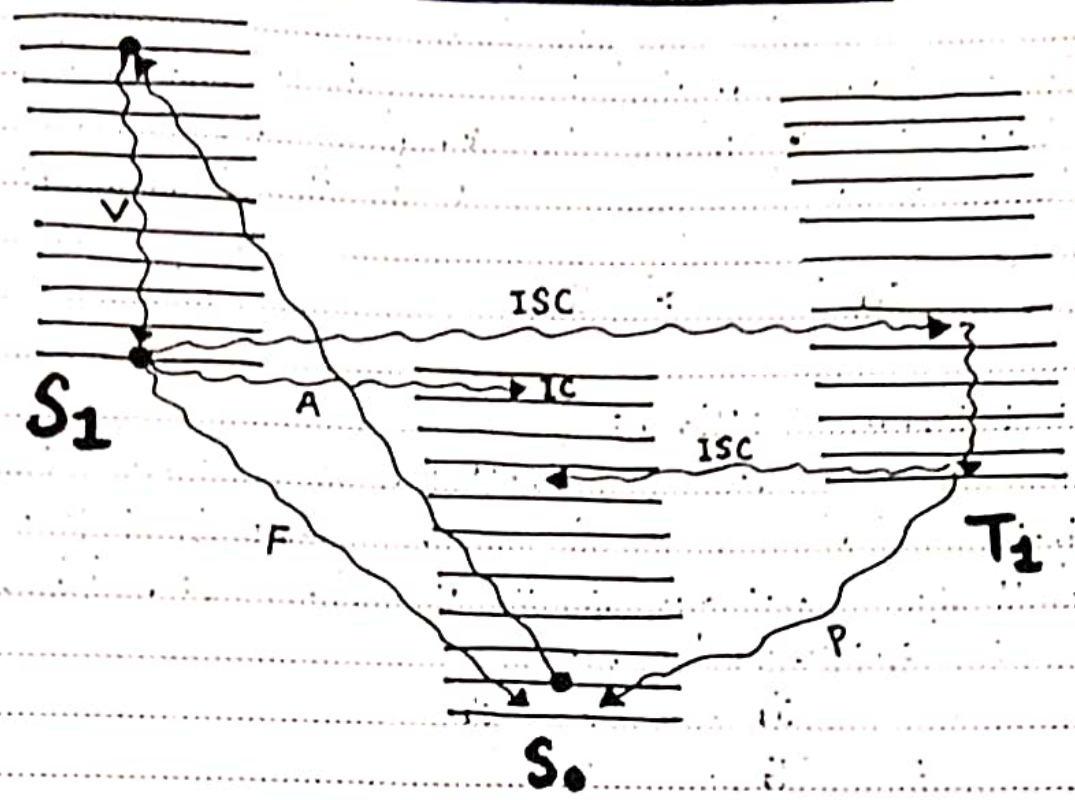
⇒ JABLONSKI DIAGRAM :-



Here,

A = Absorbance (life time = 10^{-15} sec^{-1}).

V = Vibrational cascade (life time = 10^{-10} sec^{-1}).

ISC = Inter-system crossing (life time = 10^{-6} sec^{-2}).

IC = Internal conversion (life time $\approx 10^{-10} - 10^{-6}$ sec^{-1})

F = Fluorescence (life time $\simeq 10^{-6}$ sec$^{-2} - 10^{-5}$ sec^{-1})

P = Phosphorescence (life time = 10^{-5} sec$^{-1} - 10^{-3}$ sec^{-2}).

These terms are explained below :-

Vibrational Cascade :-

Excitation results in the occupation of an excited state high in energy. The energy can be rapidly loss by the molecular collision. The process is termed as vibrational cascade.

Internal conversion :-

The conversion of one state to another state of same multiplicity without the loss of energy is called internal conversion. It is a spin allowed process and is represented by

$$S_1 \longrightarrow S_0$$

Inter-system crossing :-

The conversion of one state to another state of different multiplicity without the loss of energy. It is a spin forbidden process and represented by.

$$S_1 \longrightarrow T_1$$

or $T_1 \longrightarrow S_0$

Fluorescence :-

The conversion of one state to another state of same multiplicity by the loss of energy is called fluorescence. It is a spin allowed process and represented by

$$S_1 \longrightarrow S_0.$$

Phosphorescence :-

The conversion of one state to another state of different multiplicity by the loss of energy is called phosphorescence. It is a spin forbidden process and represented by

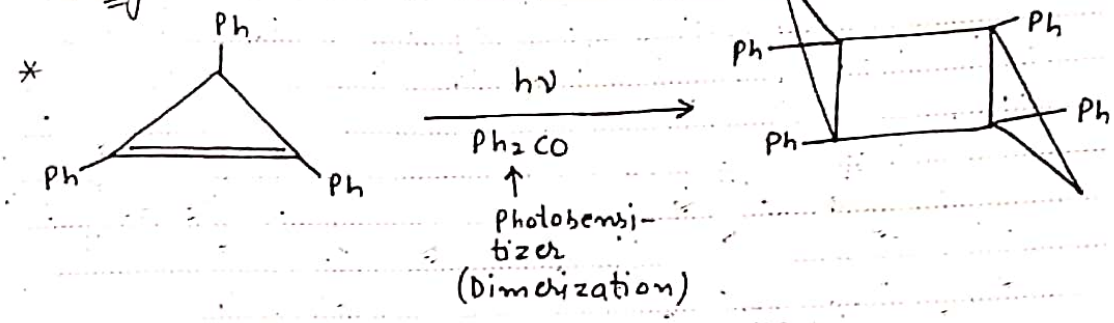
$$T_1 \longrightarrow S_0$$

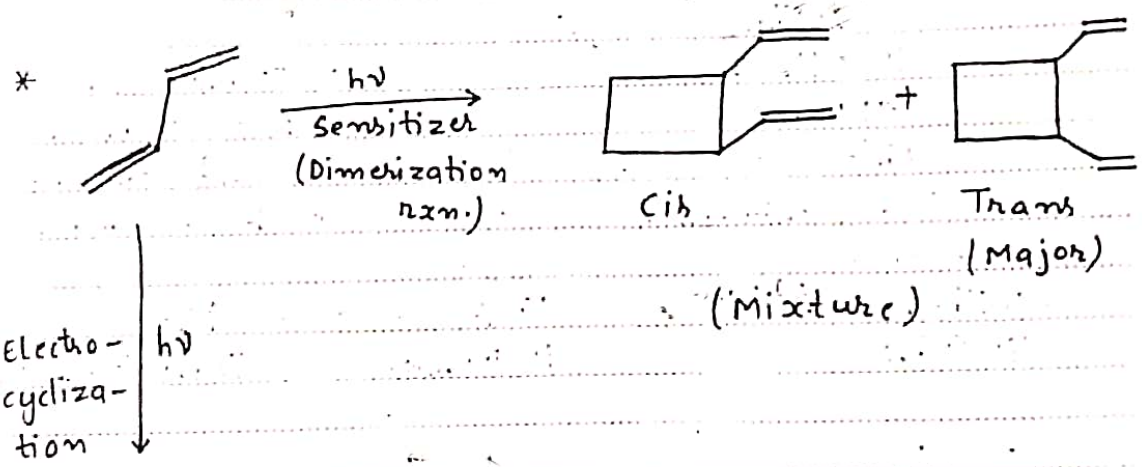
× × × × × ×

⇒ SENSITIZATION AND QUENCHING:-

The excitation of a molecule by the transfer of an excitation energy from another excited species is termed as sensitization and the deactivation of an excited species is known as quenching.

E.g.





⇒ INTRAMOLECULAR REACTIONS OF AN OLEFINIC BOND :-

These reactions fall into three categories :-

① Cis-Trans isomerization / Geometrical isomerization.
② Cyclization.
③ Rearrangement.

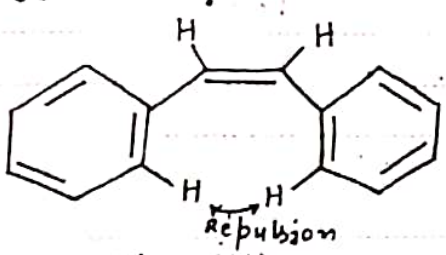
These are discussed below:-

① Cis-trans isomerization :-

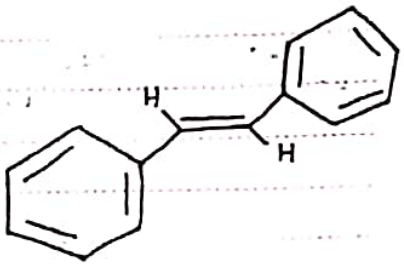
Here, we convert cis to trans and trans to cis-isomers.

E.g.:

*



- Cis-stilbene
- Less stable
- Short or no conjugation



- Trans-stilbene
- More stable.
- Long conjugation
- More λmax.

Stilbene (cis-trans) $\xrightarrow{313\,nm}$ 93% cis-isomer + 7% Trans-isomer.

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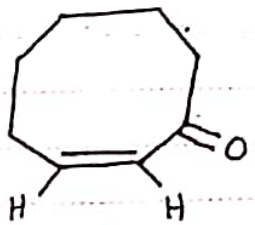
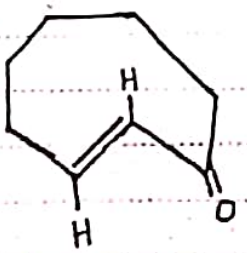


$\xrightarrow{h\nu}$

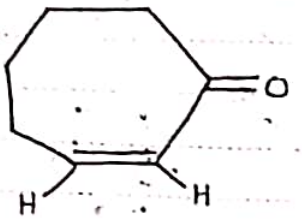


Cis-cyclo-octanone

Trans-cyclo-octanone

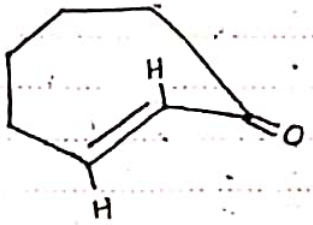
→ Stable above 0°.

*



Cis-
- cyclo-heptenone

$h\nu$

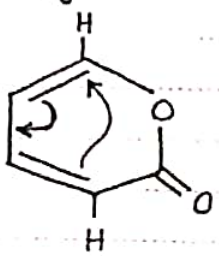


Trans-
cycloheptenone
- stable at below 0°C.

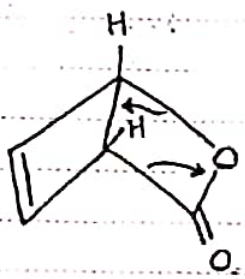
② Cyclization :-

E.g.

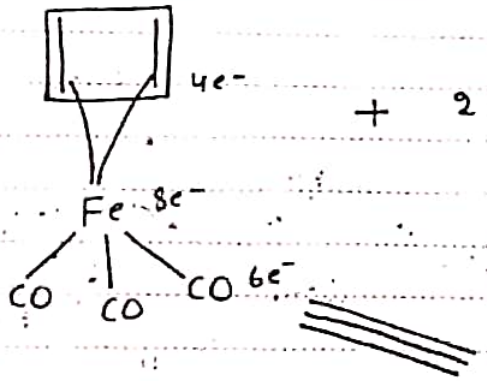
*



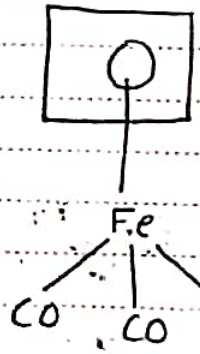
$h\nu$
cyclization



$h\nu$
$Fe(CO)_5$
↓
(18e⁻)

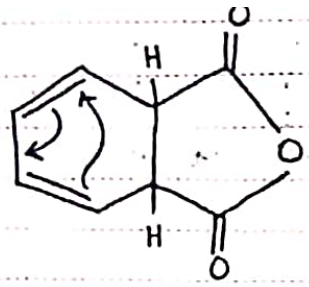


+ 2CO↑ + CO_2↑



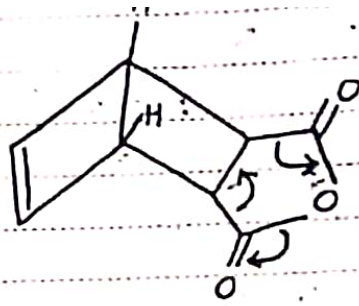
18e⁻ system.

*

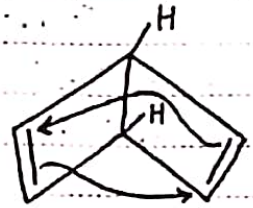


$h\nu$

Cyclization



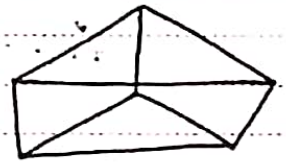
$Pb(OAc)_4$



Dewar Benzene

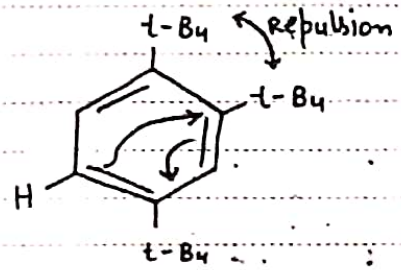
$h\nu$

Intramolecular [2+2]



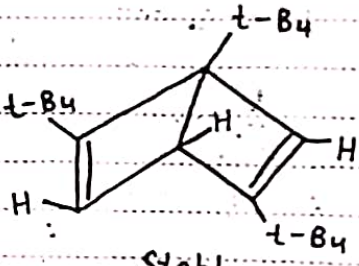
Prismate.

←

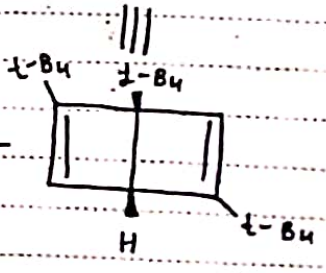


$h\nu$

Cyclization



Stable



Intramolecular [2+2]