

Photochemistry of Olefins

- Photochemistry of olefins involves only two types of electronic ~~transitions~~ excitations: σ, π^* & $\pi - \pi^*$.
- Promotion of an e^- from σ to π^* requires more energy ($< 150 \text{ nm}$) & hence difficult to achieve under experimental conditions
- π, π^* excitation is experimentally accessible as it requires the absorption of light of about $180 - 210 \text{ nm}$ for nonconjugated olefins and of abt 220 nm or more for conjugated olefins.
- ∴ Most of the photochemical reactions of olefins studied involve π, π^* excitation.
- Initial excitation (π, π^*) usually occurs with no change in multiplicity & so a single excited state is obtained.
- Singlet excited state of olefins have less tendency to intersystem crossing and they are capable of initiating many photochemical rxns.
- T_1 states are generated by intermolecular energy transfer from a triplet donor to an olefin molecule.
- The photochemistry of singlet excited state of an olefin differs considerably from that of its triplet state.

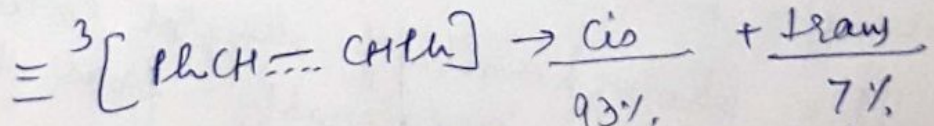
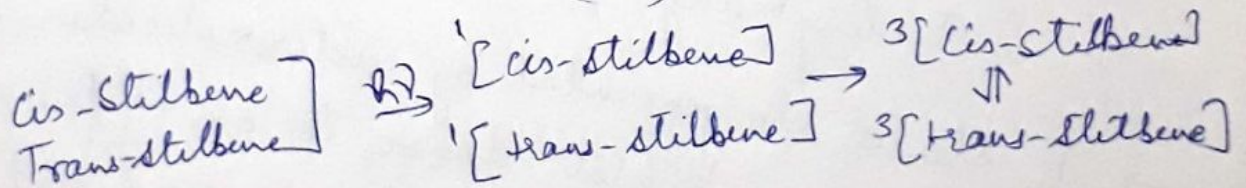
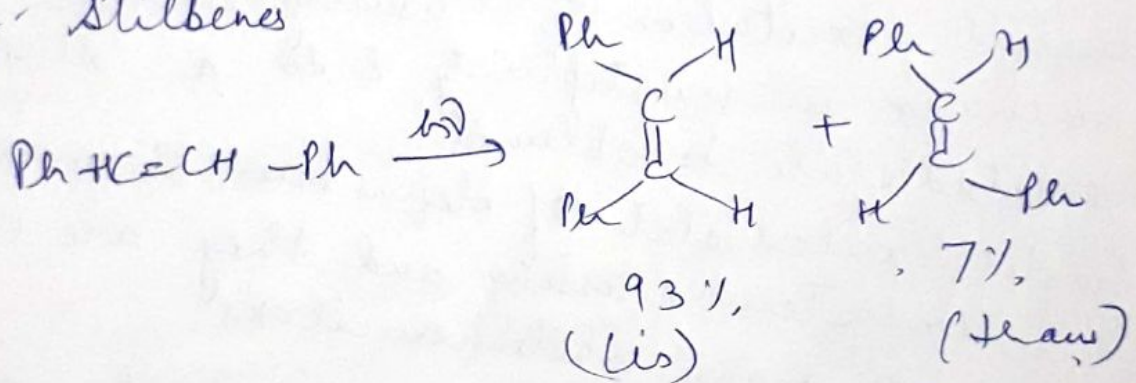
Cis-Trans Isomerization :

→ Olefins usually undergo cis-trans isomerization upon irradiation with UV light.

- The process can be done by
- a) direct irradiation of olefins
 - or
 - b) by irradiation in the presence of sensitizer.
 - or
 - c) it may either take place through a singlet or triplet excited species.

→ Isomerization in the triplet state possesses a lower barrier to rotation around the Carbon-Carbon bond.

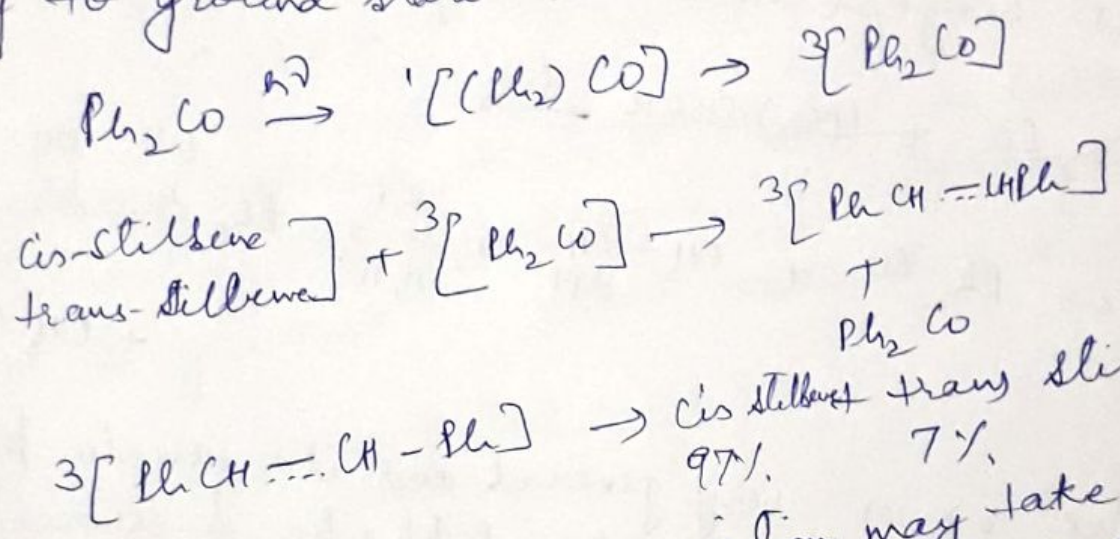
for eg. Stilbenes



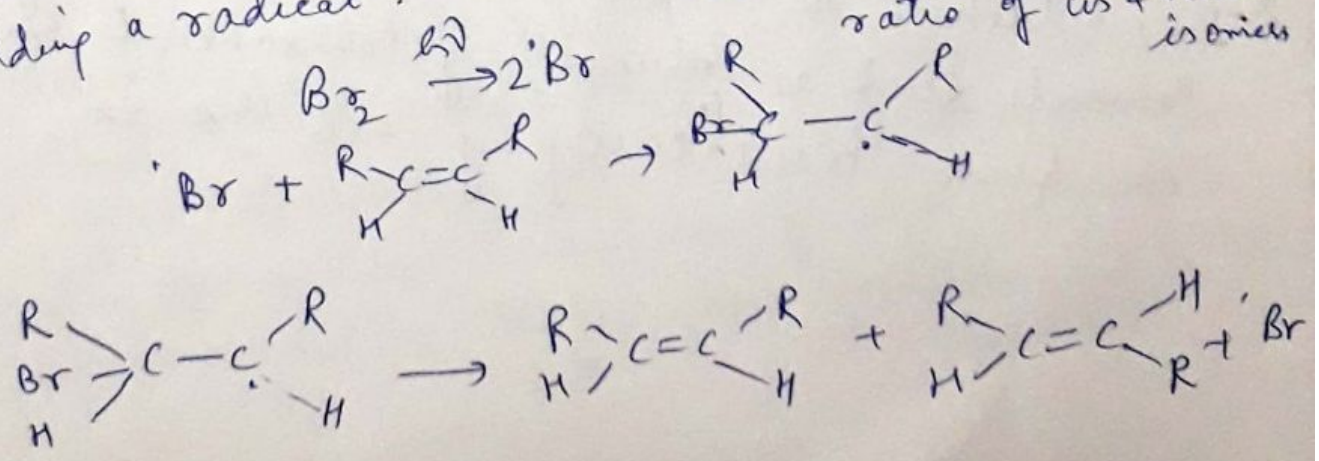
Initial absorption of light by either of these isomers is rapidly followed by inter system crossing to respective triplet states. Photoisomerization then occurs via IC (Interconversion) via a common triplet inter-mediate.

* Photoisomerization of ~~the~~ stilbene can be sensitized by an excited triplet molecule having more triplet energy than *cis*- (50 Kcal/mol) & *trans*-stilbene (57 Kcal/mol).

→ Energy transfer from T_1 of donor to either stilbene generates corresponding triplet state which either ~~can~~ interconverts to the triplet of other isomer or goes to a common triplet intermediate and in either case, final decay to ground state isomer occurs.



* Sometimes *cis-trans* isomerization may take place in the presence of halogens. It appears that under these conditions, there is a photochemical production of halogen atoms which add to the olefin yielding a radical. Elimination of halogen atom from the radical yields a constant ratio of *cis* & *trans* isomers.



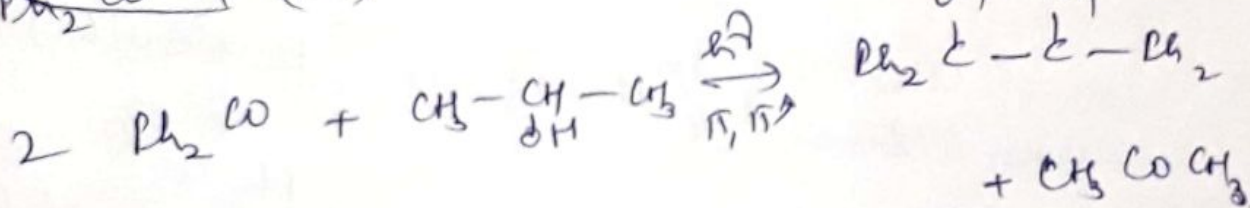
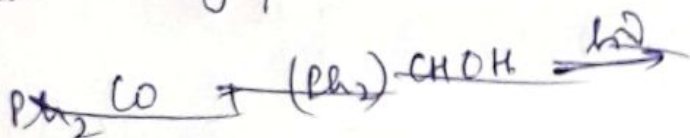
Photoreduction:-

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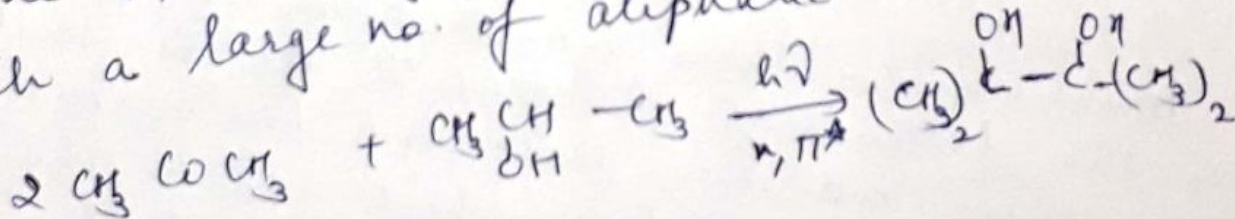
The photoreduction of benzophenone leading to benzpinacol is one of the oldest and most thoroughly investigated photochemical rxns.

→ The reaction is carried out by irradiating a soln of benzophenone in isopropyl alcohol with a light of λ 345 nm.

→ Isopropyl^{alcohol} does not absorb light at this λ but benzophenone undergoes an n, π^* transition



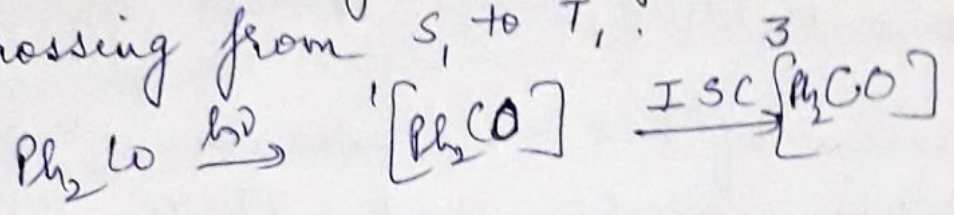
The rxn is very general and it can be performed with a large no. of aliphatic & aromatic ketones



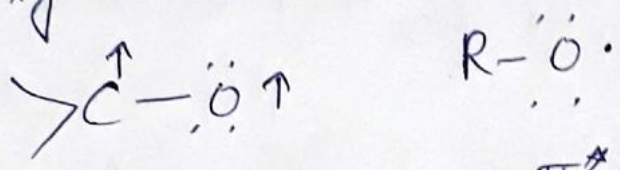
* In addition to isopropyl alcohol, a variety of solvents such as toluene, cyclohexane & methanol have been used for carrying out the rxn.

Mechanism

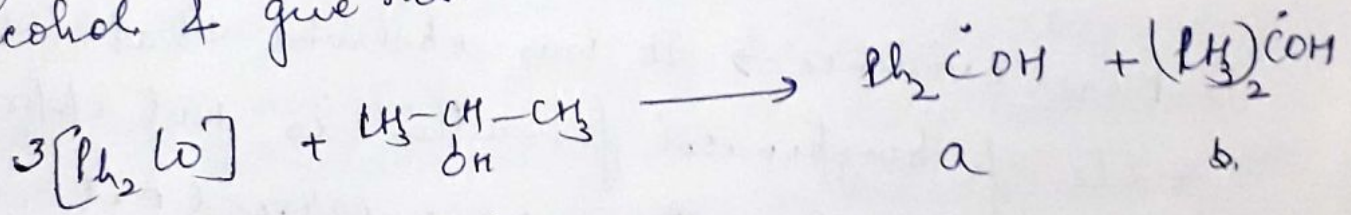
In case of benzophenone, initial light absorption is followed by rapid intersystem crossing from S_1 to T_1 .



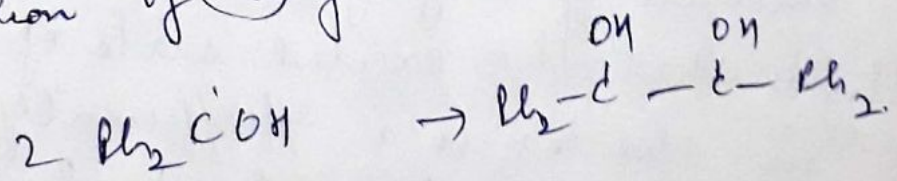
~~This~~ The carbonyl n, π^* triplet has a structure which closely resembles the structure of alkoxy radicals



Like alkoxy radicals, the n, π^* triplet is capable of abstracting the α -hydrogen of isopropyl alcohol & give rise to two radicals a & b.

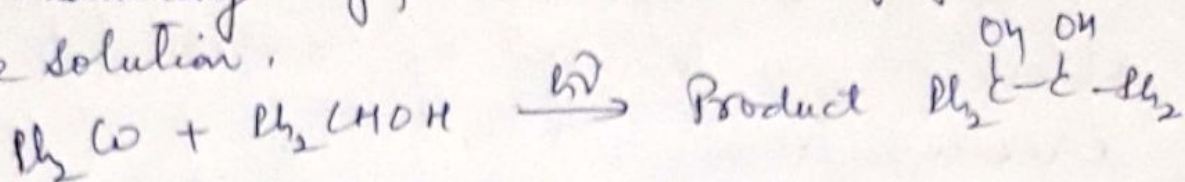


Combination of two units of (a) give rise to benzpinacol

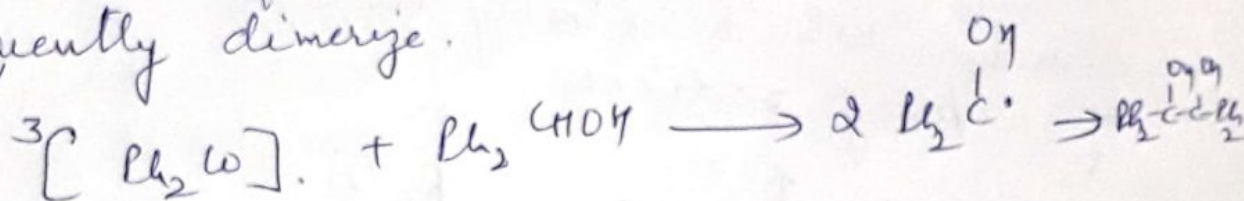


Quantum yield (ϕ) for benzpinacol formation is about 1, This confirmed that the second unit of (a) does not form as a result of the absorption of a fresh quantum of light, rather it is generated by the rxn b/w benzophenone & (b).

Benzopinacol formation can also be achieved ⁽²⁰⁾ by irradiating benzophenone and benzhydrol in benzene solution.



- The Mechanism of this rx is similar to that of the above except that there is simultaneous formation of two radicals, which subsequently dimerize.



Evidences to show that Benzophenone's triplet state participate

i) First Evidence → It was observed that the rate of benzopinacol formation is not appreciably decreased when the rx is carried out with lesser amounts of benzhydrol in benzene solution. This shows that the excited state of benzophenone involved in the rx is a sufficiently long lived species capable of waiting for benzhydrol molecule. ∴ it should be a T₁ rather than S₁ species.

ii) Quenching Studies: Addition of small amount of (2,1,7-naphthalene) naphthalene to the irradiation mixture reduces the quantum yield to a significant extent. Since naphthalene does not

Absorb light of λ needed for an n, π^* excitation in benzophenone, it is obviously an example of energy transfer in which excited benzophenone molecules return to the ground state with simultaneous excitation of naphthalene. (21)

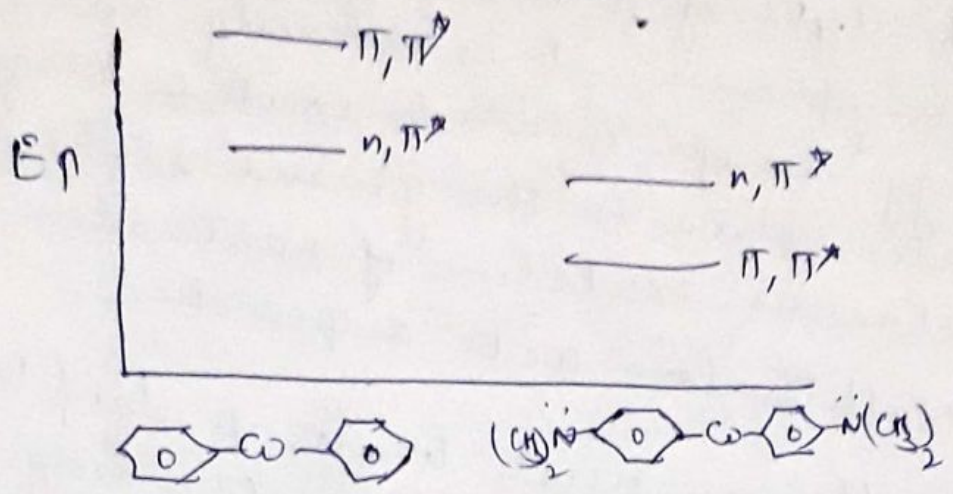
\therefore Naphthalene acts as quencher.

\rightarrow Benzophenone must be in a triplet state which only has a sufficiently long life to undergo collisions for the observed energy transfer with very low concentrations of naphthalene.

Imp: Michler's ketone does not undergo photo-reduction on irradiation with isopropyl alcohol. ?

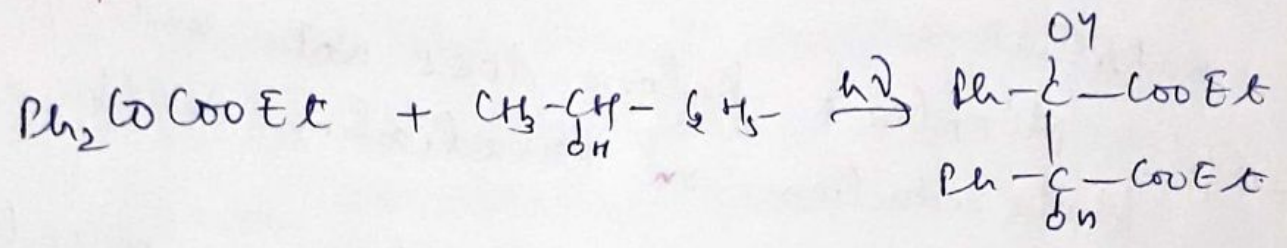
\rightarrow Hydrogen abstraction reaction is much more efficient in n, π^* state of ketones rather than in the π, π^* state as the latter does not have an odd e^- as in the oxygen n orbital in n, π^* state & \therefore , lacks characteristics of n, π^* triplet.

\rightarrow Conjugation of lone pair of e^- situated on nitrogen atom with the aromatic ring lowers the energy required for the π, π^* transition in this molecule. π, π^* transition thus becomes the lowest triplet of the system & occurs more readily than n, π^* transition. (fig)

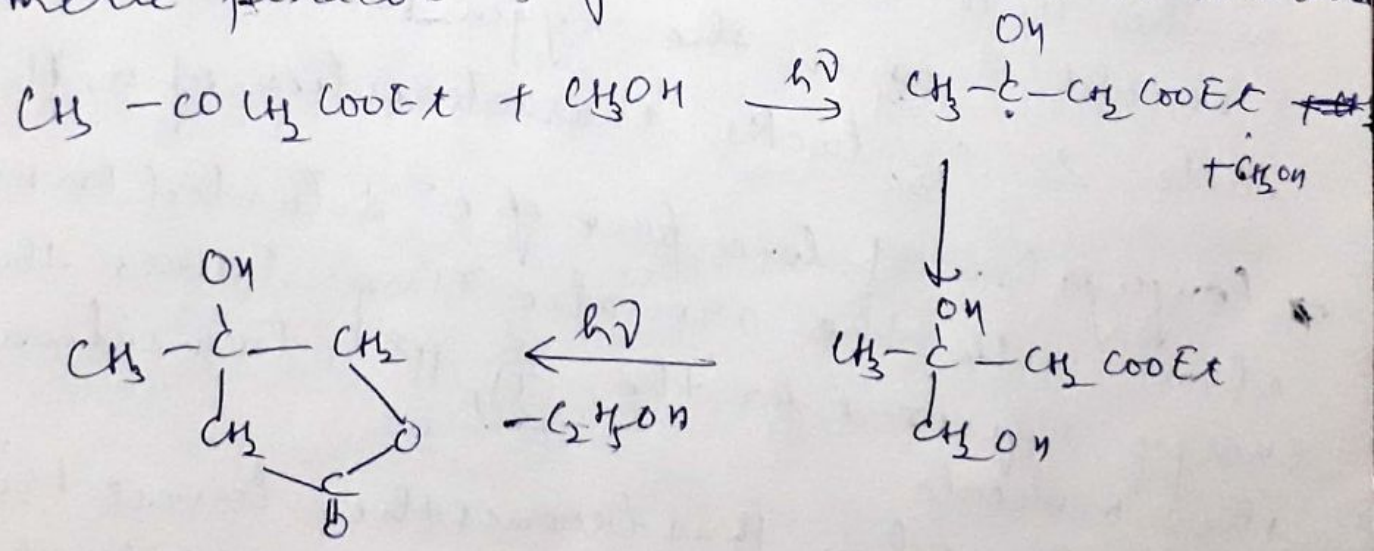


(Fig) ...

* α -Keto esters also undergo photoreduction to yield pinacol.



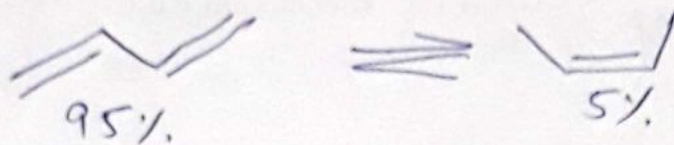
However, ethyl acetoacetate yields solvent add^{-uct} as the major product instead of expected dimeric pinacol & further converted to lactone



Photochemistry of Butadiene

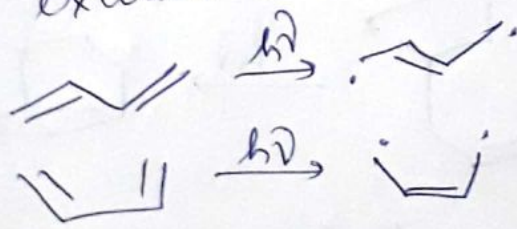
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Butadiene exists in solution as a mixture of *S-trans* (95%) and *S-cis* (5%) conformers

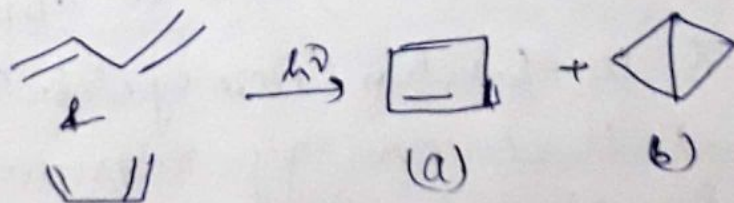


→ Irradiation of butadiene promotes an electron from ψ_2 to ψ_3 (π, π^* transition) which results in the increased bonding b/w C_2 & C_3 at the expense of C_1-C_2 & C_3-C_4 .

In other words, the lowest excited states of *S-trans* & *S-cis* butadiene should exhibit still large barriers to rotation about C_2-C_3 bond because of its double bond character. Thus, conformational character of butadienes are retained in excited state.

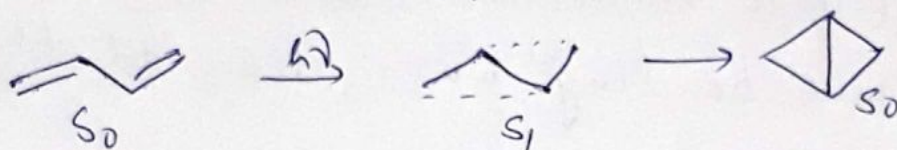
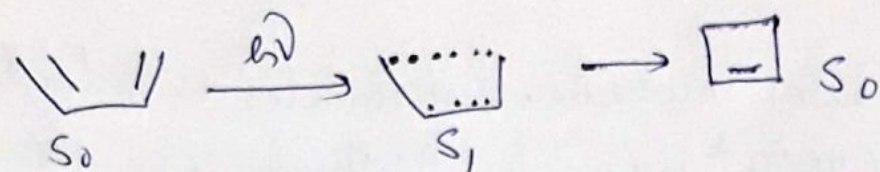


Direct irradiation of butadiene yields cyclobutene & bicyclo [1.1.0] butane.

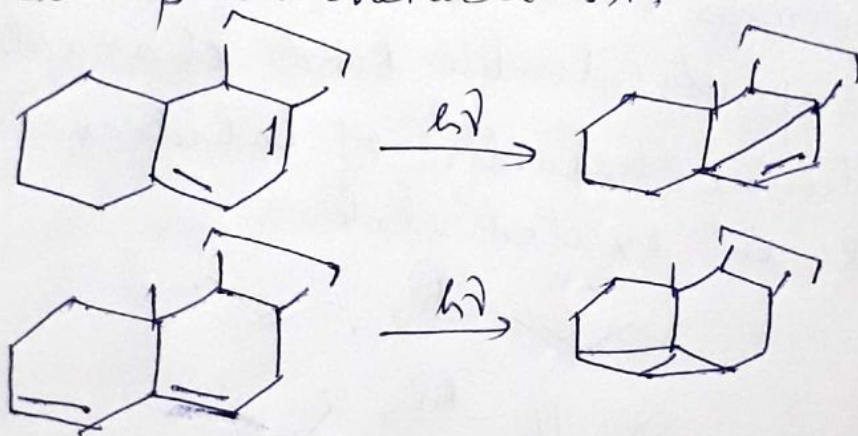


Formation of these products occurs directly from S_1 state of butadiene & assuming that

The conformational characters of butadiene⁽²⁴⁾ are retained in S_1 state, it appears quite reasonable to speculate that S_1 -cis butadiene is precursor of cyclobutene while excited state resembling S_1 -trans butadiene give rise to bicyclobutane.



Formation of cyclobutene & bicyclobutane on irradiation of 1,3-butadiene is a fairly general photochemical rx.



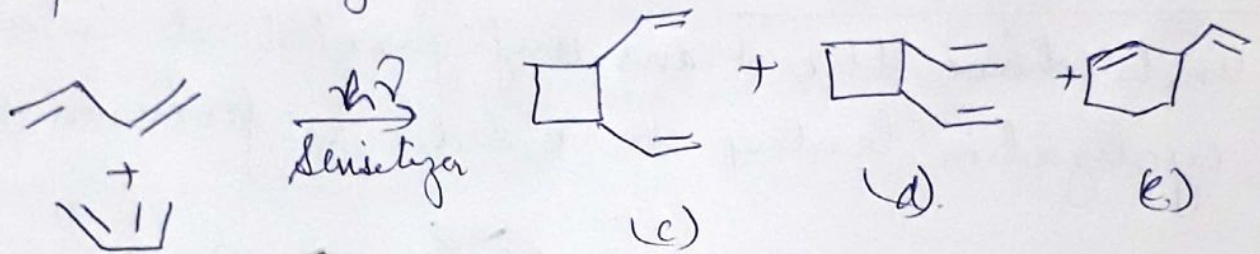
The single excitation energies of the two conformers of butadiene are not exactly known ($\sim 110-120 \text{ kcal/mol}$), but it appears from the product composition (more cyclobutene than bicyclobutane) that energy required for the singlet excitation of S_1 -cis butadiene is lower than that required for S_1 -trans isomer.

→ The triplet excitation energies for *s-cis* & *s-trans* have been found to be 53 & 60 kcal/mol respectively.

→ Large energy gap b'n S_1 & T_1 , shows that there will be no ~~an~~ ISC in butadienes.

Photochemistry of T_1 states of Butadienes

→ It occurs through energy transfer from triplet sensitizers

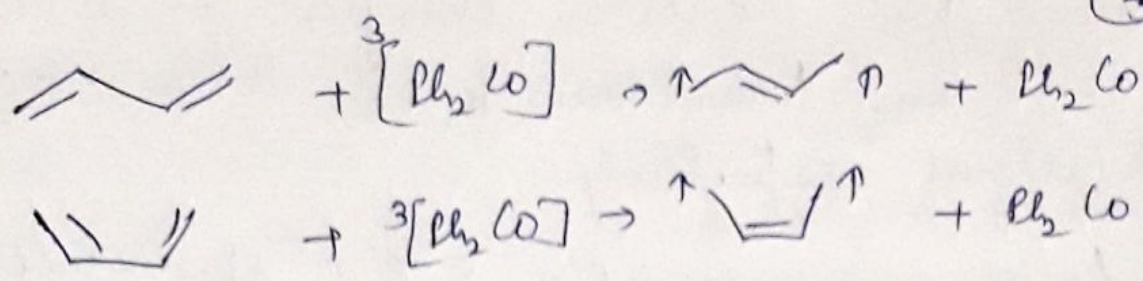


Moreover, ~~energy~~ composition of dimer mixture varies with the triplet energy of the sensitizers to populate T_1 state of butadiene.
eg.

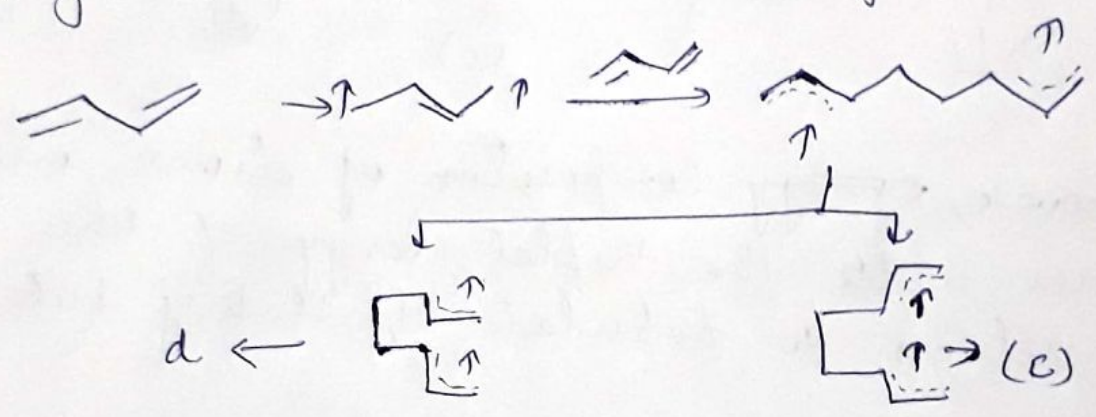
Sensitizer	E_T	c	d	e
1) Benzophenone	69	80	16	4
2) Benzil	54	49	8	43

Mechanism:-

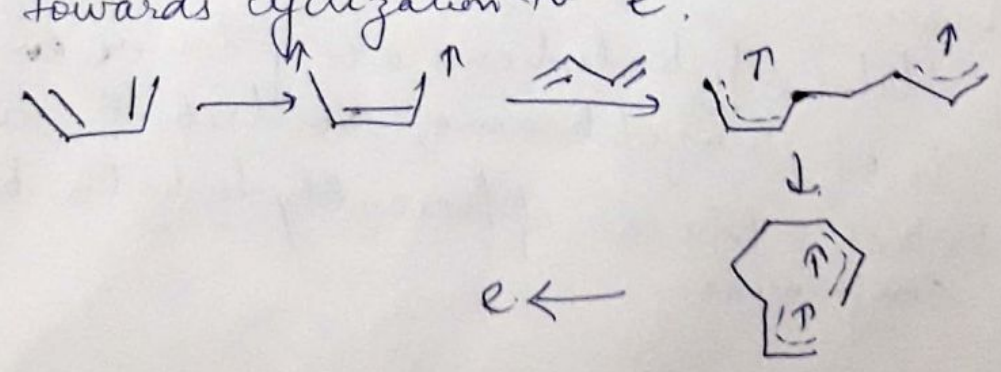
T_1 states of butadienes are of lower energy than T_1 of benzophenone, so triplet energy transfer takes place efficiently to both butadiene conformers



Trans triplet of butadiene is formed predominantly
 b'coz diene is almost trans,
 subsequent reaction of trans triplet with
 S-trans butadiene leads to an intermediate
hexadienyl biradical in which both allylic
 units have the trans configuration & so a
 cyclization leading to c & d is favoured.



A similar rxn of cis triplet, formed in small amount
 with a molecule of S-trans butadiene leads to a
 biradical in which one allylic unit has cis
 configuration & in one conformation, it is favourably
 disposed towards cyclization to e.



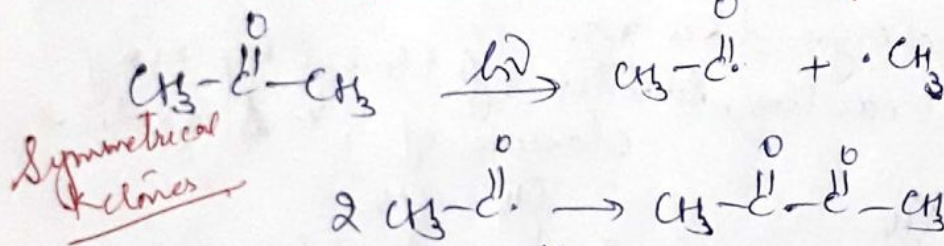
In contrast to benzophenone (E_T 69 kcal/mol),⁽²⁹⁾
 a triplet sensitizer ($E_T < 60$ kcal/mol but > 53 kcal/mol)
 preferentially should form cis-butadiene triplet
 by energy transfer to s-cis-butadiene.

This explains predominance of c when benzil
 is employed as a sensitizer.

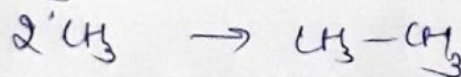
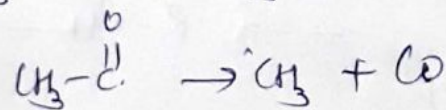
As the triplet energy of photosensitizer is
 decreased below 53 kcal/mol, there will not
 be any energy transfer since excitation of
 diene now requires more energy than the
 sensitizer can provide.

Extra

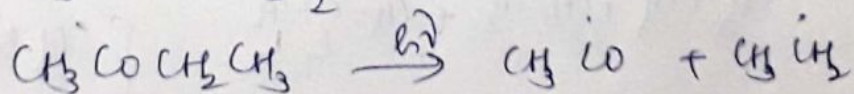
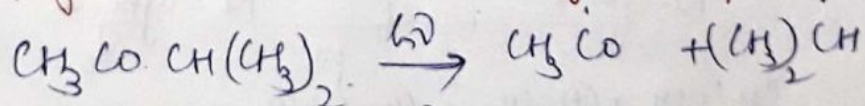
Norrish Type I Rxn:- (α cleavage) ∴ Homolytic fission of
 α carbon-carbon bond)



$h\nu$ $\pi^* \pi$ excited state of acetone



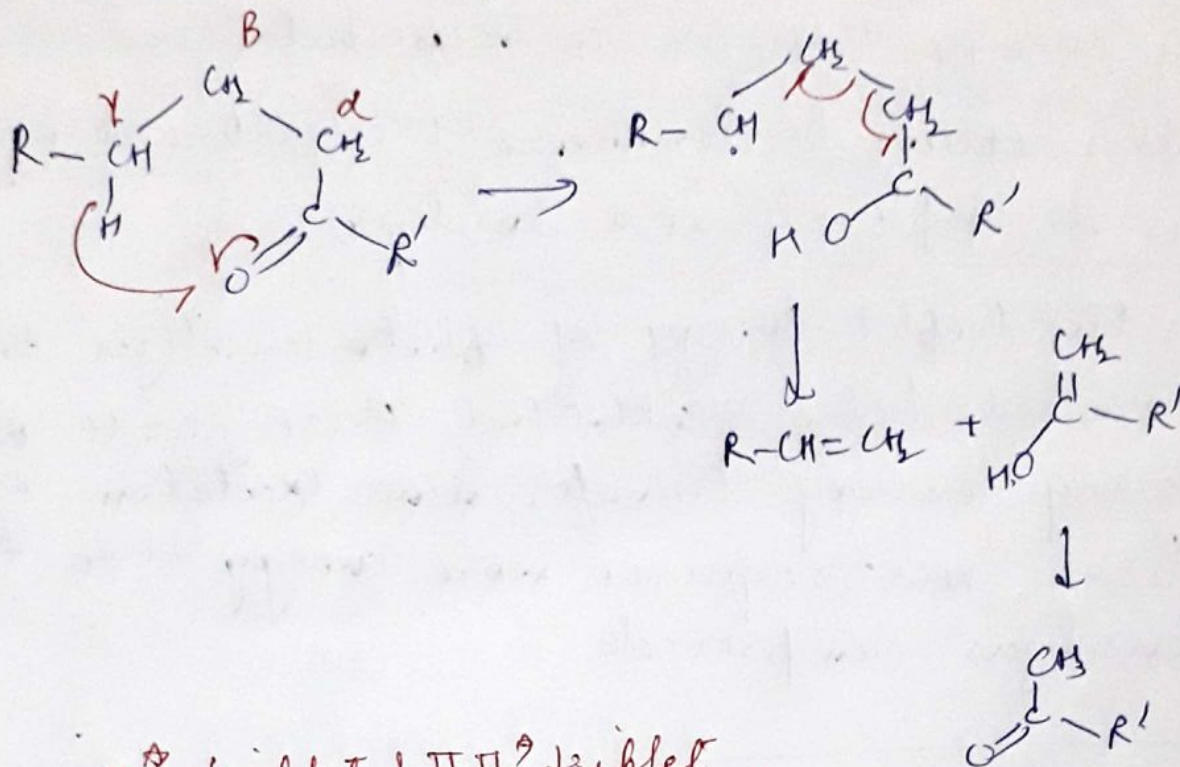
Unsymmetrical ketones → generate more stable of two possible radicals.



Norrish Type II :-

(28)

→ Ketones possessing γ hydrogen atom undergo photochemical rx. & form olefin & enol of smaller ketone.



Both n, π^* triplet & π, π^* triplet participate in intramolecular hydrogen abstraction while ketones with a low lying π, π^* state do not undergo this rx. γ -hydrogen abstraction, sometimes followed by ring closure of 1,4-diradical.

