
ISC
S_1
vc
$h\nu$
ISC
T_1
$h\nu$
$h\nu_f$
vc
$h\nu_p$
S_0

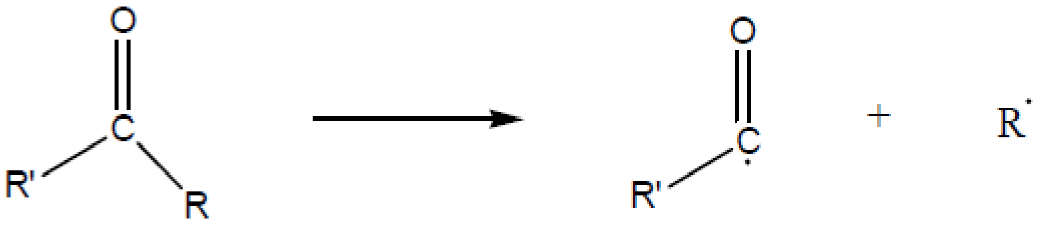
- A quencher is defined as a molecular entity that deactivates (quenches) an excited state of another molecular entity, either by energy tranfer, electron transfer, or by a chemical mechanism.

Fate of excited molecules

- both singlet and triplet states undergo chemical reaction but due to longer lives, mostly triplet states reacts chemically and singlet states have physical decay.

- Chemical reactions :

1. Simple Cleavage into Radicals:



- aldehydes and ketones absorbs in 230-330nm
- result from an n - π* singlet–singlet transition.
- norrish type I reaction
- in secondary process acyl group loses CO group to give alkyl radical

Decomposition into Molecules:

- Aldehydes (though not generally ketones) can also cleave in this manner

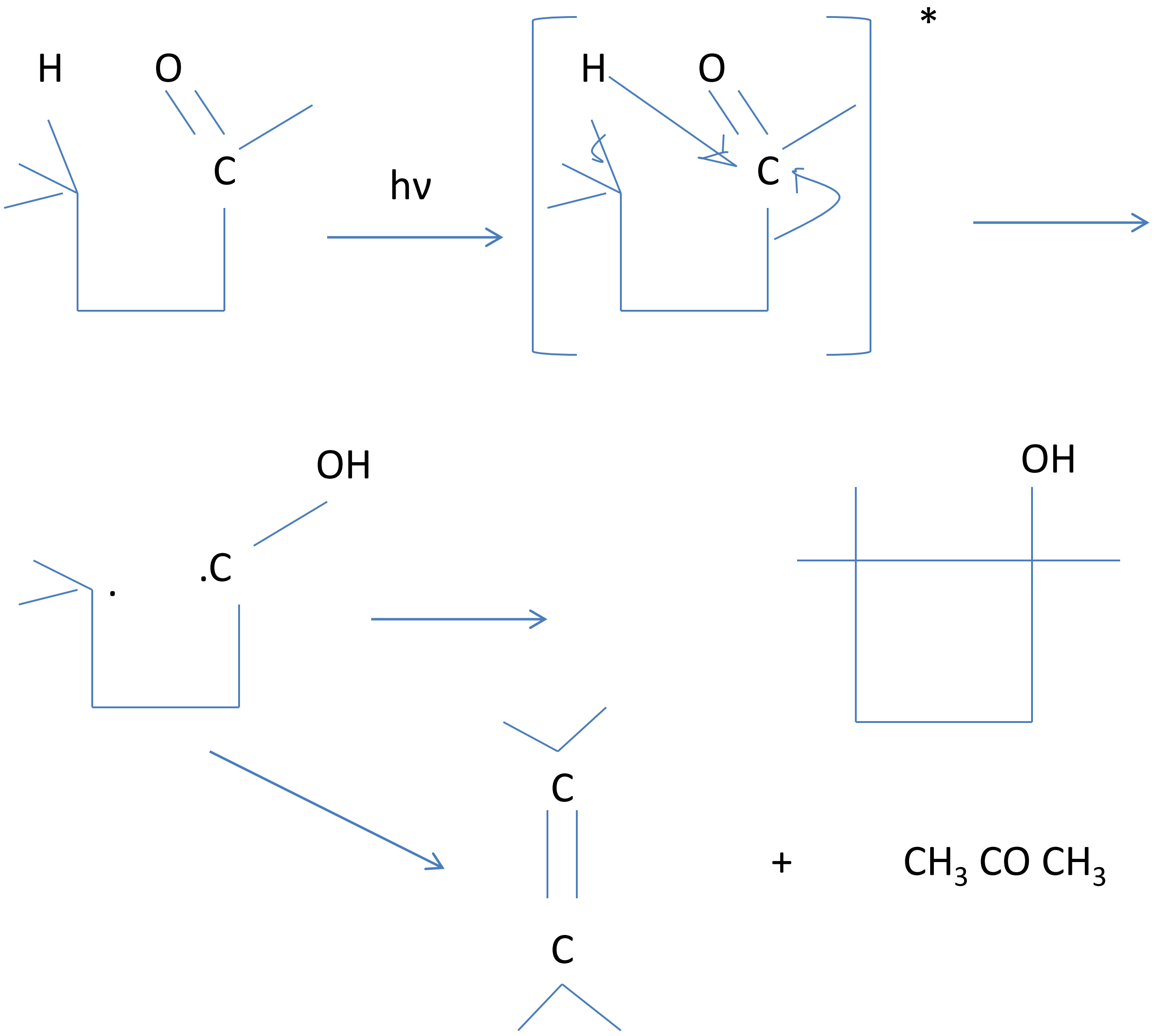
- norrish type II reaction

- involves intramolecular abstraction of the γ hydrogen followed by cleavage of the resulting diradical (a secondary reaction) to give an enol that tautomerizes to the aldehyde or ketone product

- Both singlet and triplet n,π* states undergo the reaction.

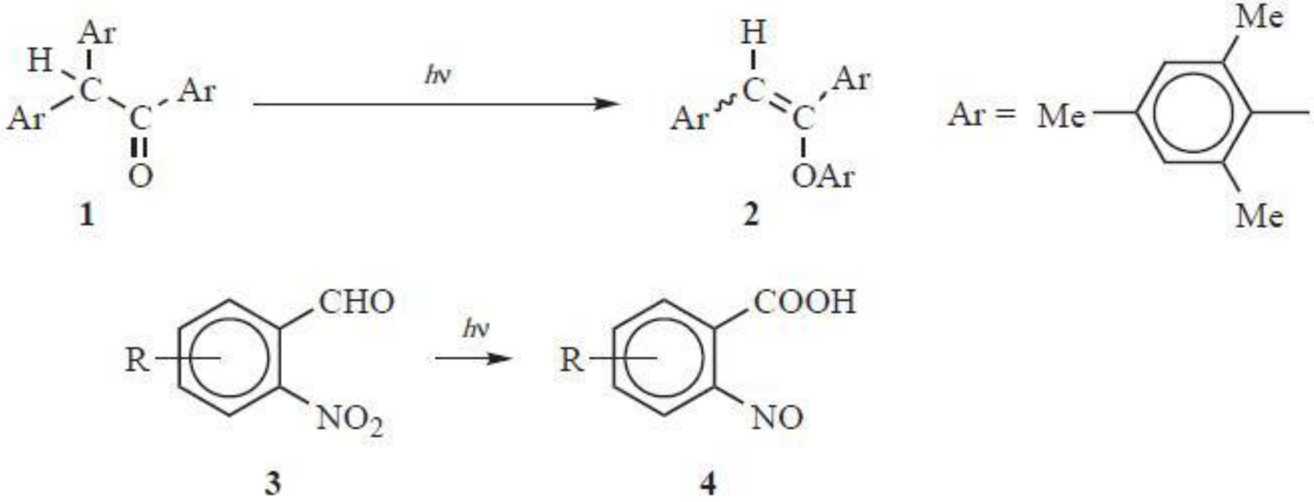
- extrusion reaction

- $\mathrm{RCHO} \xrightarrow{h\nu} \mathrm{R\text{-}H + CO}$


H
O
C
hν
H
O
C
*
OH
.C
.
OH
C
C
+
$CH_3\ CO\ CH_3$

3. Intramolecular Rearrangement:

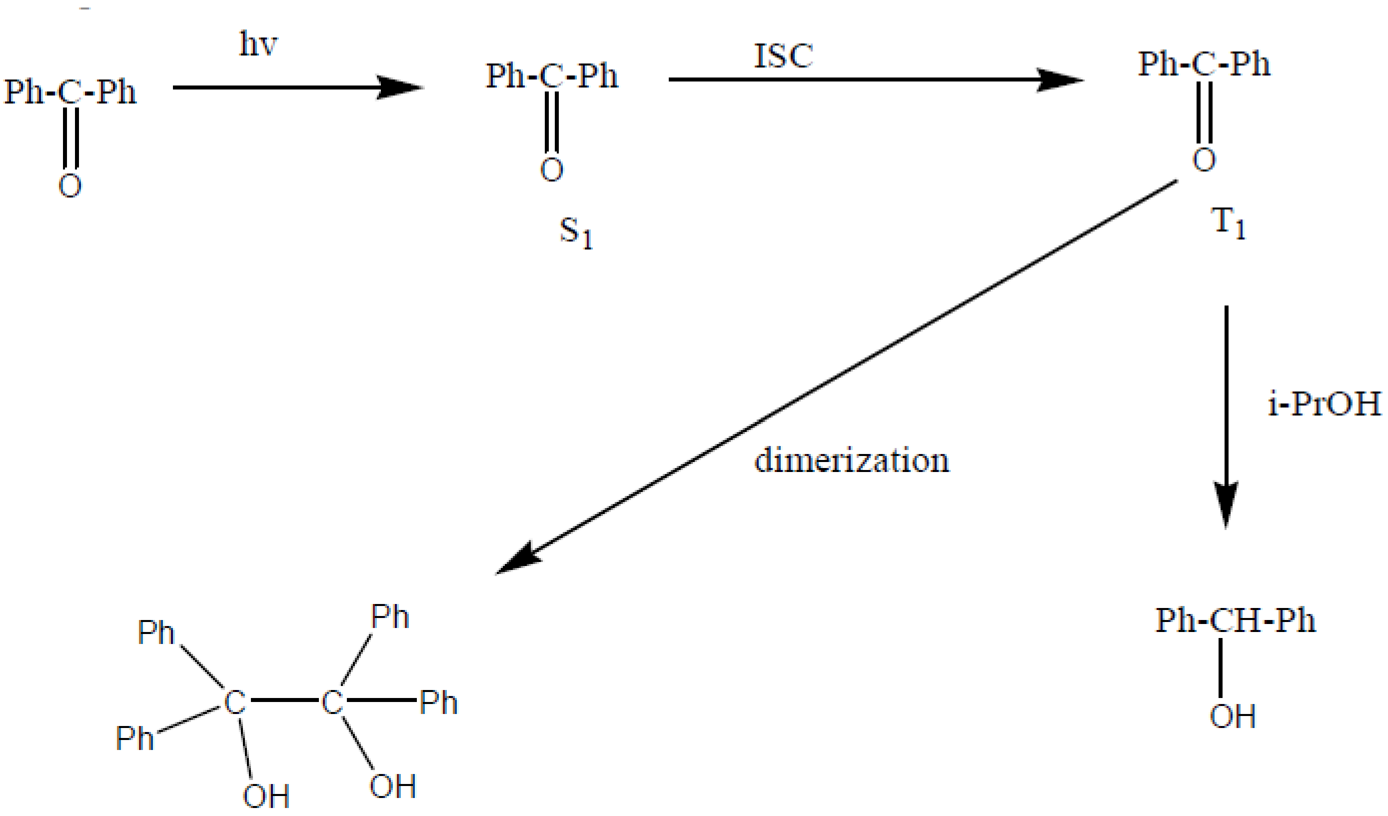
- trimesityl compound to the enol ether , and irradiation of onitrobenzaldehydes to give o-nitrosobenzoic acids .



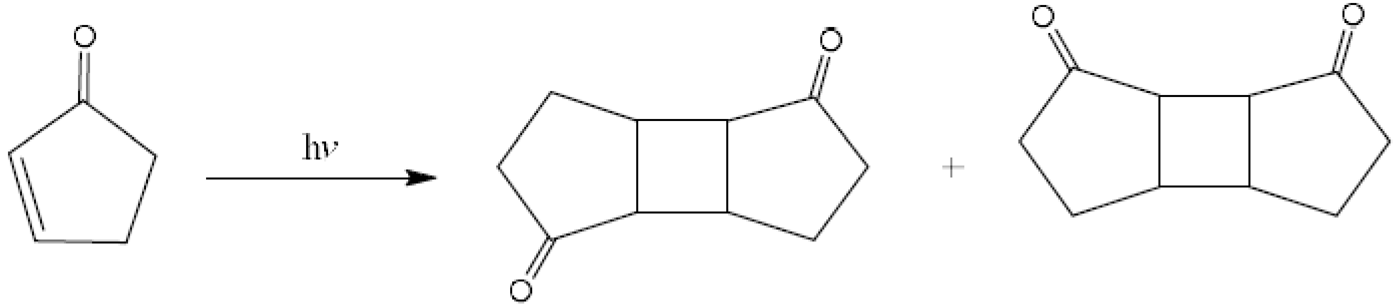
4. Photoisomerization:

- cis trans isomerization
- e.g. cis stilbene to trans stilbene

5. Hydrogen-Atom Abstraction:


Ph-C-Ph
O
hv
Ph-C-Ph
O
S1
ISC
Ph-C-Ph
O
T1
dimerization
i-PrOH
Ph
Ph
C
C
Ph
Ph
OH
OH
Ph-CH-Ph
OH

6. Photodimerisation



Quantum yield

- for a reaction

$$A \xrightarrow{h\nu} P$$

$$\phi = \frac{\text{number of molecules of P formed}}{\text{Number of quanta abosrbed by A}}$$

Energy transfer:

- $D \xrightarrow{h\nu} {}^1[D] \longrightarrow {}^3[D] \xrightarrow{[A]} {}^3[A] + D \longrightarrow \text{Products}$

• above shows triplet- triplet transfer of energy. Beside this, singlet-singlet transfer also takes place.

•read it from text book “Reaction Mechanism, Singh & Mukherjee”.

Questions:

Q. Discuss jablonski diagram.

Q. Write short note on :

- (a) singlet and triplet excited states.
- (b) internal conversion
- (c) florescence and phosphorescence
- (d) photosensitizer
- (e) quenchers

Q. Discuss different types of photochemical reactions with examples.

Q. Discuss energy transfer.

Thank You