Photo chemistry

Molecules $\xrightarrow{absorb}$ Photon → Two effect
Possible

I Primary Effect:

(i) Excitation of molecule.
(ii) Isomeric Change → new molecule.
(iii) Dissociation of molecule.
(iv) Ionisation of molecule

II Secondary Effect:

(i) Photosensitization
(ii) Delayed photo chemical change
(iii) Rise in T
(iv) fluorescence
(v) Phosphorescence.

UV → 100-400 nm
Visible → 400- 750nm
IR → 750- 2,500nm

Photo chemical Reactions.

Sub $\xrightarrow{\text{absorb}}$ ligh Energy.

I. $A \xrightarrow[h\nu]{\text{absorb}} A^*$ → Primary process.

II. $A^* \xrightarrow[\text{Intra Molecular rearrangement}]{\text{Photolysis}}$ new B → 2° process. [unimolecular reaxn]

$A^* + A \longrightarrow C$ → 2° process. [bimolecular reaxn]

(i) Photo synthesis

Plants $\xrightarrow{h\nu}$ Carbohydrates [stored chemical Energy]

(ii) Vision

Photo receptor in eye ⇒ rhodopsin $\xrightarrow{h\nu}$ isomerises

(iii) Vitamin D → skin $\xrightarrow{h\nu}$ vit. D

7-dehydrocholesterol.

(iv) Ozone $\xrightarrow[h\nu]{UV}$ photo. Chemical dissocn.

Mol. O_2 → O-atoms

↓

O_3

P.C.R.	Thermal Reacn
1. absorbn of light	absorbn or evolution of heat
2. only in presence of light	in both dark & light
3. ΔG → + or − ve	ΔG = always −ve
4. T has little effect	T - significant effect

Laws of Photochemical reaxn

Grotthus - Draper law

Sub- which absorb light involve in P.C.R. otherwise

Only the light which is absorbed by a substance can bring about a P.C.R.

Lamberts law

When a beam of monochromatic radia passes thro' a homogeneous absorbing medium the rate of decrease of intensity of the radiation with thickness of absorbing medium is proportional to intensity of the incident radiation

$$\frac{-dI}{dx} = kI$$

Lambert - Beer's law

$$\frac{-dI}{dx} = k'IC$$

as well as Conc of the soln

Stark - Einstein law:

Each molecule taking part in a photochemical reaxn absorbs one quantum of radiation.

$h = 6.6024 \times 10^{-27}$ erg. sec.

$E = Nh\nu$ erg per mole

$N = 6.023 \times 10^{23}$

Characteristics of Photochemical reaxn:

1. These reaction requires photons to interact chemical species
2. light has particular wavelength
   specific
3. It depends upon the intensity of the light
4. It is not necessary for an excited molecule to show always chemical change.
5. ΔG may be +ive or -ive

Photo chemistry of ketones

→ 4 important primary photo chemical processes.

→(i) Cleavage of the bond α- to the Carbonyl gps → α- cleavage (or) Norrish Type

→ 2- α bonds in the substrate - not identical - weaker bond - cleaved.

(ii) cleavage of bond β to the carbonyl gp - intramolecular hydrogen abstraction

→ β- cleavage or Norrish Tye-2

(iii) If Intermolecular reaxn, hydrogen abstraction ~~by~~ from the carbonyl oxygen.

(iv) Addition of Carbonyl Oxygen atom ex $\left[-C=\underline{\underline{O}} \quad -\overset{H}{\overset{|}{C}}=\underline{\underline{O}} \right]$ to a carbon-carbon double bond

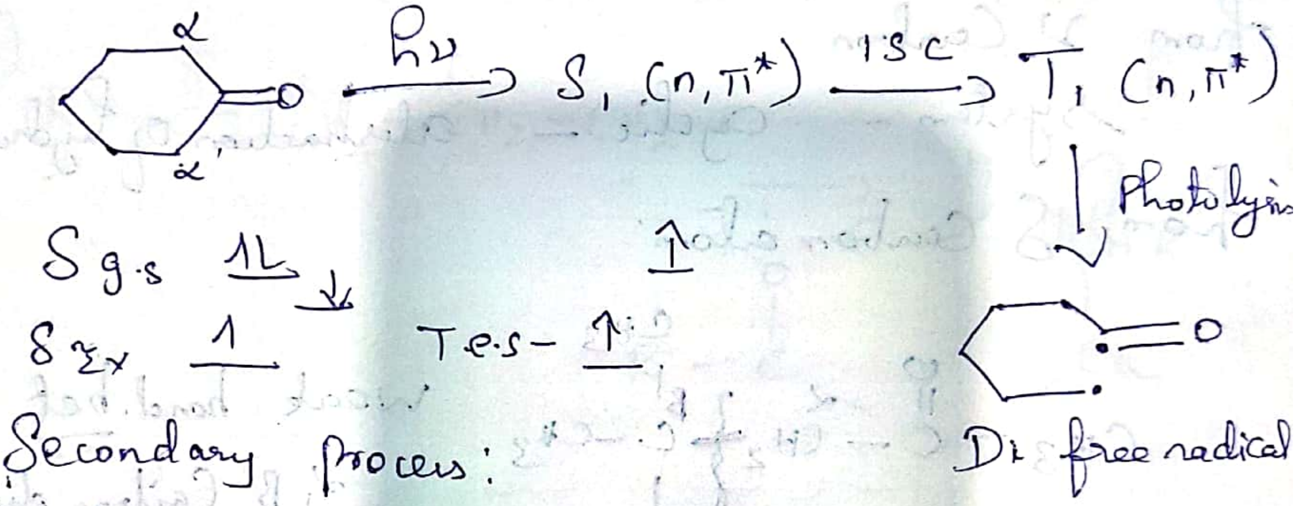
→ Primary reactions Occur from $\underline{n, \pi^*}$ triplet state (T_1)

→ $\underline{\text{Reaxn}}$ Products - isolated - 2° $\underline{\text{reaxn}}$

→ Structural Variations in ketone & Choice of solvent → Mechanism

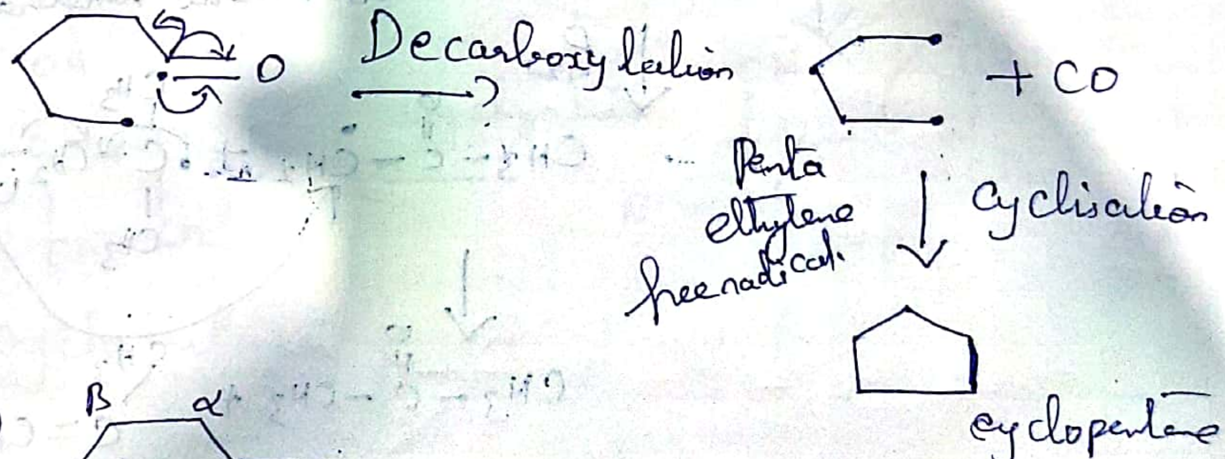
Norrish Type-I Process:

Primary process: Photolysis of cyclohexanone

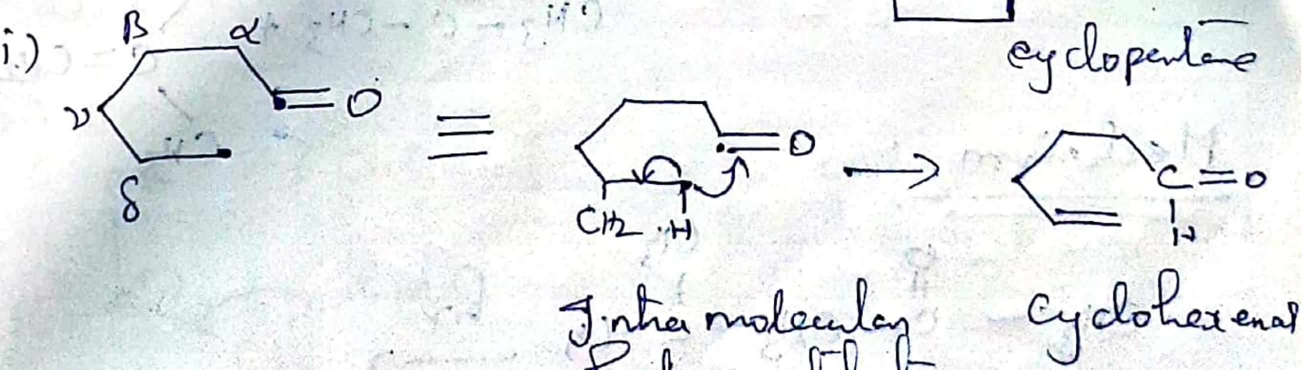


Secondary process:

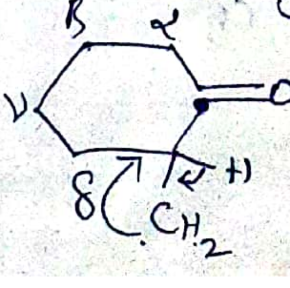
(i)



(ii)



Intramolecular hydrogen abstraction.



(Six membered cyclic T.S)

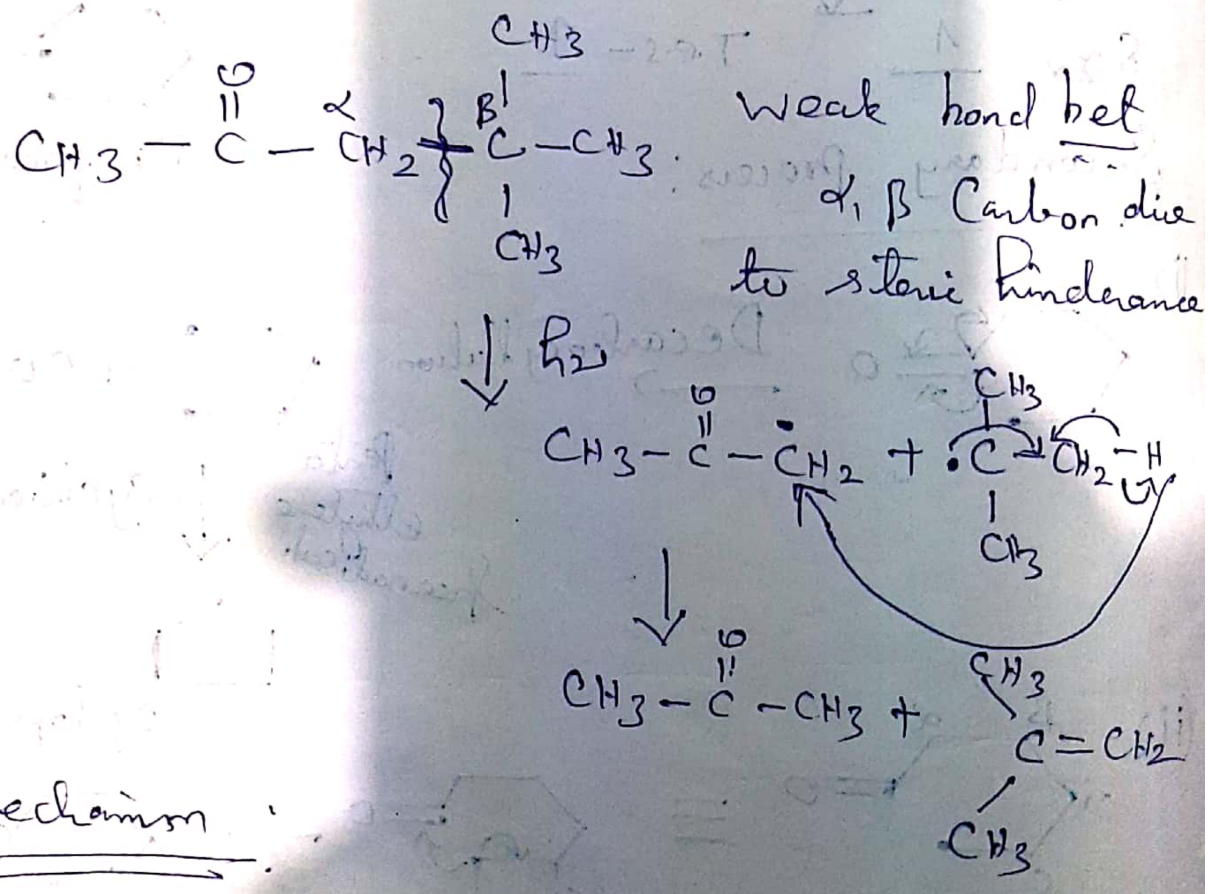
Norrish Type-II process: (β-cleavage)

Possible.

→, bond between α & β Carbon is weak

→ If reaction occurs in Open chain Compd Abstraction of hydrogen atom takes place from γ Carbon

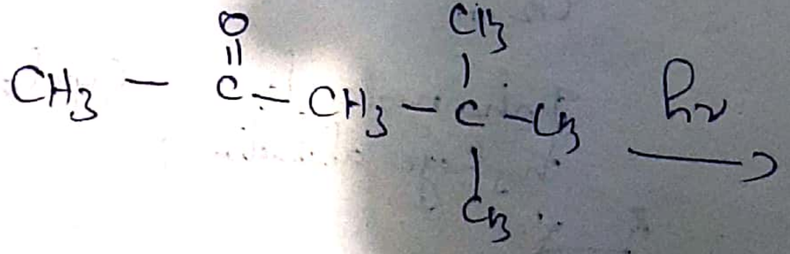
System - cyclic - abstraction of hydrogen from δ-Carbon atom



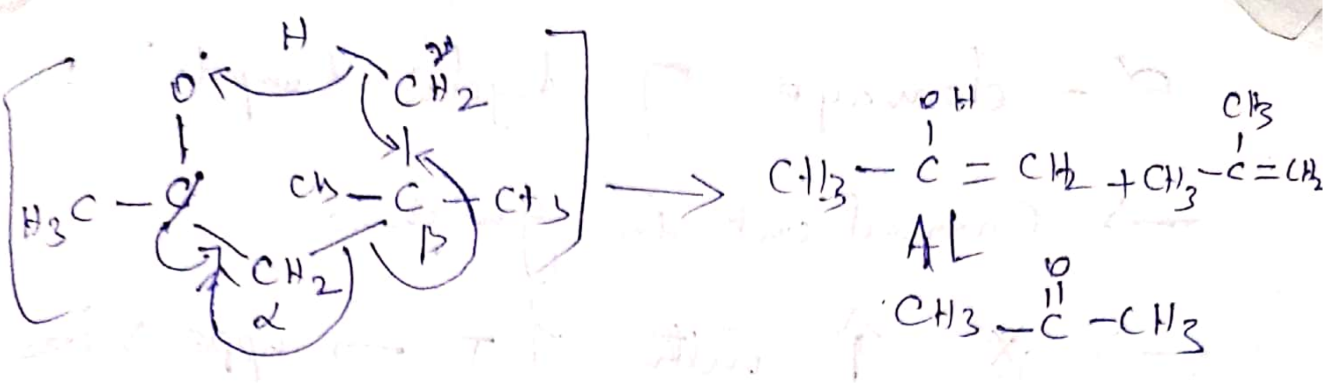
$$CH_3-\overset{O}{\overset{\|}{C}}-\overset{\alpha}{CH_2}-\overset{\beta}{C}(CH_3)_2-CH_3 \xrightarrow{h\nu} CH_3-\overset{O}{\overset{\|}{C}}-\dot{C}H_2 + \dot{C}(CH_3)_2-CH_2-H \rightarrow CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + (CH_3)_2C=CH_2$$

weak bond bet α, β Carbon due to steric hindrance

Mechanism :

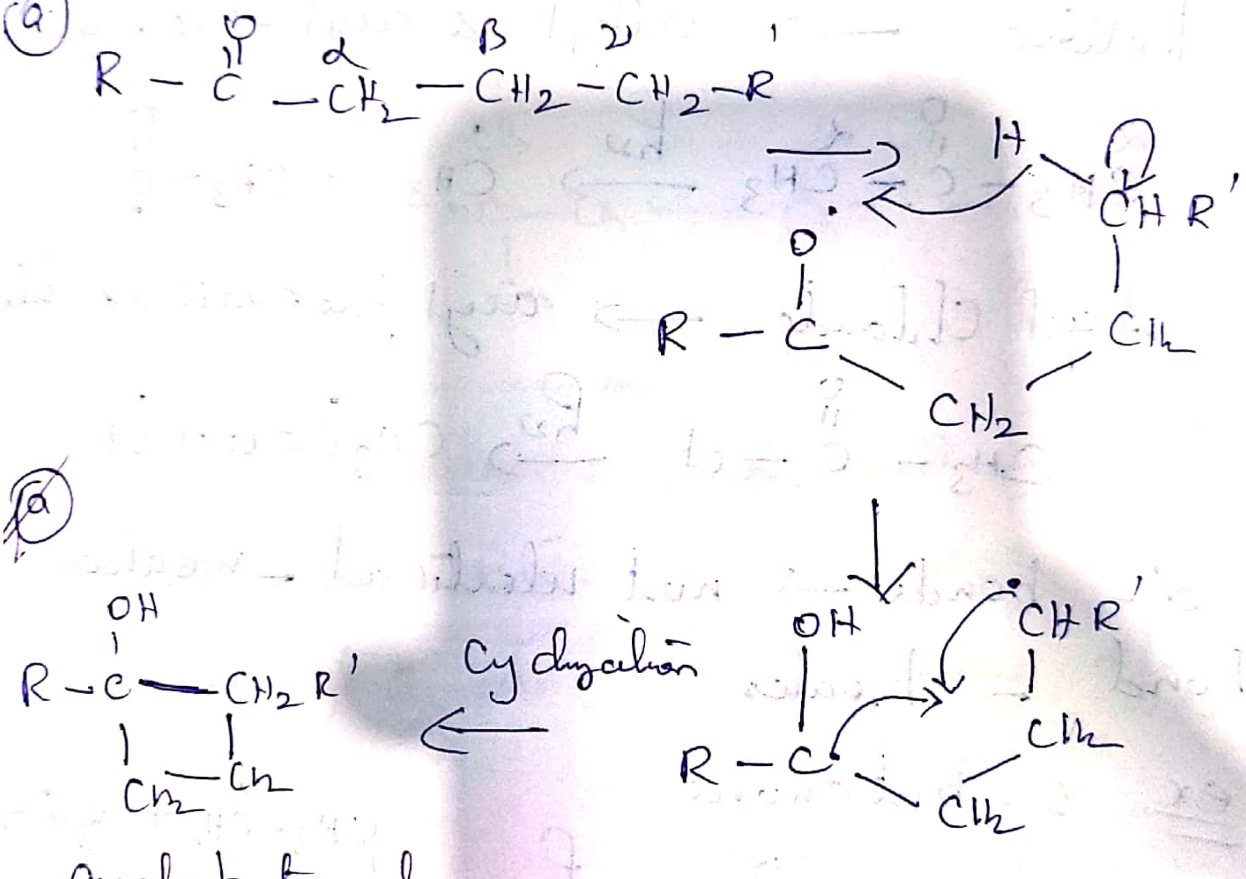


$$CH_3-\overset{O}{\overset{\|}{C}}-CH_3-C(CH_3)_2-CH_3 \xrightarrow{h\nu}$$



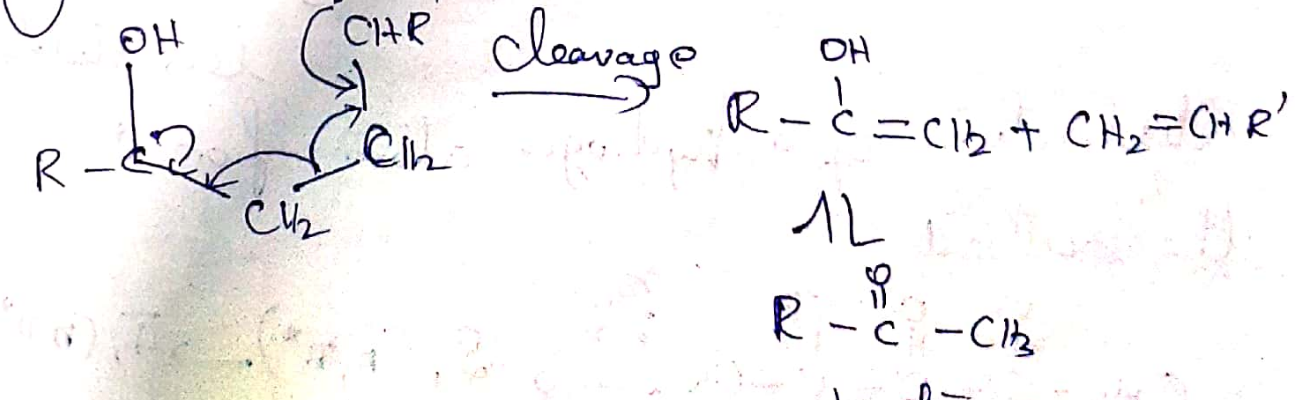
TS

(a)



cyclobutanal.

(b)



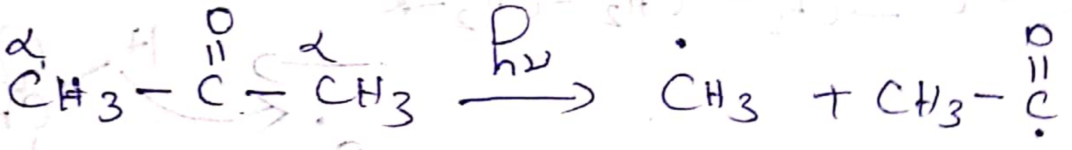
Ketone.

α- cleavage of Acyclic Compds:

→ Carried out in gas phase.

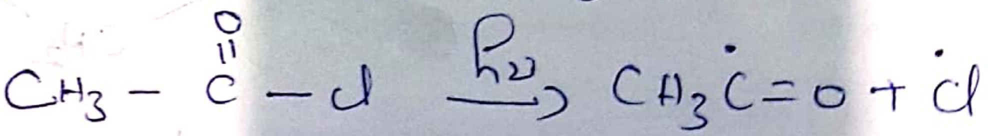
→ Φ ↑ with ↑ T → upper Vibrational level Significant.

(i) ketone → alkyl & acyl free radica



$$\overset{\alpha}{C}H_3-\overset{O}{\overset{\|}{C}}-\overset{\alpha}{C}H_3 \xrightarrow{h\nu} \dot{C}H_3 + CH_3-\overset{O}{\overset{\|}{\dot{C}}}$$

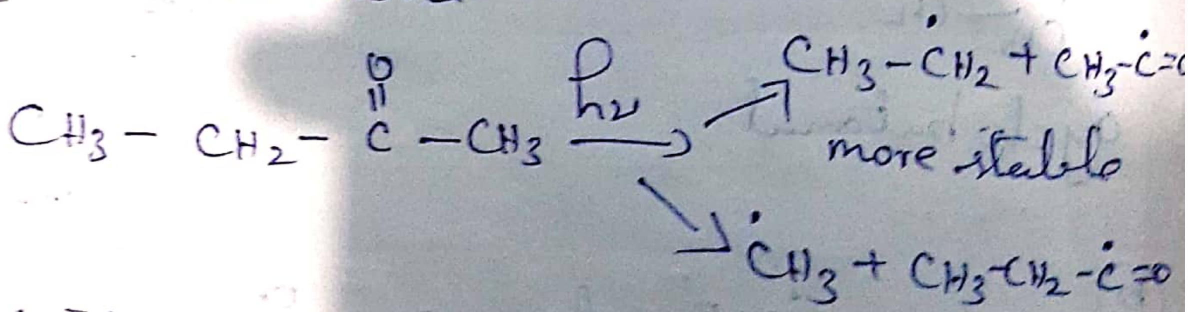
(ii) Acyl Chloride → acyl free radical & chlo



$$CH_3-\overset{O}{\overset{\|}{C}}-Cl \xrightarrow{h\nu} CH_3\dot{C}=O + \dot{C}l$$

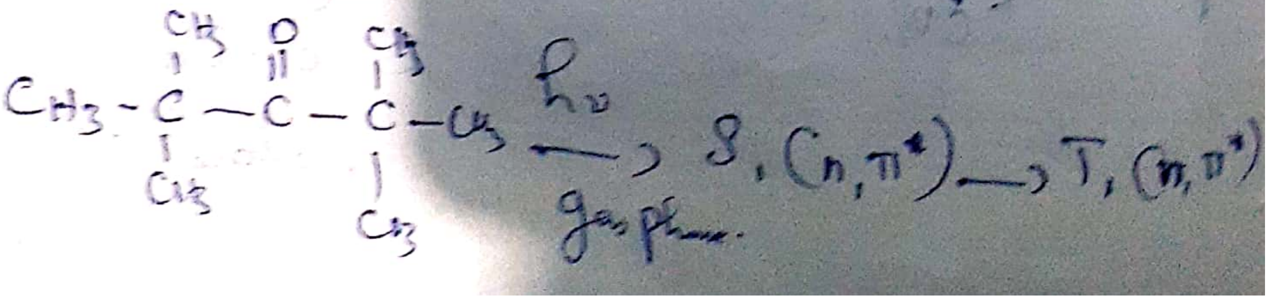
α- bonds → not identical – weaker bond – breaks

ex 2-butanone

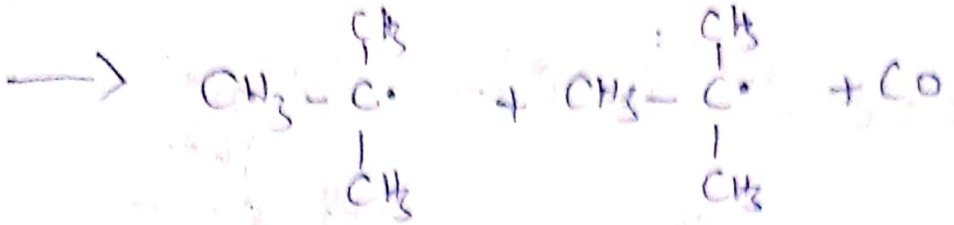


$$CH_3-CH_2-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow{h\nu} CH_3-\dot{C}H_2 + CH_3-\dot{C}=O \text{ (more stable)};\quad \dot{C}H_3 + CH_3-CH_2-\dot{C}=O \text{ (less stable)}$$

abstraction of a hydrogen atom from the solvent

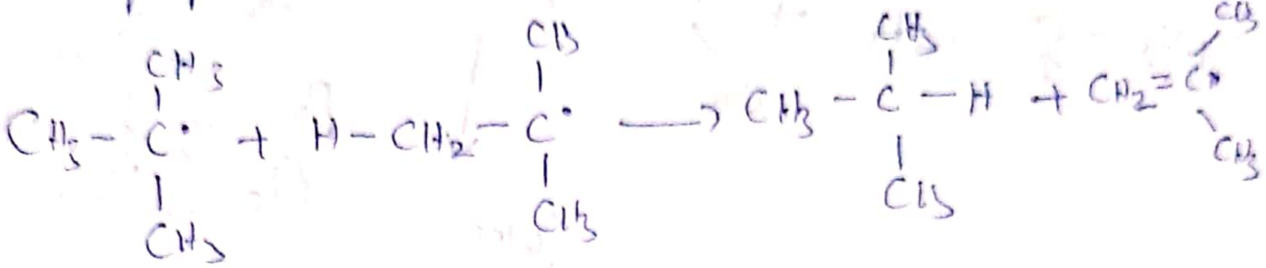


$$CH_3-\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}-\overset{O}{\overset{\|}{C}}-\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}-CH_3 \xrightarrow[\text{gas phase}]{h\nu} S_1(n,\pi^*) \longrightarrow T_1(n,\pi^*)$$



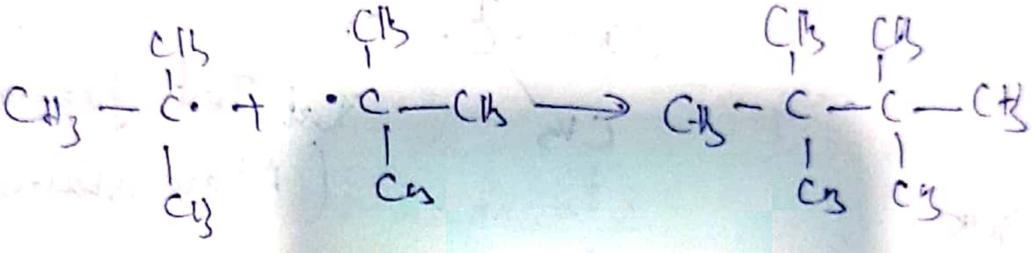
$$\longrightarrow CH_3-\overset{CH_3}{\underset{CH_3}{C\cdot}} + CH_3-\overset{CH_3}{\underset{CH_3}{C\cdot}} + CO$$

(i) Disproportionation



$$CH_3-\overset{CH_3}{\underset{CH_3}{C\cdot}} + H-CH_2-\overset{CH_3}{\underset{CH_3}{C\cdot}} \longrightarrow CH_3-\overset{CH_3}{\underset{CH_3}{C}}-H + CH_2=\overset{CH_3}{\underset{CH_3}{C\cdot}}$$

(ii) Re Combination



$$CH_3-\overset{CH_3}{\underset{CH_3}{C\cdot}} + \cdot\overset{CH_3}{\underset{CH_3}{C}}-CH_3 \longrightarrow CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{CH_3}{\underset{CH_3}{C}}-CH_3$$

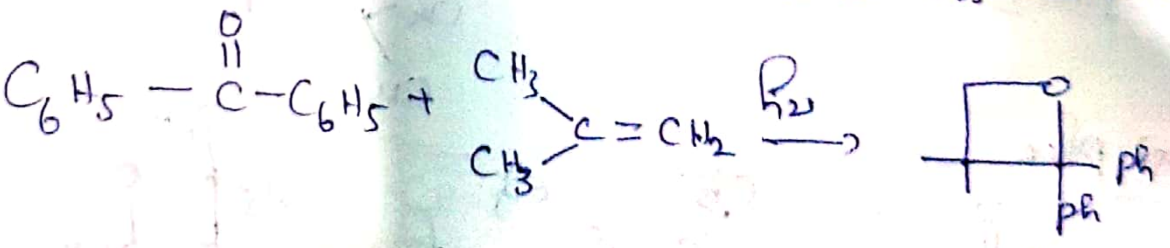
Photo cyclo Addition of ketones with unsatd Compds

Paterno-Buchi Reaxn:

Carbonyl compds + alkene, diene, alkyne

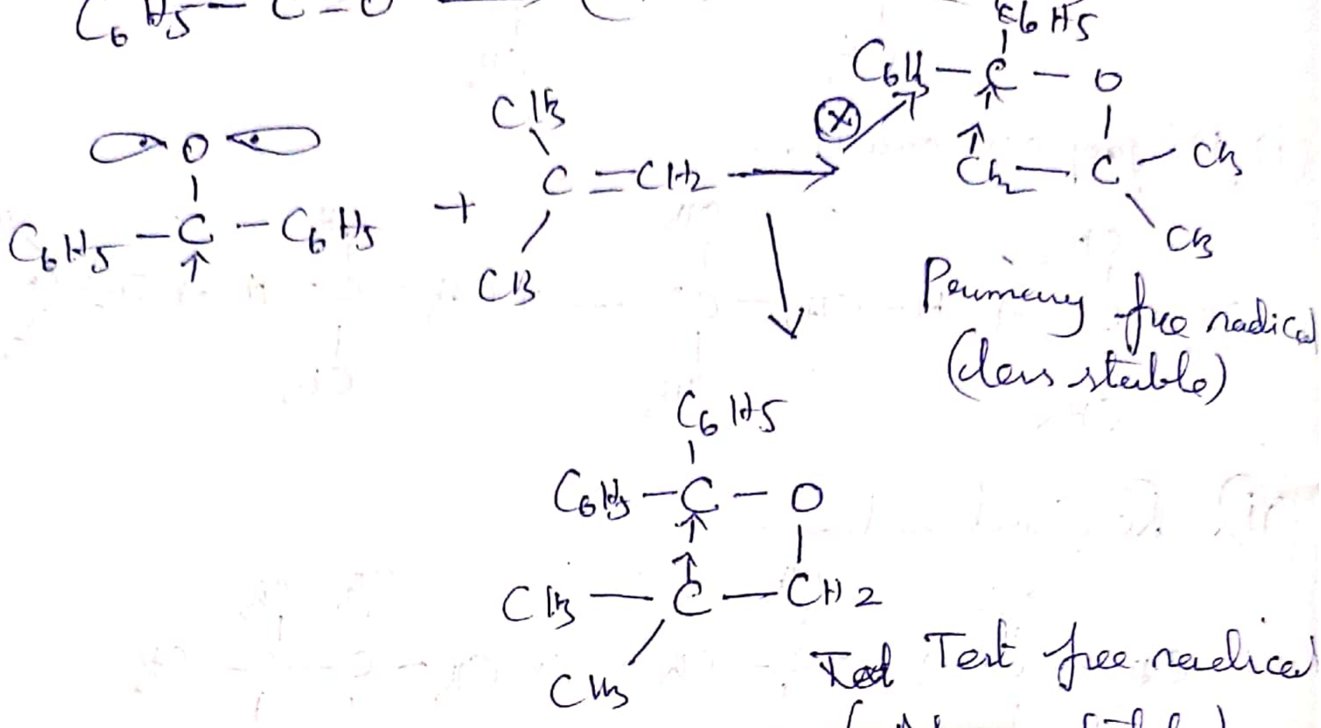
hν ↓ cycloaddn

Oxetene & its derivatives



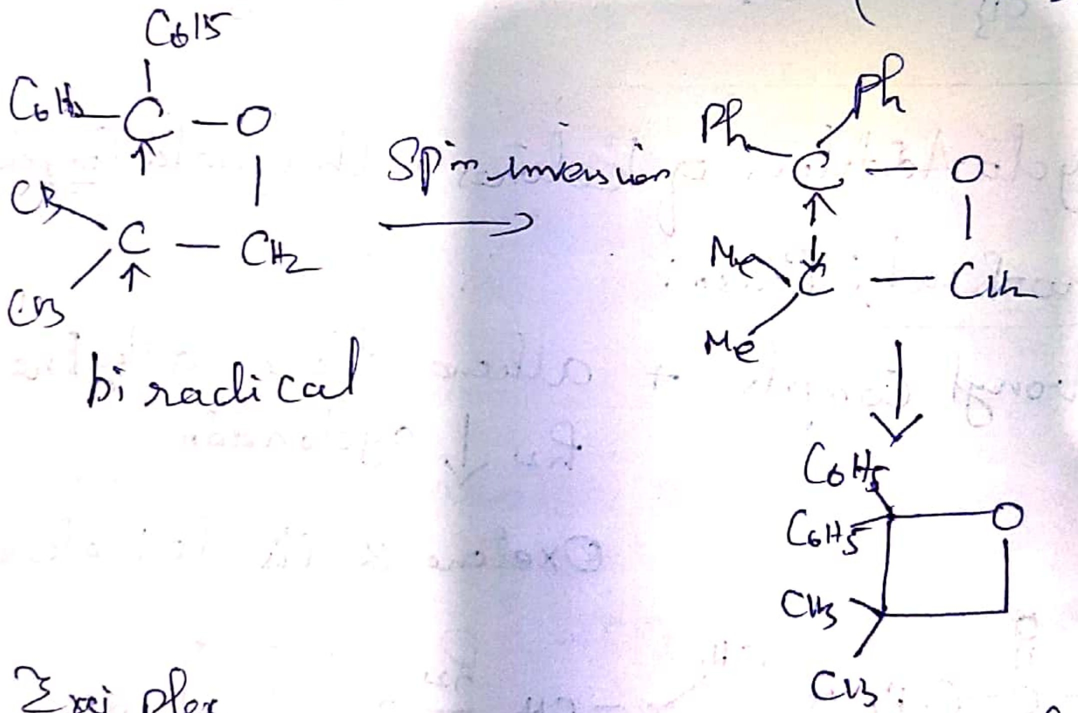
2,2-diphenyl 3,3-dimethyl Oxetane.

$C_6H_5-C=O \xrightarrow{h\nu} {}^1(n,\pi^*) \longrightarrow {}^3(n,\pi^*)$



Primary free radical (less stable)

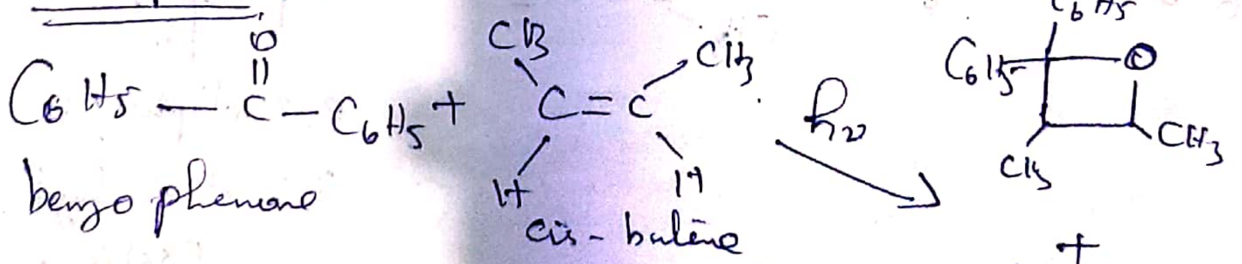
~~Ted~~ Tert free radical (More stable)



biradical

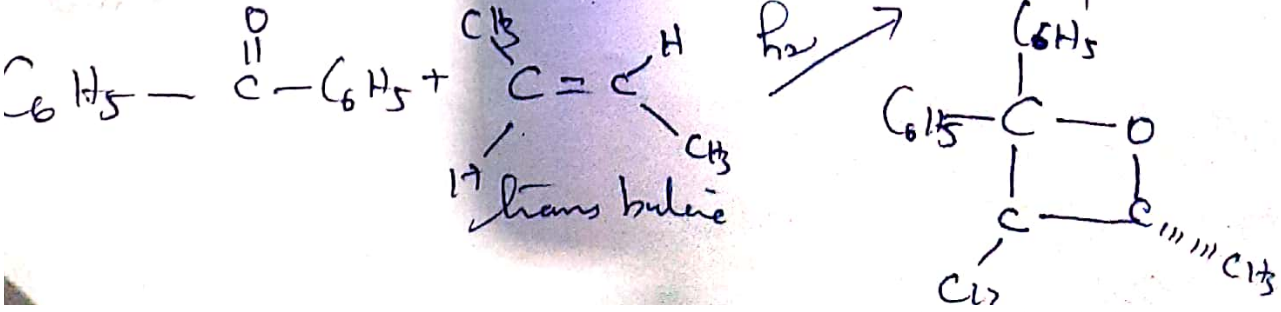
Spin inversion

Exciplex



benzophenone

cis-butene



trans butene

Exiplex → Complex bet excited ketone & olefin

biradical – predict → Major pdt.

not mechanism:

Rate Const for excited ketone → high → exciplex
↓
Collaps with biradical

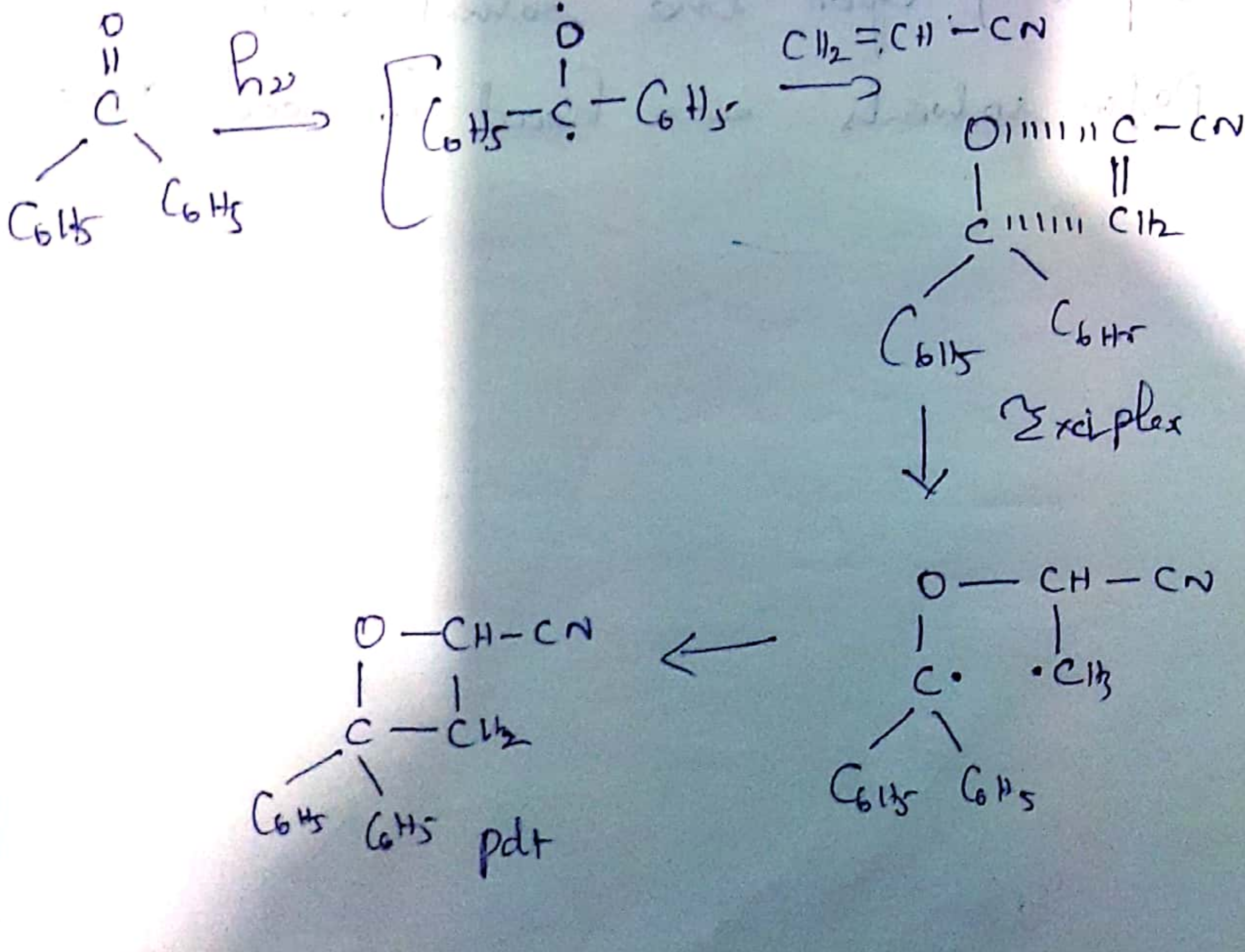
ketone $\xrightarrow{h\nu}$ ¹(ketone)

¹(ketone) → ³(ketone)

³(ketone) + olefin ⇌ exciplex

exciplex → biradical:

biradical → Oxetane.

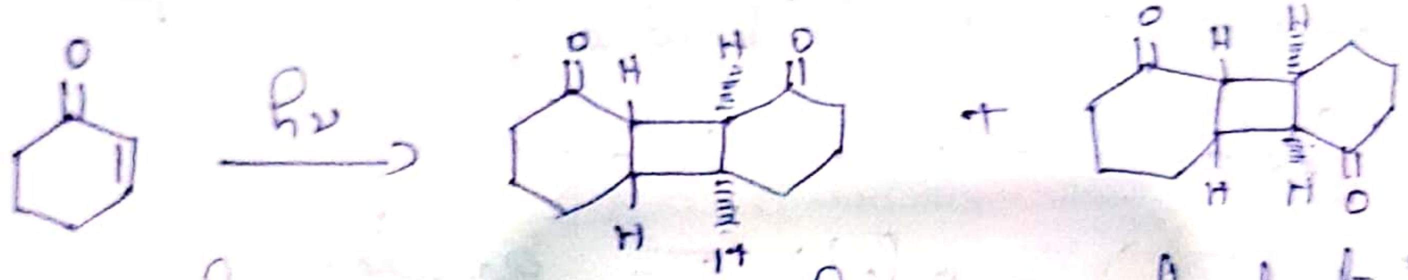


Photodimerisation of α,β-unsatd. Carbonyl Compds.

i.e. Ketones.

α,β-unsatd Carbonyl Compds $\xrightarrow{\text{intermolecular}}$ Photo cycloaddn → → cyclobutane

→ across C=C bond by $^3(\pi \rightarrow \pi^*)$ state



2-cyclohexanone

Head to head

Head to tail

Photo dimers

depending upon the solvent

Polar solvents → head to head dimer.