Photochemistry of Carbonyl Compounds:

Carbonyl compounds especially ketons, undergo many interesting & versatile reaction on irradiation. These reactions is initiated by $n-\pi^*$ transition. Promotion of an e^- will lead to either a singlet-state or a triplet state. Photochemical reactions by carbonyl groups takes place either by singlet state or by triplet or by both state

Carbonyl compounds give four primary type of photochemical reactions.

(1) Cleavage of the bond α- to the carbonyl group or Norrish type-I.

(2) Cleavage of a bond β- to the carbonyl group or Norrish Type-II.

(3) Intermolecul hydro hydrogen abstraction by carbonyl group oxygen.

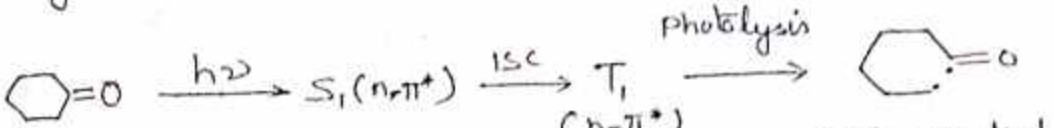
(4) Addition of carbonyl oxygen atom to a carbon-carbon double bond.

(1) Norrish Type-I Process:

The bond dissociation energy of C-C bond adjacent to a carbonyl is comparatively small and consequently photochemical excitation of ketones usually results in the homolytic fission of α-cleavage or Norrish type-I reaction. it occurs more readily in vapour phase. The reaction results in the formation of

mixture of 5-hexenal, cyclopentane and carbon monoxide.

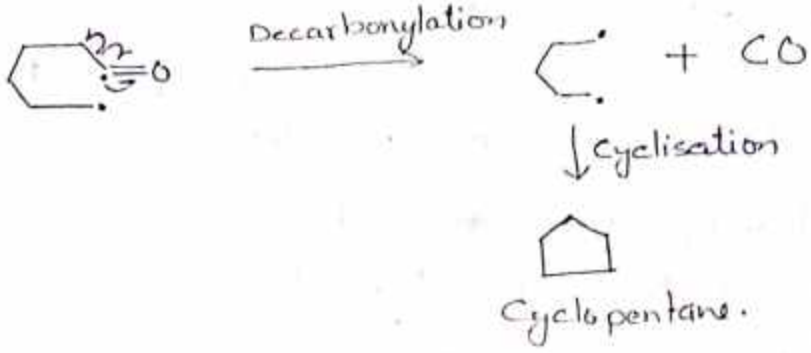
Primary process:



Cyclohexanone. Di free radical

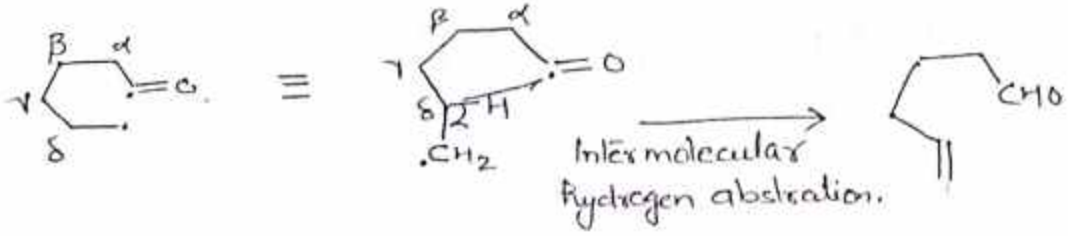
Secondary Process:

(i) Loss of CO (photo decarbonylation)



Cyclopentane.

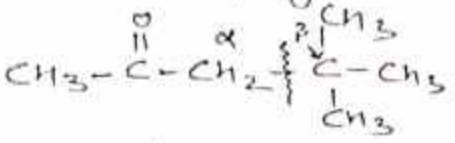
(ii) The initial diradical can undergo intermolecular hydrogen abstraction via a favoured six member TS leading to unsaturated aldehyde.



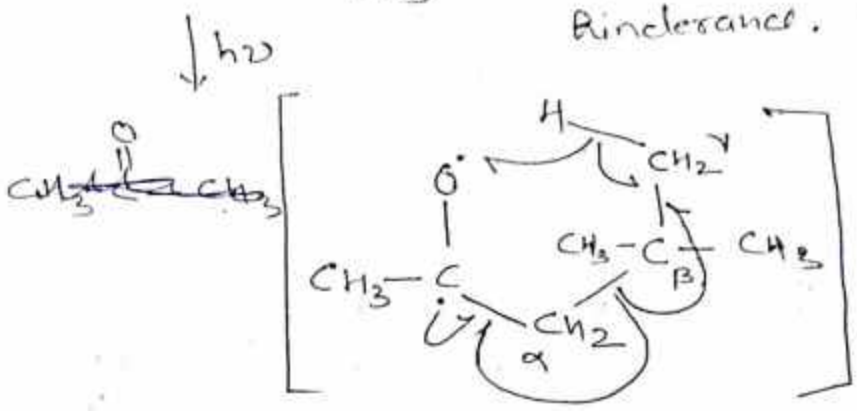
(2) Norrish Type-II or β-cleavage:-

The β-cleavage reaction occurs whenever hydrogen atoms are suitably positioned five atom from the carbonyl oxygen, i.e, at least one hydrogen on γ-carbon. This photo-decomposition also involves intra molecular hydrogen transfer and by six membered cyclic transition state (TS).

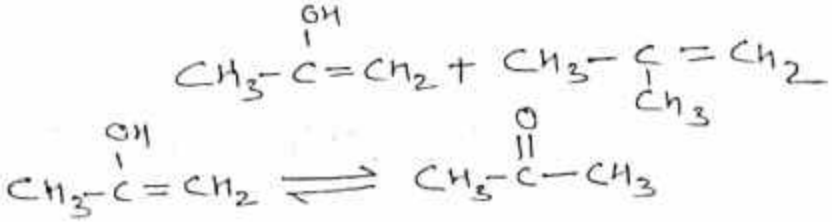
β-cleavage can possible if bond between α & β- carbon is weak. If system is cyclic then abstraction of hydrogen takes place at δ-carbon but if system is open chain then abstraction takes place from γ- carbon in the formation of six- membered cyclic TS.



weak bond between α & β carbon due to steric hinderance.

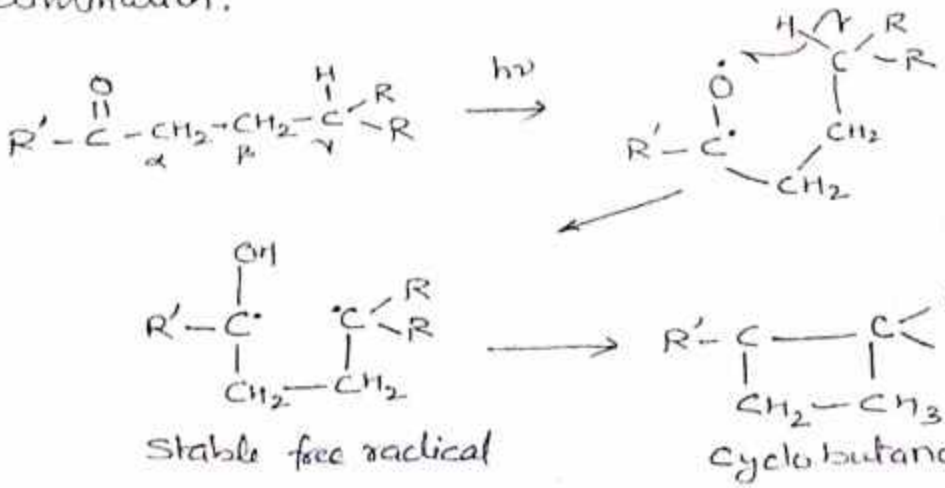


Cyclic TS.



if however, a relatively stable radical can be generated by the intermolecular hydrogen abstraction then cyclobutanol formation can complete with β- elimination.

(i)

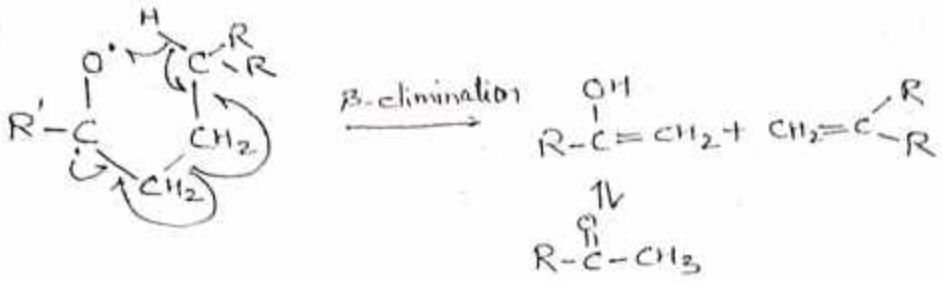


Stable free radical

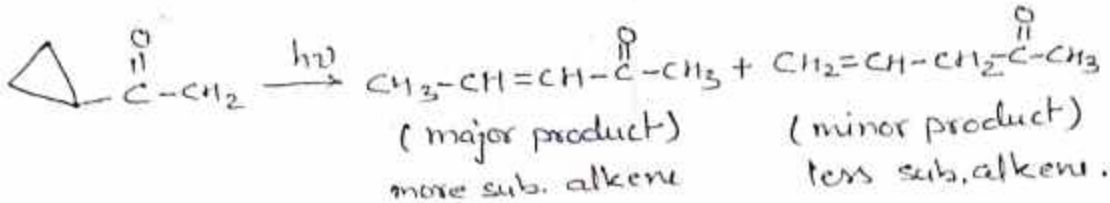
Cyclobutanol

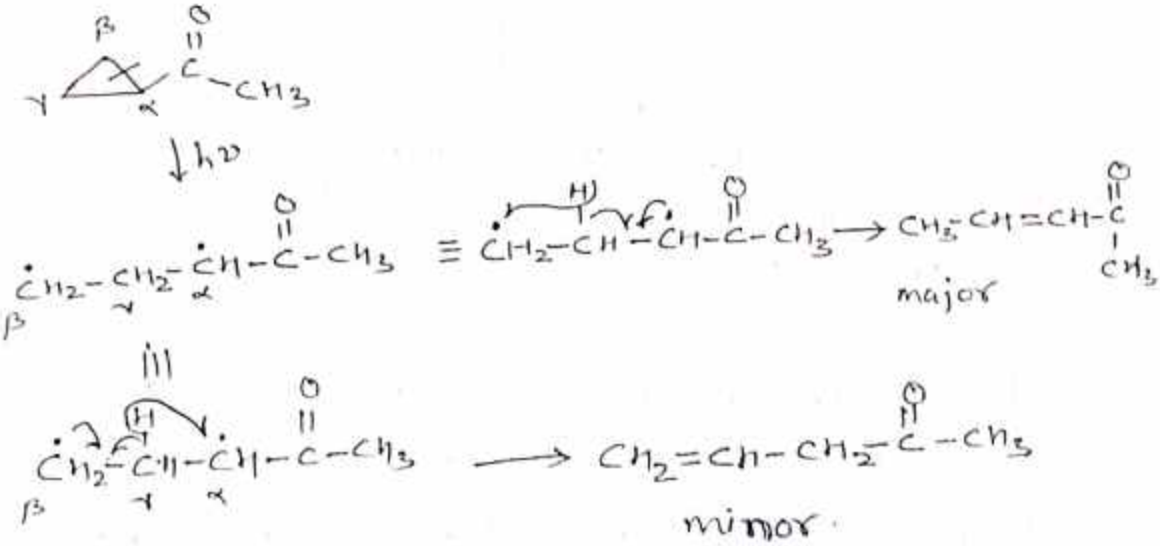
if R is alkyl or phenyl group at γ-carbon then

(iii)



Cyclopropenyl ketones are the most common compounds which undergo β-cleavage followed by hydrogen abstraction from the γ-carbon.





(3) Intermolecular Hydrogen abstraction by carbonyl oxygen (Bimolecular reaction)

Bimolecular reaction takes place between excited state of one molecule & ground state of another molecule.

When aldehyde & ketone is reacted in a solvent- specially in sec alcohol, toluene, cumenede, undergoes bimolecular reduction to form a pinacol.

The proposed mechanism involves intermolecular hydrogen abstraction by carbonyl oxygen of photo excited state.

$$Ph_2-C=O \xrightarrow{h\nu} S_1 \longrightarrow (T_1\ n\text{-}\pi^*)\ Ph_2-\dot{C}-\dot{O}$$

$$Ph_2-\dot{C}-\dot{C} + R_2CHOH \longrightarrow Ph_2-\dot{C}-OH + R_2\dot{C}-OH$$

$$R_2-\dot{C}-OH + Ph_2-C=O \longrightarrow Ph_2-\dot{C}-OH + R_2C=O$$

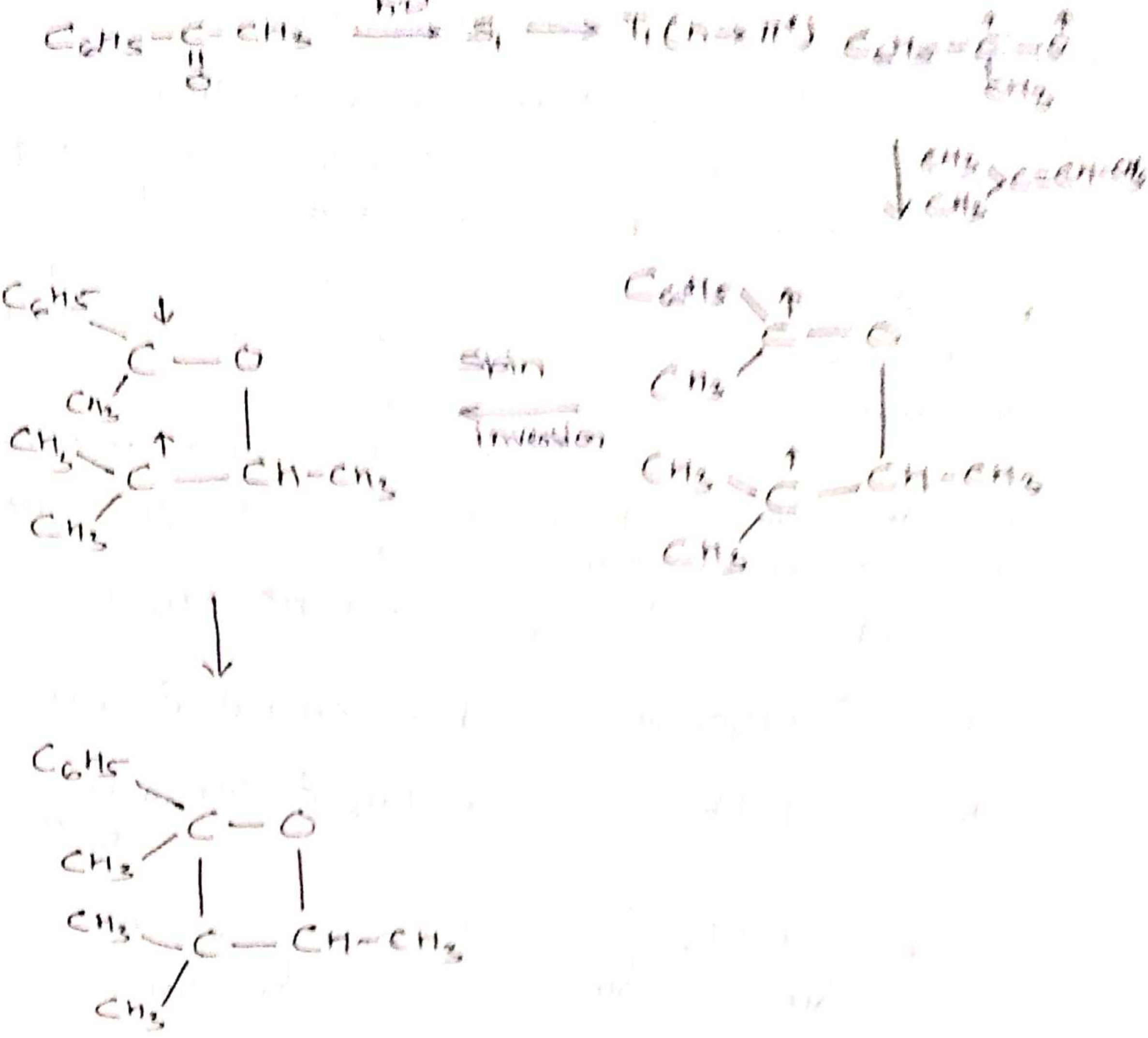
$$Ph_2-\underset{\underset{OH}{|}}{\dot{C}} + Ph_2-\underset{\underset{OH}{|}}{\dot{C}} \longrightarrow Ph_2-\underset{\underset{OH}{|}}{C}-\underset{\underset{OH}{|}}{C}-Ph_2$$

Pinacol

(4) Addition of carbonyl oxygen to carbon-carbon double bond: The Paterno-Büchi Reaction-

This primary process can occur if a ketone or aldehyde is photolysed in presence of a alken to give cycloaddition product- oxetane and its derivatives. This addition reaction is known as Paterno-Büchi Reaction.

The addition of the $n \rightarrow \pi^*$ T_1 of ketone to alkene (anti Markovnikov's addition) gives a biradical, then spin inversion & secondary cyclisation lead to an oxetane.


hν
Spin Inversion