

M.Sc. Semester-IV
Core Course-9 (CC-9)
Synthetic Organic Chemistry



II. Pericyclic Reactions
2. Classification of Pericyclic Reactions



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II Pericyclic Reactions 20 Hrs

Molecular orbital symmetry, Frontier orbitals of ethylene, 1,3-butadiene, 1, 3, 5-hexatriene, allyl system, Classification of pericyclic reactions. FMO approach, Woodward-Hoffman correlation diagram method and PMO approach for pericyclic reaction under thermal and photochemical conditions.

Electrocyclic reactions: Conrotatory and disrotatory motion, $4n$ and $(4n+2)$ systems, Cycloaddition reaction: $[2+2]$ and $[4+2]$ cycloaddition reaction, Cycloaddition of ketones, Secondary effects in $[4+2]$ cycloaddition. Stereochemical effects on rate of cycloaddition reaction, Diels-Alder reaction, 1,3-dipolar cycloaddition, Chelotropic reaction, The Nazarov reaction.

Sigmatropic rearrangement: Suprafacial and antarafacial shift involving H and carbon-moieties, Peripatetic cyclopropane bridge, Retention and inversion of configuration, $[3,3]$ -, $[1,5]$ -, $[2,3]$ -, $[4,5]$ -, $[5,5]$ -, and $[9,9]$ -Sigmatropic rearrangements, Claisen rearrangements (including Aza-Claisen, Ireland-Claisen), Cope rearrangements (including Oxy-Cope, Aza-Cope), Sommelet-Hauser rearrangements, Group transfer reaction, Ene reaction, Mislow - Evans rearrangement, Walk rearrangement.

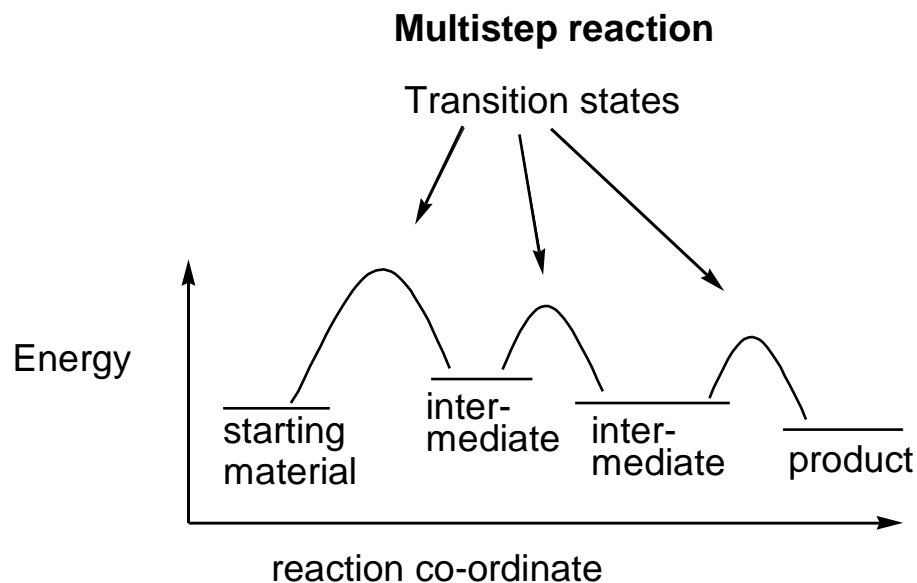
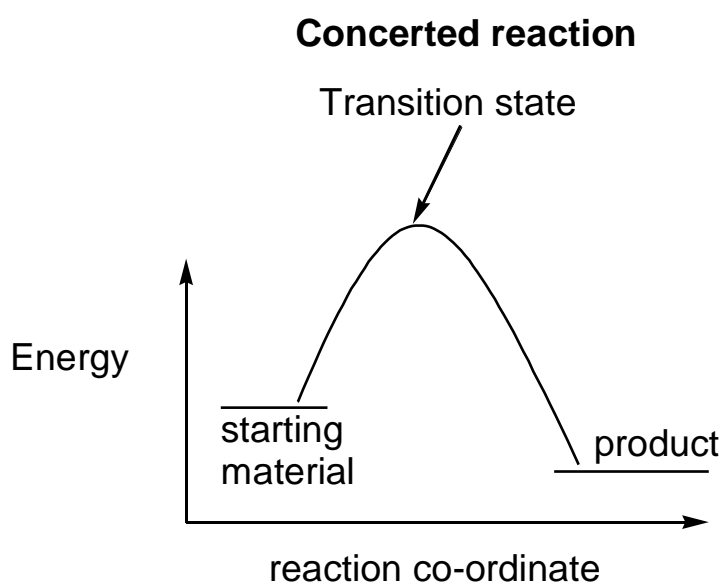
Coverage:

1. Classification of Pericyclic Reactions

Introduction: Unexpected results of cyclisation reactions

Pericyclic reactions are; “Any concerted reaction in which bonds are formed or broken in a cyclic transition 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.

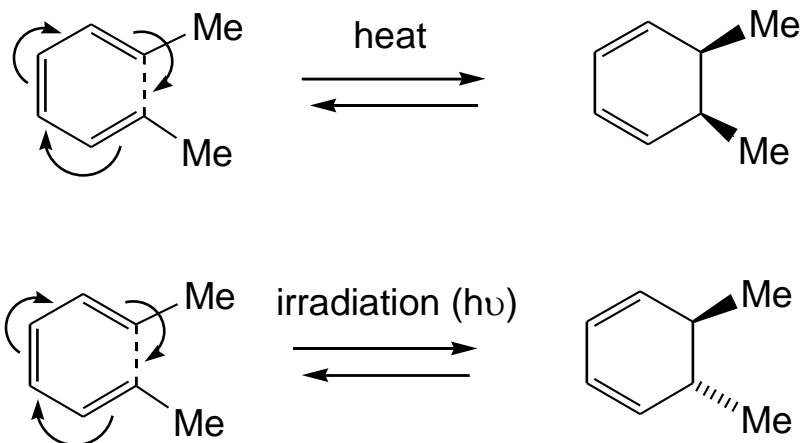


Properties of pericyclic reactions:

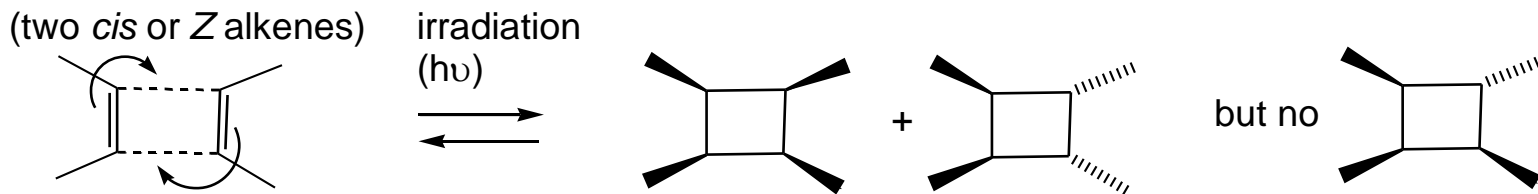
- (a) Little, if any, solvent effect
- (b) No nucleophiles or electrophiles involved.
- (c) Not generally catalysed by Lewis acids.
- (d) Highly stereospecific.
- (e) Often photochemically promoted.

Examples of pericyclic reactions:

1) Electrocyclisation reactions – Linear conjugated polyene converted into a cyclic product in one step. The mechanism is not particularly surprising, but the stereochemistry changes depending on whether heat or irradiation (typically UV-light) is used to promote the reaction. e.g.

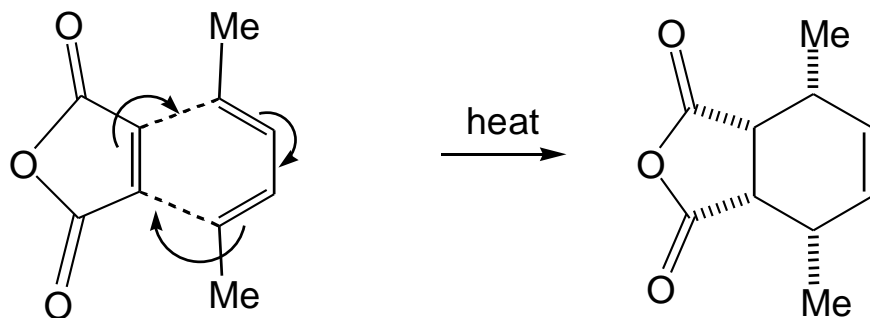


2) Cycloaddition reactions – Two linear conjugated polyenes converted onto a cyclic product in one step. Again, the stereochemistry of the reaction is remarkably reproducible. e.g.



Examples of pericyclic reactions, continued:

Example of a cycloadditions to give a 6-membered ring:

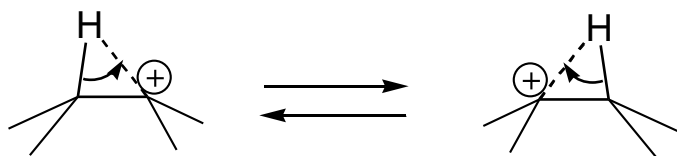


(one *cis* or *Z* alkene, and a *E,E*-diene)

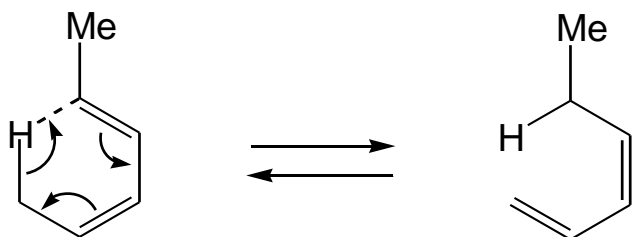
One diastereoisomer is favoured.

(Diels-Alder reaction!)

3) Sigmatropic rearrangement reactions: This involves a concerted migration of atoms or of groups of atoms. E.g. migration of a σ -bond.



This would be classified as a [1,2]-sigmatropic rearrangement (or shift).

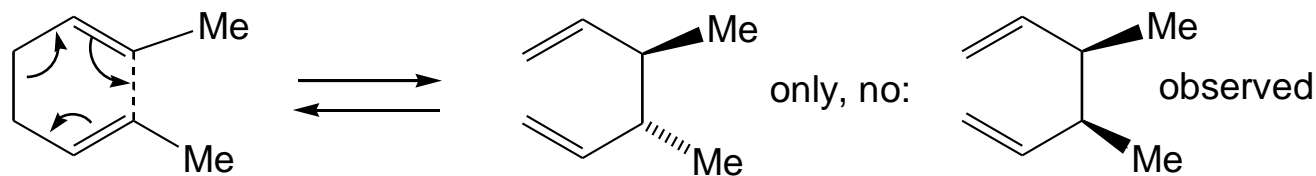


This would be classified as a [1,5]-sigmatropic rearrangement (or shift).

The numbering refers to the number of atoms in the transition state on either side of where bonds are made or broken.

Examples of pericyclic reactions, continued:

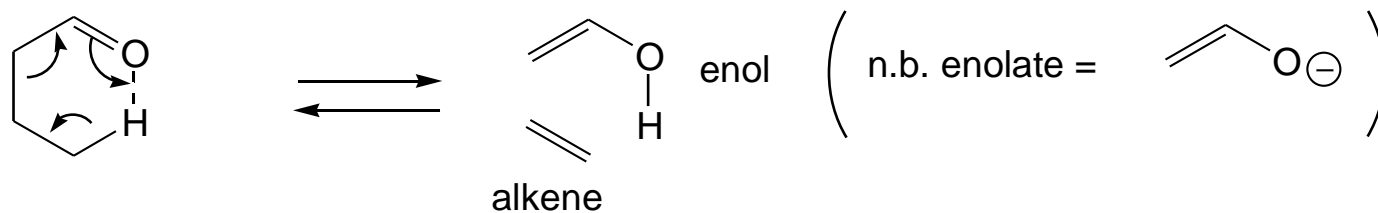
3) Sigmatropic rearrangement reactions: A high level of stereochemical control is often observed.



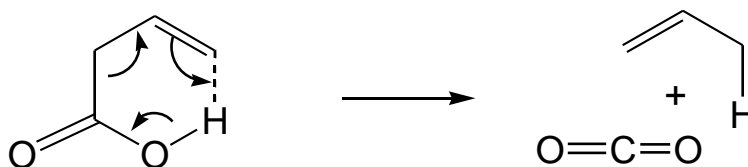
This would be classified as a [3,3]-sigmatropic rearrangement (or shift).

Other concerted reactions:

a) Ene reaction (synthetic chemists), or Norrish rearrangement (photochemists) or McLafferty rearrangement (for mass spectrometrists).

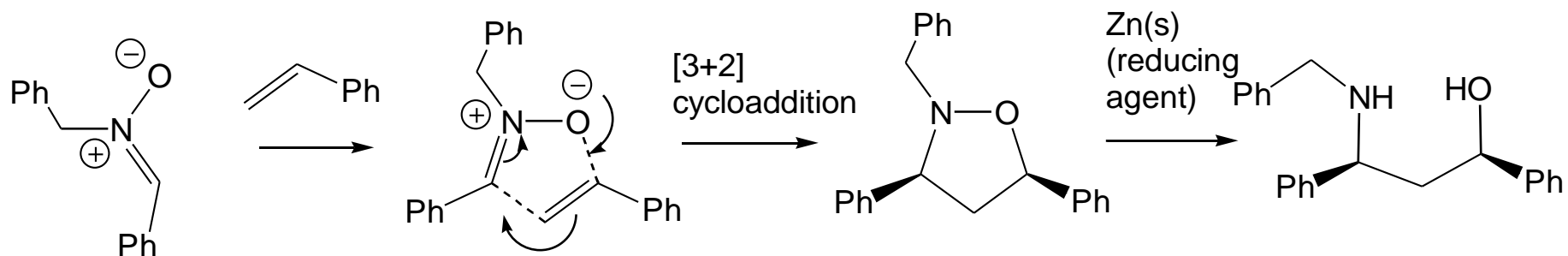


b) Decarboxylation reaction:

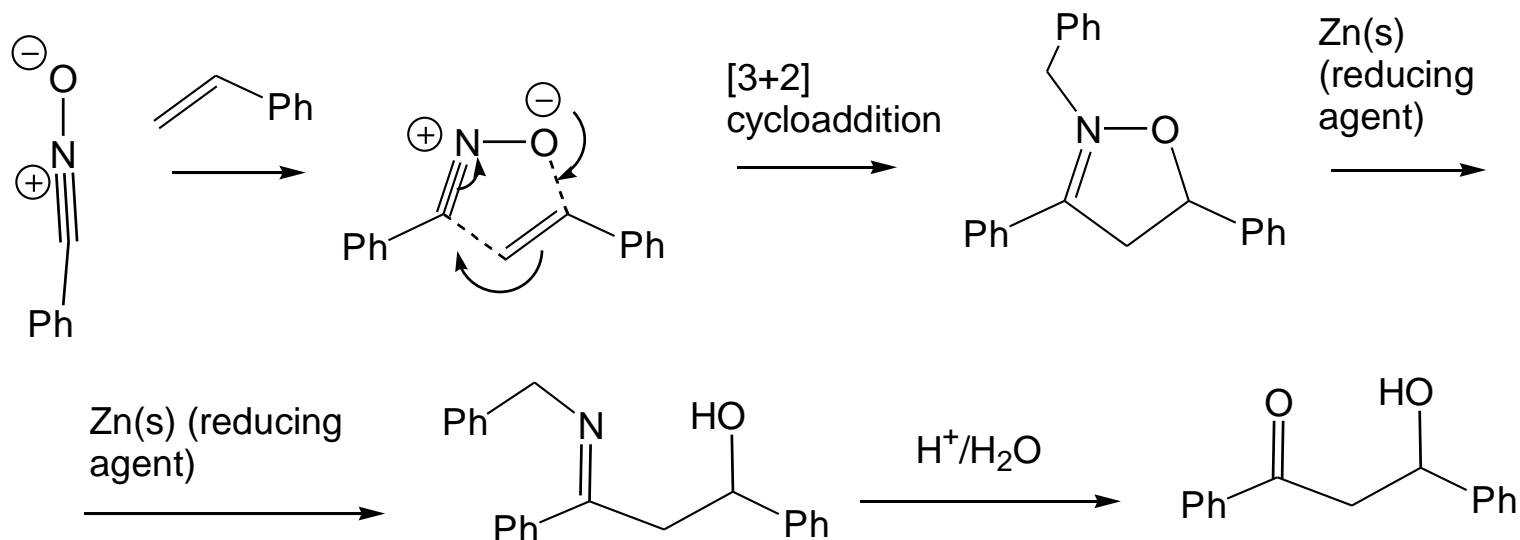


1,3-Dipolar cycloaddition reactions

The cycloaddition of nitrones to alkenes (below) is a 6-electron process which proceeds in a suprafacial manner. The cycloaddition product can be reductively opened, thus providing a stereoselective method for the synthesis of 1,3-aminoalcohols.

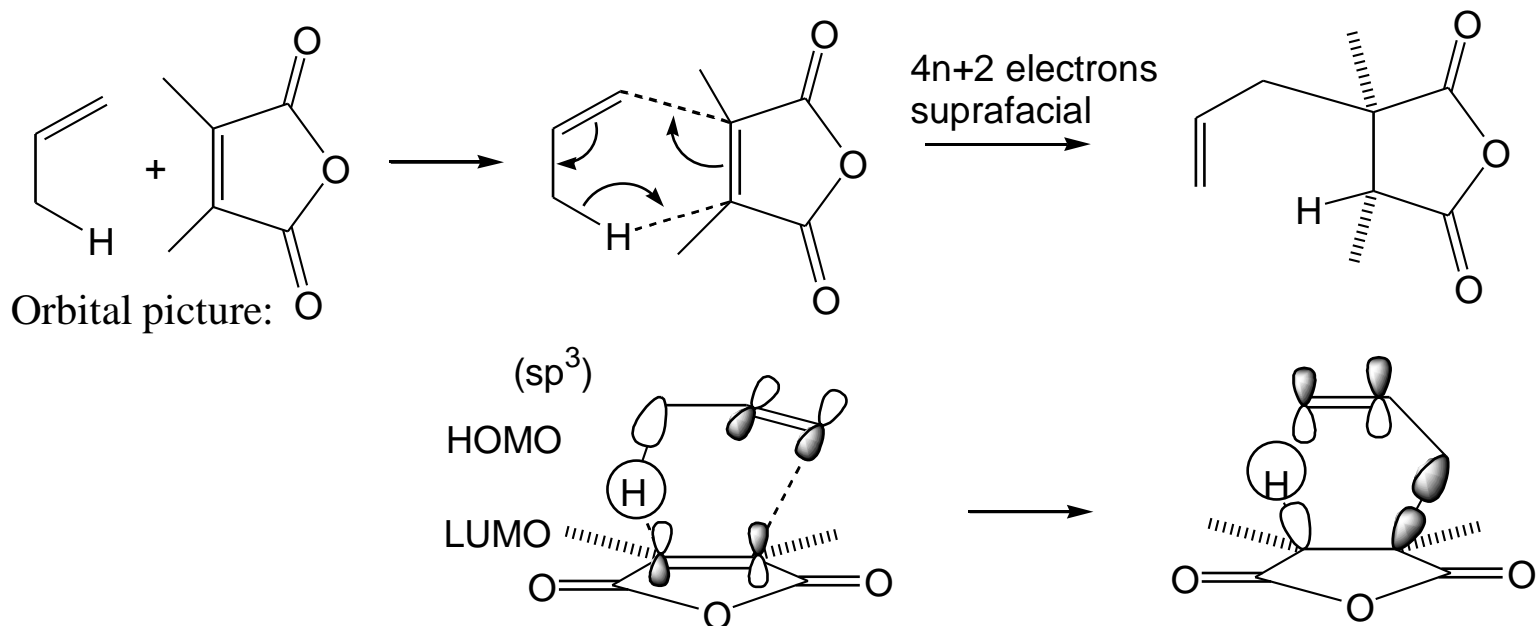


A similar cycloaddition of nitrile oxides provides a method for the synthesis of 3-hydroxy ketones, all these reactions involve $4n+2$ electrons and are suprafacial:



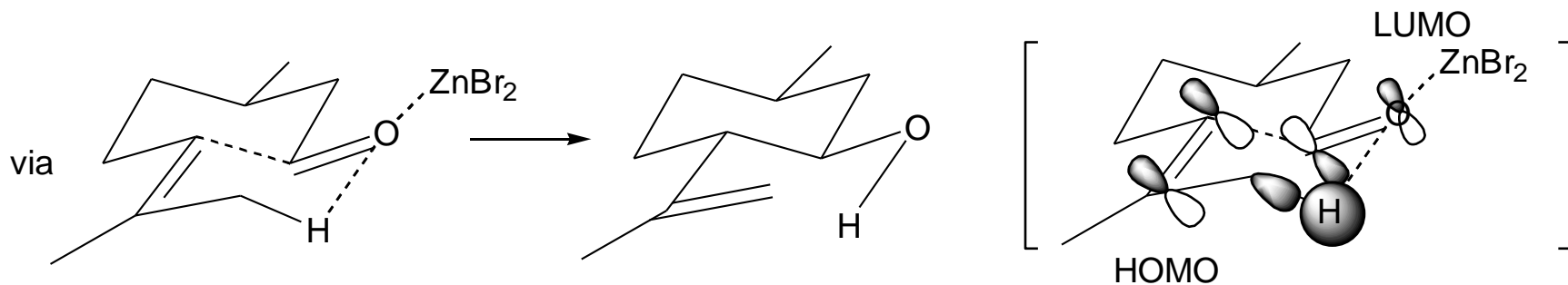
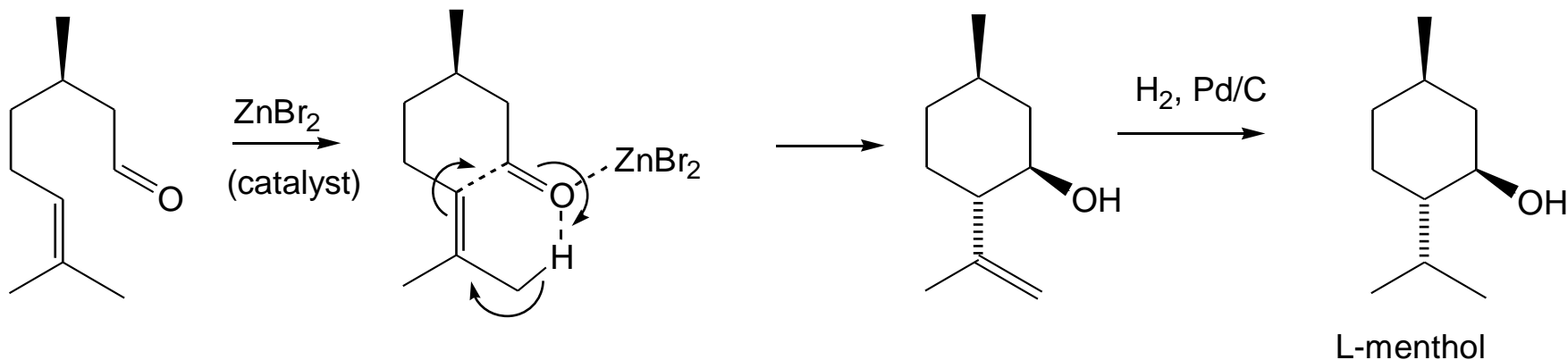
The Ene reaction; a type of cycloaddition

The ene reaction involves a cycloaddition between two alkenes, but with the formation of only a single C-C bond. A C-H bond is also formed in the process:



Menthol is prepared through an ene reaction:

The reaction below uses a mild Lewis acid. The chirality of the product comes entirely from the single chiral centre of the starting material. Note that the lone pair on the carbonyl oxygen is available for participation in this cyclisation.



This process allows menthol to be made more efficiently than through extraction from natural sources. How would you make the starting material?

Note

- The electrocyclic reactions and sigmatropic rearrangements are intramolecular reactions.
- The cycloaddition reactions are usually intermolecular reactions.

Common features among the pericyclic reactions

- are concerted reactions
- are highly stereoselective
- are not affected by catalysts

The configuration of the product formed depends on:

- The configuration of the reactant
- The number of conjugated double bonds or pairs of electrons in the reacting system
- Whether the reaction is a thermal or a photochemical reaction

A photochemical reaction takes place when a reactant absorbs light

A thermal reaction takes place without the absorption of light

Theory of Conservation of Orbital Symmetry

Explains the relationship among the structure and configuration of the reactant, the conditions (thermal or photochemical) under which the reaction takes place, and the configuration of the products.

States that in-phase orbitals overlap during the course of a pericyclic reaction.

Thank You



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