PHOTOCHEMISTRY

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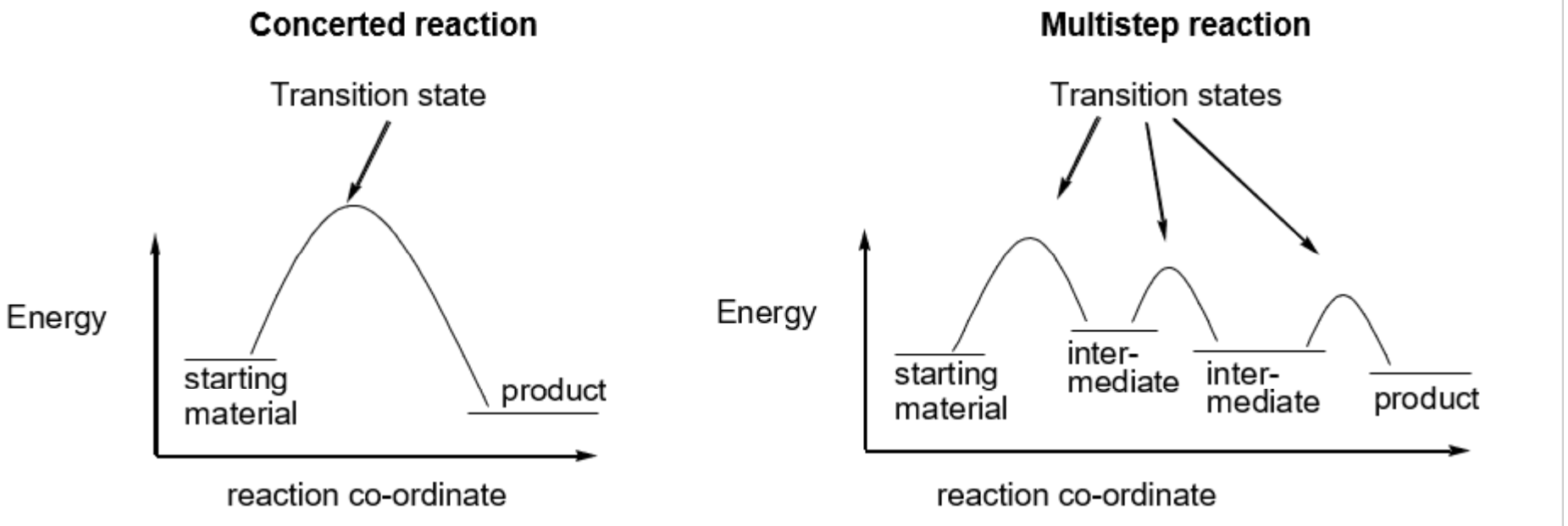
PERICYCLIC REACTION

- **Pericyclic** reactions are "Any concerted reaction in which bonds are formed or broken in a cyclic transitions state". (electrons move around in a circle). i.e. there is a single transition state from start to finish, in contrast to a stepwise reaction



- Pericyclic reactivity can be understood interms of frontier molecular orbital (FMO) theory and the outcome of reactions can be predicted using the Woodward-Hoffmann rules.

- **.** Pericyclic reactions require light or heat and are completely stereospecfic; that is, a single stereoisomer of the reactant forms a single stereoisomer of the product.

Properties of pericyclic reactions:

(a)Little, if any, solvent effect

(b)No nucleophiles or electrophiles involved.

(c) Not generally catalysed by Lewis acids.

(d)Highly stereospecific.

(e)Often photochemically promoted.

Classification:

1. Cycloaddition reaction .
2. Electrocyclic ring closing and ring opening reaction
3. Sigmatropic Rearrangements
4. Cheletropic

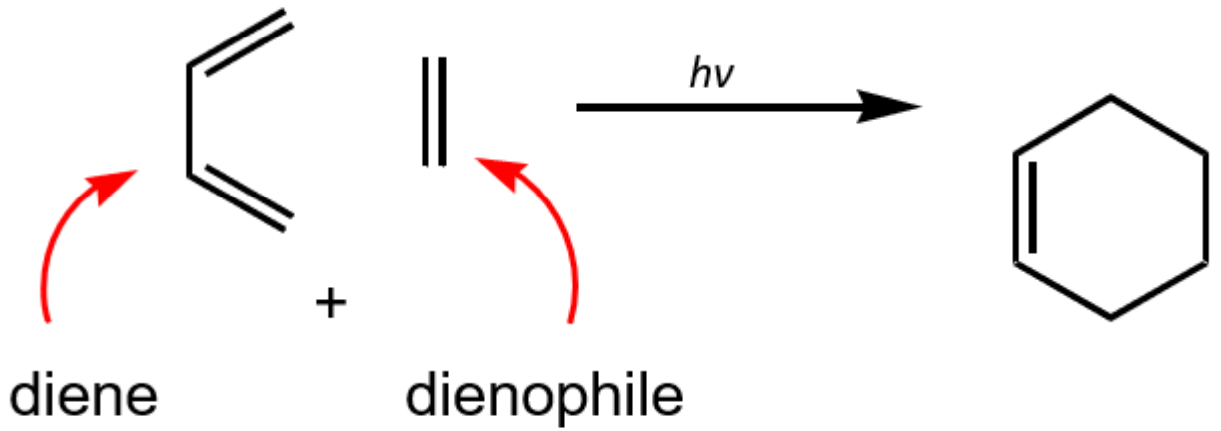
- Group Transfer

Cycloaddition reaction

- A **cycloaddition** is a pericyclic chemical reaction, in which "two or more unsaturated molecules (or parts of the same molecule) combine with the formation of a cyclic adduct in which there is a net reduction of the bond multiplicity." The resulting reaction is a cyclization reaction. Designated as [A+B].
- A and B refers to number of atoms containing π-electrons
- Three important classes of cycloaddition reactions
  - (i) Diels-Alder reaction
  - (iii) [2+2] Cycloaddition
  - (ii) [1,3]-Dipolar cycloaddition

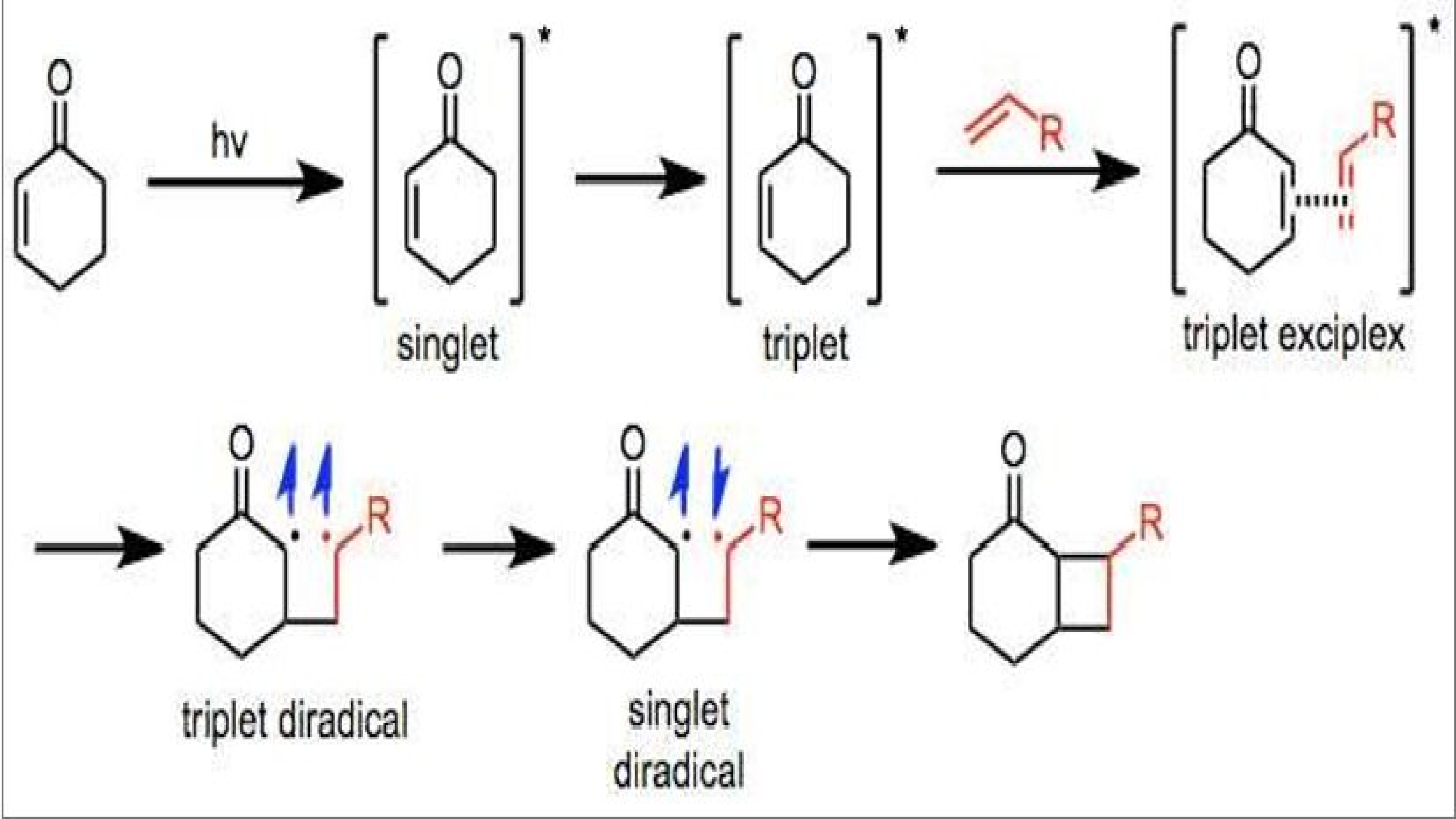
Diels-Alder Reaction

- Discovered by Professor Otto Diels and his student Kurt Alder in 1928 and received Nobel prize in 1950
- Reaction between a conjugated diene and dienophile.
- Highly effective method for the formation of cyclohexene ring



[2+2] Cycloaddition reaction

The **[2+2] photocycloaddition** is a cycloaddition-type reaction – it generally entails the formation of new molecules by the reaction of two unsaturated molecules via two atoms from each molecules (hence "[2 + 2]").


hv
singlet
triplet
R
triplet exciplex
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singlet
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Sigmatropic Rearrangements

•Molecular rearrangements in which a σ-bonded atom or group, flanked by one or more π-electron systems, shifts to a new location with a corresponding reorganization of the π-bonds are called sigmatropic reactions. The total number of σ-bonds and π-bonds remain unchanged. Diffenent type of sigmatropic rearrangement reaction are-

- (3,3)-sigmatropic rearrangement
- (2,3)-sigmatropic rearrangement
- (1,5)-sigmatropic rearrangement

•Electrocyclic Reactions

•An electrocyclic reaction is a reversible reaction that involves ring closure of a conjugated polyene to a cycloalkene, or ring opening of a cycloalkene to a conjugated polyene.

- For example, ring closure of 1,3,5-hexatriene forms 1,3cyclohexadiene, a product with one more ! bond and one fewer " bond than the reactant. Ring opening of cyclobutene forms 1,3butadiene, a product with one fewer ! bond and one more " bond than the reactant.