

3.10. Pericyclic reactions

3.10.1. Pericyclic reaction

A concerted reaction which proceeds via cyclic transition state is called pericyclic reaction

3.10.2. Principle of Conservation of Orbital Symmetry or Woodward Hoffman Rules

The theory is based on the following points:

- The ground state of all the molecules contains a pair of electron in HOMO (Highest Occupied Molecular Orbital).
- The overlap of positive lobes of one orbital with the positive lobes of another orbital is allowed. Likewise negative lobes of one orbital overlaps with the negative lobes of another orbital.
- A symmetric orbital interacts with a symmetric orbital and vice versa.
- Cycloaddition reaction can be classified according to the facility of the interacting orbital, i.e. “suprafacial” or “antarafacial”.

3.10.3. Categories

Pericyclic reactions are of five categories

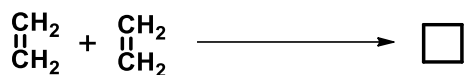
- Cycloaddition reaction
- Electrocyclic reaction
- Sigmatropic rearrangement
- Cheletropic reaction
- Group transfer and elimination reaction.

- Cycloaddition Reactions

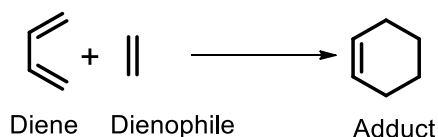
It is the combination of two π -electron system having m and n electrons respectively to form a ring of (m+n) members.

Examples:

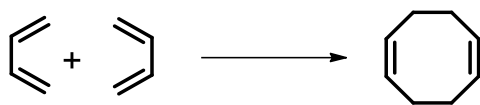
- [2+2] cycloaddition



- [4+2] cycloaddition: It is a Diels-Alder addition reaction



➤ [4+4] cycloaddition



❖ Endo product preferred over exo product for [4+2] cycloaddition reaction.

❖ Woodward Hoffman rule for (i+j) Cycloadditions

i+j	Thermal	Photochemical
4n (2+2, 4+4,.....)	Supra, antara Antara, supra	Supra, supra Antara, antara
4n+2 (4+2, 6+4.....)	Supra, supra Antara, antara	Supra, antara Antara, supra

• Electrocyclic Reaction:

- (i) A conjugated polyene undergoes isomerization and forms cyclic compound under the influence of heat or light.
- (ii) A new single bond is formed.
- (iii) A double bond is disappeared and the remaining double bond shift their positions.



- Electrocyclic reactions are completely stereospecific and stereoselective.
- A stereospecific reaction is one where a given isomer gives one product where as other stereoisomer gives the opposite product.
- Woodward Hoffman rule for Electrocyclic Reactions

Number of p-electrons	Reaction	Motion
4n	Thermal	Conrotatory
4n	Photochemical	Disrotatory
4n+2	Thermal	Disrotatory
4n+2	Photochemical	Conrotatory

- **Sigmatropic Rearrangement**

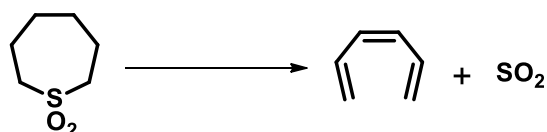
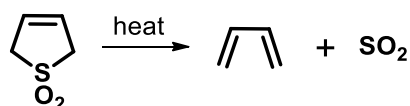
- Sigmatropy refers to migration of a sigma bond.
- It is a concerted reaction in which a sigma bond migrates along with the group attached to it, to a new position.
- This reaction is classified as [i, j] order, where i and j refers to the number of atom to which each end of the migrating bond joins.
- Claisen and Cope rearrangement are the example of [3,3]-sigmatropic rearrangement.

➤ **Symmetry rule for sigmatropic rearrangement**

i, j	Thermal Reaction	Photochemical Reaction
1, 3	Antarafacial	Suprafacial
1, 5	Suprafacial	Antarafacial
1, 7	Antarafacial	Suprafacial
3, 3	Suprafacial	Antarafacial

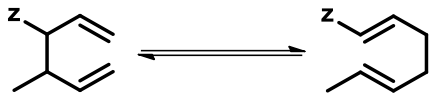
- **Cheletropic Reactions**

The reaction in which two sigma bonds are formed or broken in a concerted manner that terminates at a single atom is called cheletropic reaction.



- **Cope Rearrangement**

This is reaction where 1,5-dienes are thermally isomerized by 3,3-sigmatropic shift is known as Cope rearrangement.



Z may be different groups like alkyl-, aryl-, acyl-groups etc

3.10.4. Principles and Applications of Photochemical Reactions in Organic Chemistry

3.10.4a. Quantum Yield:

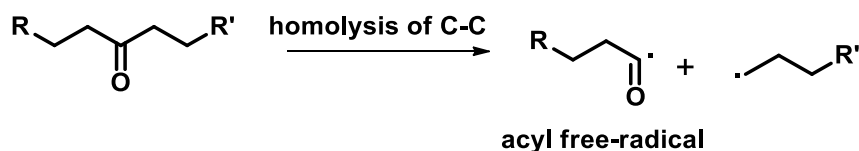
The efficiency of a photochemical reaction is shown in terms of quantum yield (ϕ) which is defined as as the number of molecules reacting per quantum of light absorbed.

$$\phi = \frac{\text{number of molecules reacting in a given time}}{\text{number of quantum of radiation absorbed in the same time}}$$

3.10.4b. Photochemical Reactions:

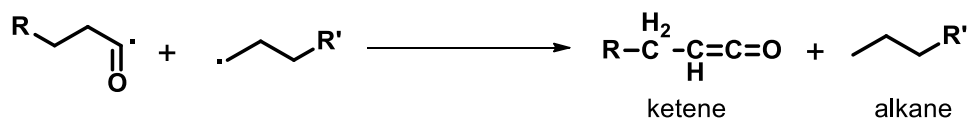
3.10.4b.I. Photolysis of Carbonyl Compounds:

- Norrish type I reaction or α -cleavage: A reaction in which C-C bond α to the carbonyl group takes place is known as Norrish type I reaction.

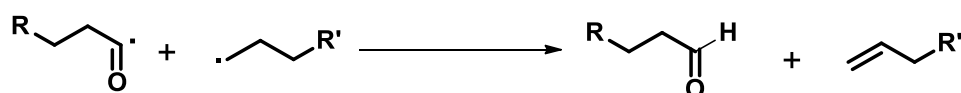


This acyl-radical can further undergoes the following reactions

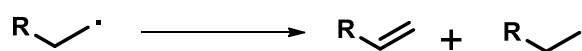
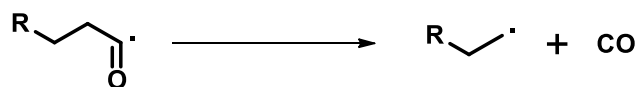
(a) Disproportionation reaction:



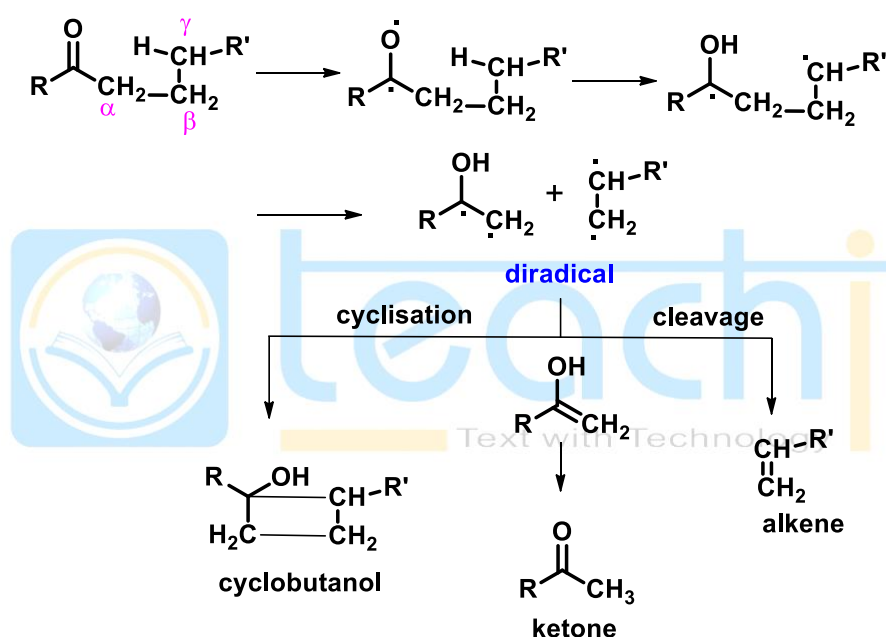
(b) Intermolecular hydrogen atom abstraction by the acyl radical:



(c) Decarbonylation followed by disproportionation reaction:



- Norrish type II reaction or β -cleavage
 - (a) In this reaction carbonyl compound contains at least one H-atom at γ -carbon.
 - (b) Intramolecular abstraction of γ -H atom occurs followed by α - β bond is cleaved.
 - (c) Cyclization of the diradicals affords aldehyde or ketone.

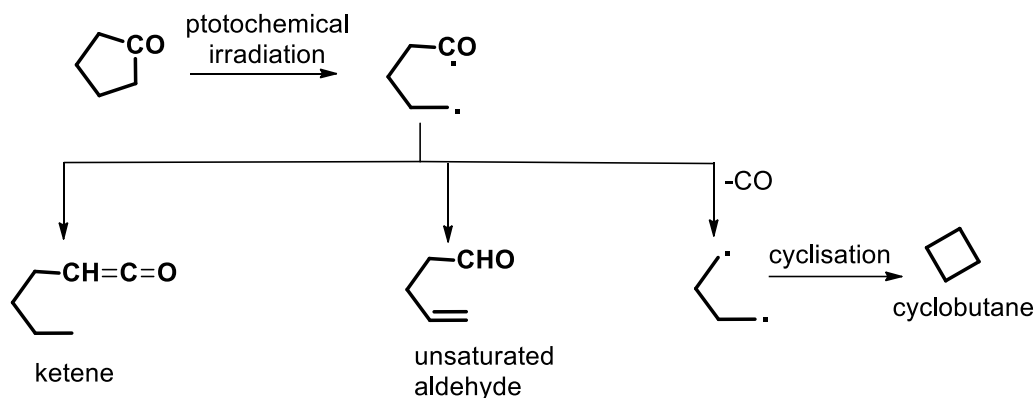


NB: (i) If α -carbon contains only H-atom on it, the major product is the carbonyl compound, where as if it has alkyl substituent, the major product would be cyclobutanol derivative.

(ii) This reaction is will favorable if the bond between α - β bond is weak.

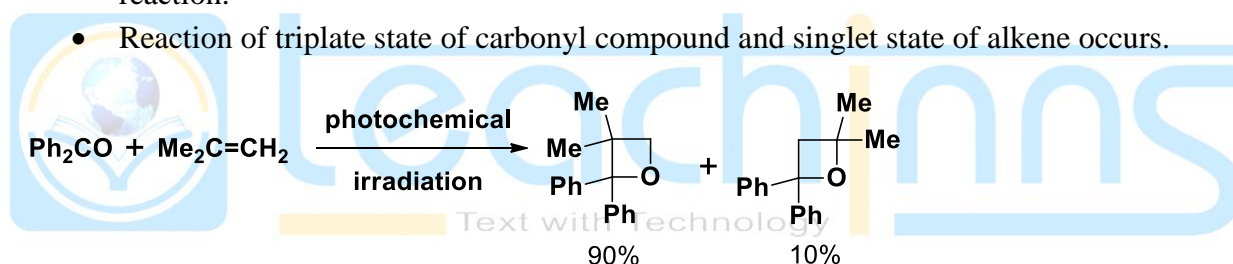
3.10.4b.II. Photochemical cleavage of cyclic ketones:

Photochemical cleavage of smaller cyclic ketone is demonstrated by Norrish type-I reaction and the diradical formed may undergo the following types of Intramolecular reaction.



3.10.4b.III. Photochemical Addition Reaction (Paterno Buchi Reaction)

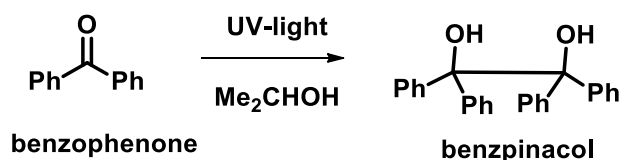
- Photochemical addition of alkenes to carbonyl compound is known as Paterno Buchi reaction.
- Reaction of triplate state of carbonyl compound and singlet state of alkene occurs.



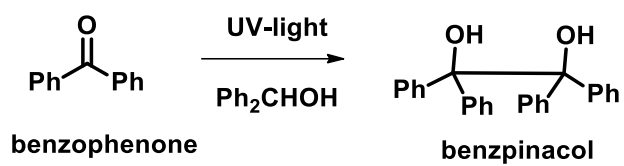
- Acetylene can also participate in Paterno-Buchi reaction and this reaction proceeds via an unstable oxetene derivative.

3.10.4b.IV Photochemical Dimerization or Photoreduction

- Upon irradiation with UV light of a diaryl or aryl alkyl ketone in presence of H-donor solvent like 2-propanol, dimerisation occurs and pinacol derivative is formed.
- The photo reduction of benzophenone leads to form benzpinacol.



- Benzpinacol is also formed by irradiating benzophenone and benzhydrol in benzene solution.



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