

Chapter 30 – Orbitals and Organic Chemistry: Pericyclic Reactions

Chapter Outline

- I. Molecular orbitals and pericyclic reactions of conjugated pi systems (Section 30.1).
 - A. Molecular orbitals of conjugated π systems.
 1. The p orbitals of the sp^2 -hybridized carbons of a polyene interact to form a set of π molecular orbitals.
 2. The energies of these orbitals depend on the number of nodes they have.
 - a. The molecular orbitals with fewer nodes are bonding MOs.
 - b. The molecular orbitals with more nodes are antibonding MOs.
 3. A molecular orbital description can be used for any conjugated π system.
 - a. In the ground state, only the bonding orbitals are used.
 - b. On irradiation with UV light, an electron is promoted to an antibonding orbital.
This is known as an excited state.
 - B. Molecular orbitals and pericyclic reactions.
 1. The mechanisms of pericyclic reactions can be explained by molecular orbital theory.
 - a. A pericyclic reaction can take place only if the lobes of the reactant MOs have the correct algebraic sign in the transition state.
 - b. If the symmetries of both reactant and product orbitals correlate, the reaction is symmetry-allowed.
 - c. If the symmetries don't correlate, the reaction is symmetry-disallowed.
The reaction may still take place, but only by a nonconcerted, high-energy pathway.
 2. A modification of MO theory states that only two MOs need be considered (frontier orbitals):
 - a. The highest occupied molecular orbital (HOMO).
 - b. The lowest unoccupied molecular orbital (LUMO).
- II. Electrocyclic reactions (Sections 30.2 – 30.4).
 - A. General description of electrocyclic reactions Section 30.2).
 1. Nature of electrocyclic reactions.
 - a. An electrocyclic reaction involves the cyclization of a conjugated polyene.
One π bond is broken, a new σ bond is formed and a cyclic compound results.
 - b. Electrocyclic reactions are reversible.
 - i. The triene–cyclohexadiene equilibrium favors the ring-closed product.
 - ii. The diene–cyclobutene equilibrium favors the ring-opened product.
 2. Stereochemistry of electrocyclic reactions.
 - a. A specific E,Z bond isomer yields a specific cyclic stereoisomer under thermal conditions.
 - b. The stereochemical results are opposite when the reactions are carried out under photochemical conditions.
 3. Orbital explanation for outcomes of electrocyclic reactions.
 - a. The signs of the outermost lobes of the interacting orbitals explain these results.
For a bond to form, the lobes must be of the same sign.
 - b. The outermost π lobes of the polyene must rotate so that the lobes that form the bonds are of the same sign.
 - i. If the lobes are on the same side of the molecule, the lobes must rotate in opposite directions – disrotatory motion.

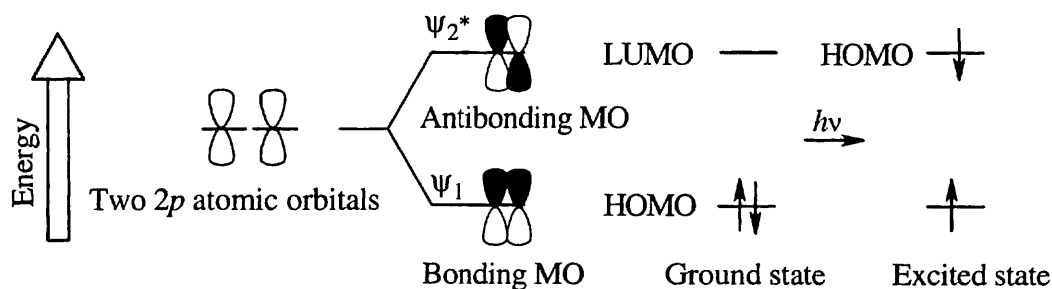
- ii. If the lobes of the same sign are on opposite sides of the polyene, both lobes must rotate in the same direction – conrotatory motion.
- B. Stereochemistry of thermal electrocyclic reactions (Section 30.3).
 1. The stereochemistry of an electrocyclic reaction is determined by the symmetry of the polyene HOMO.
 2. The ground-state electronic configuration is used to identify the HOMO for thermal reactions.
 - a. For trienes, the HOMO has lobes of like sign on the same side of the molecule, and ring-closure is disrotatory.
 - b. For dienes, ring closing is conrotatory.
 3. In general, polyenes with odd numbers of double bonds undergo disrotatory thermal electrocyclic reactions, and polyenes with even numbers of double bonds undergo conrotatory thermal electrocyclic reactions.
- C. Stereochemistry of photochemical electrocyclic reactions (Section 30.4).
 1. UV irradiation of a polyene causes excitation of one electron from the ground-state HOMO to the ground-state LUMO.
 2. UV irradiation changes the symmetry of HOMO and LUMO and also changes the reaction stereochemistry.
 - a. Photochemical electrocyclic reactions of trienes occur with conrotatory motion.
 - b. Photochemical electrocyclic reactions of dienes occur with disrotatory motion.
 3. Thermal and photochemical electrocyclic reactions always take place with opposite stereochemistry.
- III. Cycloaddition reactions (Sections 30.5 – 30.6).
 - A. General description of cycloaddition reactions (Section 30.5).
 1. A cycloaddition reaction is a reaction in which two unsaturated molecules add to give a cyclic product.
 2. Cycloadditions are controlled by the orbital symmetry of the reactants.

Reactions that are symmetry-disallowed either don't take place or occur by a higher-energy nonconcerted pathway.
 3. The Diels–Alder cycloaddition is an example.
 - a. Reaction occurs between a diene and a dienophile to yield a cyclic product.
 - b. The products have a specific stereochemistry.
 - c. The reaction is known as a $[4 + 2]$ cycloaddition.
 4. Cycloadditions can only occur if the terminal π lobes have the correct stereochemistry.
 - a. In suprafacial cycloadditions, a bonding interaction takes place between lobes on the same face of one reactant and lobes on the same face of the other reactant.
 - b. Antarafacial cycloadditions occur between lobes on the same face of one reactant and lobes on opposite faces of the other reactant.
 - c. Often, antarafacial cycloadditions are symmetry-allowed but geometrically constrained.
 - B. Stereochemistry of cycloadditions (Section 30.6).
 1. A cycloaddition reaction takes place when a bonding interaction occurs between the HOMO of one reactant and the LUMO of the other reactant.
 2. The symmetries of the terminal lobes of the HOMO and LUMO of the reactants in a $[4 + 2]$ thermal cycloaddition allow the reaction to proceed with suprafacial geometry.
 3. For $[2 + 2]$ cycloadditions:
 - a. Orbital symmetry shows that thermal cyclization must occur by an antarafacial pathway.
 - b. Because of geometrical constraints, thermal $[2 + 2]$ cycloadditions aren't seen.

- c. Photochemical [2 + 2] cycloadditions take place because the addition can occur by a suprafacial pathway.
 - 4. Thermal and photochemical cycloadditions always take place by opposite stereochemical pathways.
- IV. Sigmatropic rearrangements (Sections 30.7 – 30.8).
- A. General description of sigmatropic rearrangements (Section 30.7).
 - 1. In a sigmatropic rearrangement, a σ -bonded atom or group migrates across a π electron system.
 - a. A σ bond is broken, the π bonds move, and a new σ bond is formed in the product.
 - b. The σ bonded group can be either at the end or in the middle of the π system.
 - c. The notation [3,3] indicates the positions in the groups to which migration occurs.
 - 2. Sigmatropic rearrangements are controlled by orbital symmetry.
 - a. Migration of a group across the same face of the π system is suprafacial rearrangement.
 - b. Migration from one face to the other face is antarafacial rearrangement.
 - c. Both types of rearrangements are symmetry-allowed, but suprafacial rearrangements are geometrically easier.
 - B. Examples of sigmatropic rearrangements (Section 30.8).
 - 1. The [1,5] migration of a hydrogen atom across two double bonds of a π system is very common.
Thermal [1,3] hydrogen shifts are unknown.
 - 2. The Cope rearrangement and the Claisen rearrangement involve reorganization of an odd number of electron pairs and proceed by suprafacial geometry.
- V. A summary of rules for pericyclic reactions (Section 30.9).
- A. Thermal reactions with an even number of electron pairs are either conrotatory or antarafacial.
 - B. A change from thermal to photochemical, or from even to odd, changes the outcome to disrotatory/suprafacial.
 - C. A change of both thermal and even causes no change.

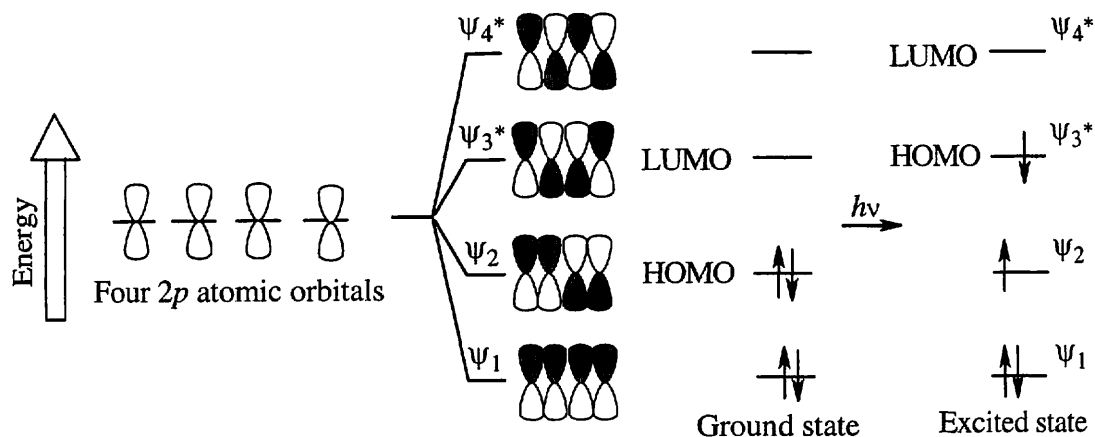
Solutions to Problems

30.1 For ethylene:



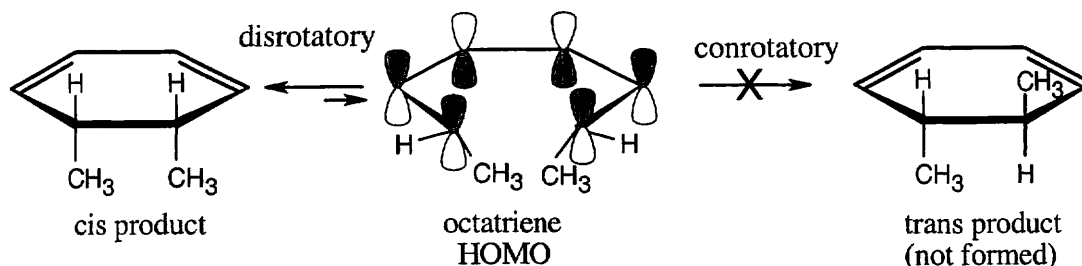
The two π electrons of ethylene occupy ψ_1 in the ground state, making ψ_1 the HOMO and ψ_2^* the LUMO. In the excited state, one electron occupies ψ_1 and the other occupies ψ_2^* , making ψ_2^* the HOMO. Since all orbitals are occupied in the excited state, there is no LUMO.

For 1,3-butadiene:



In the ground state, ψ_2 is the HOMO, and ψ_3^* is the LUMO. In the excited state, ψ_3^* is the HOMO, and ψ_4^* is the LUMO.

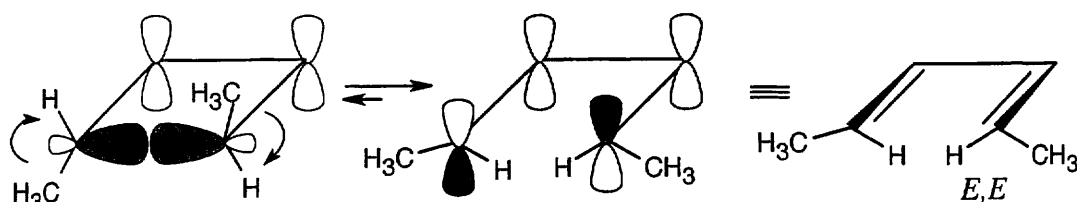
30.2



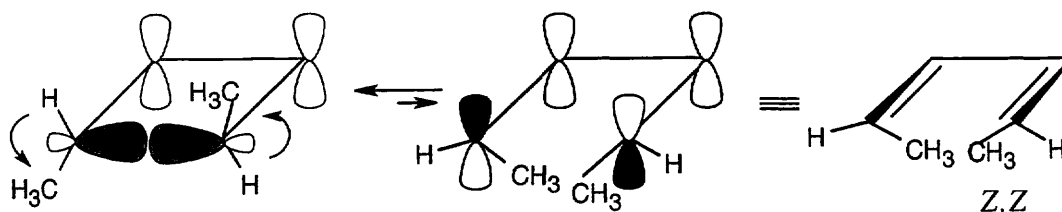
The symmetry of the octatriene HOMO predicts that ring closure occurs by a disrotatory path and that only *cis* product is formed.

30.3 Note: *Trans*-3,4-dimethylcyclobutene is chiral; the *S,S* enantiomer will be used for this argument.

Path A:

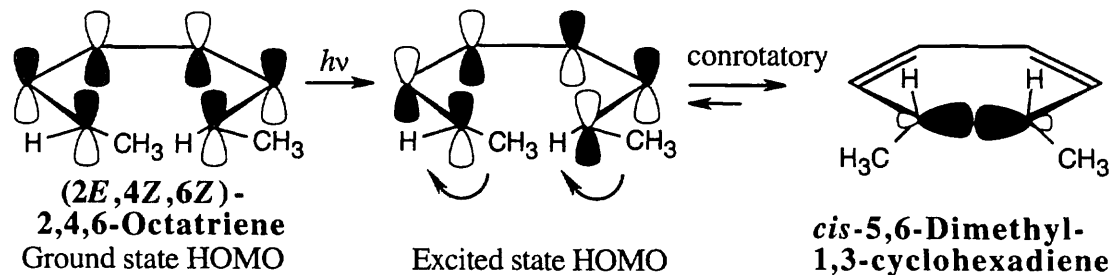
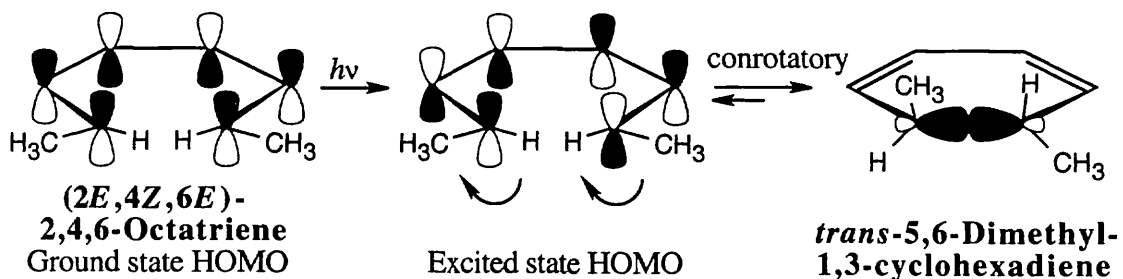


Path B:



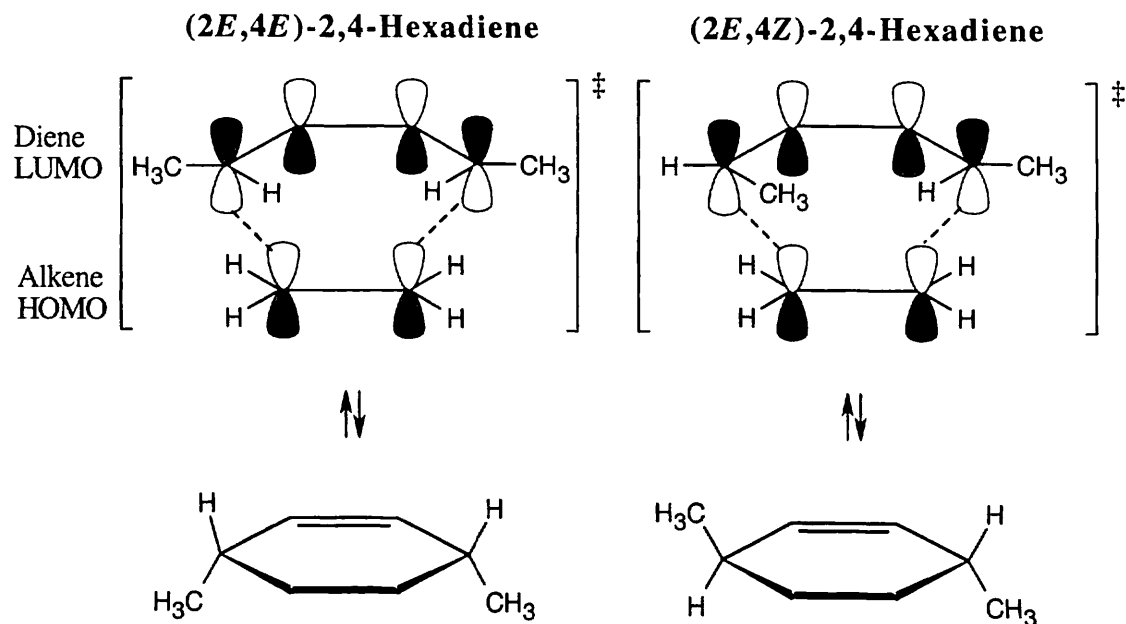
Conrotatory ring opening of *trans*-3,4-dimethylcyclobutene can occur in either a clockwise or a counterclockwise manner. Clockwise opening (**path A**) yields the *E,E* isomer; counterclockwise opening (**path B**) yields the *Z,Z* isomer. Production of (2*Z*,4*Z*)-hexadiene is disfavored because of steric strain between the methyl groups in the transition state leading to ring-opened product.

30.4



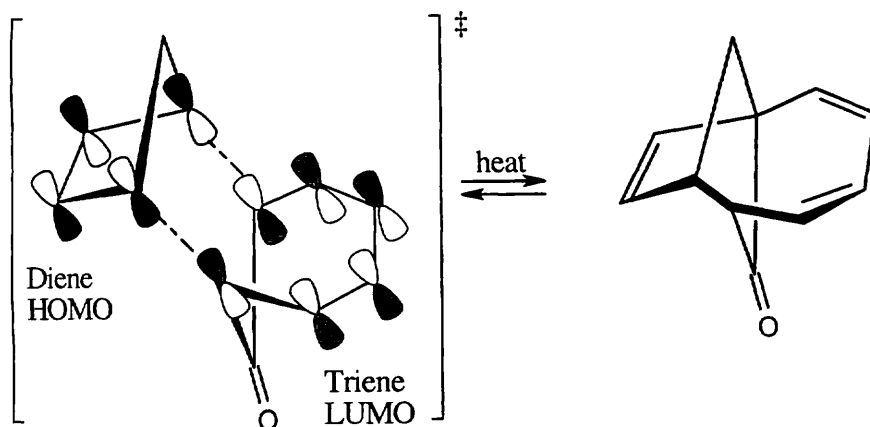
Photochemical electrocyclic reactions of 6 π electron systems always occur in a conrotatory manner.

30.5



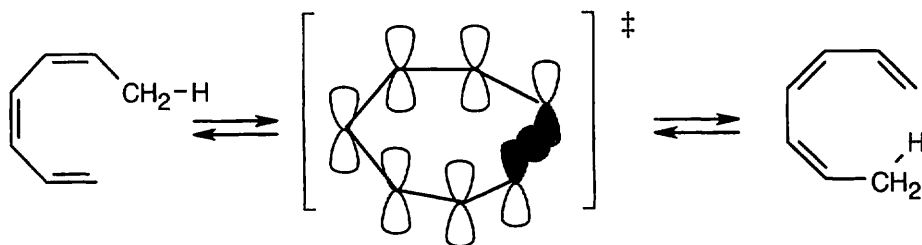
The Diels–Alder reaction is a thermal [4 + 2] cycloaddition, which occurs with suprafacial geometry. The stereochemistry of the diene is maintained in the product.

30.6

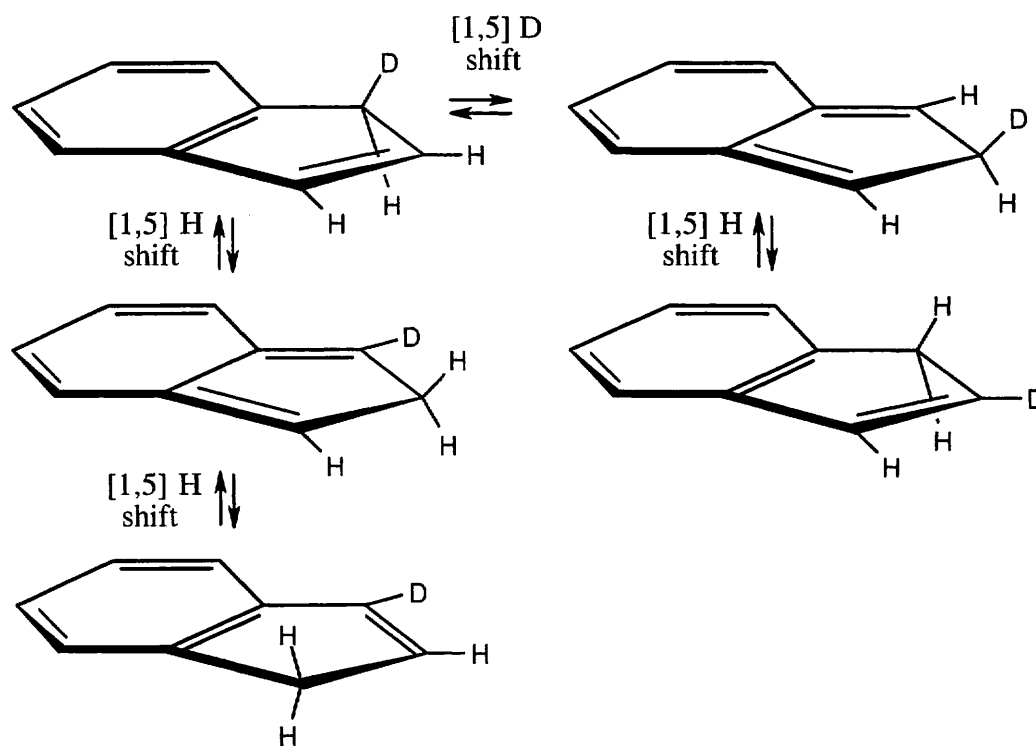


The reaction of cyclopentadiene and cycloheptatrienone is a [6 + 4] cycloaddition. This thermal cycloaddition proceeds with suprafacial geometry since five electron pairs are involved in the concerted process. The π electrons of the carbonyl group do not take part in the reaction.

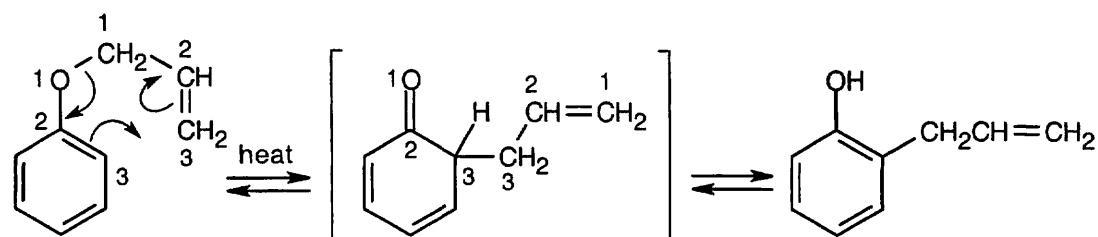
30.7 This [1,7] sigmatropic reaction proceeds with antarafacial geometry because four electron pairs are involved in the rearrangement.



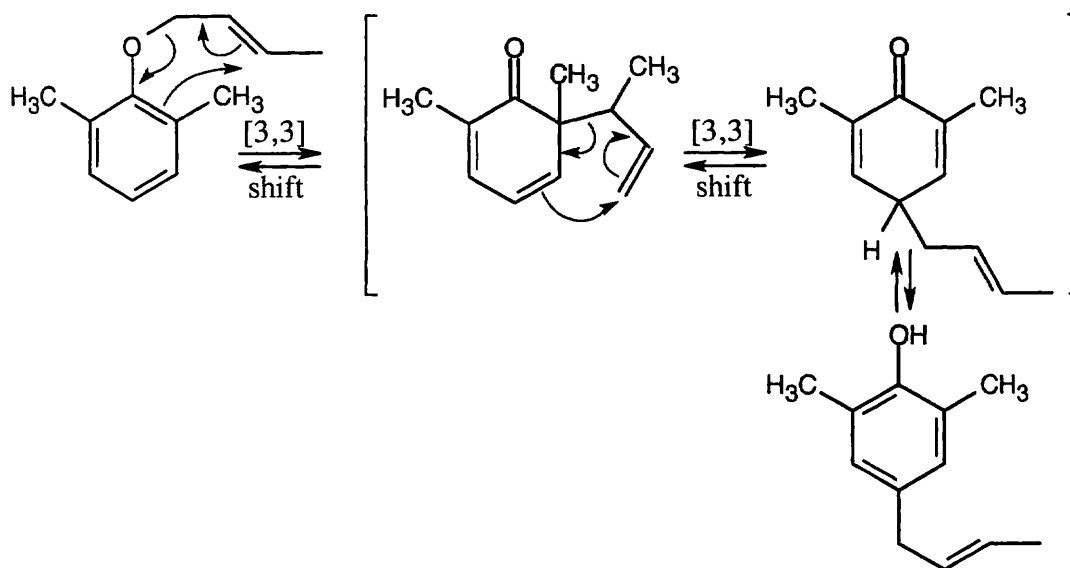
- 30.8** Scrambling of the deuterium label of 1-deuterioindene occurs by a series of [1,5] sigmatropic rearrangements. This thermal reaction involves three electron pairs – one pair of π electrons from the six-membered ring, the π electrons from the five-membered ring, and two electrons from a carbon-deuterium (or hydrogen) single bond – and proceeds with suprafacial geometry.



30.9



The Claisen rearrangement of an unsubstituted allyl phenyl ether is a [3,3] sigmatropic rearrangement in which the allyl group usually ends up in the position *ortho* to oxygen. In this problem both *ortho* positions are occupied by methyl groups. The Claisen intermediate undergoes a second [3,3] rearrangement, and the final product is *p*-allyl phenol.

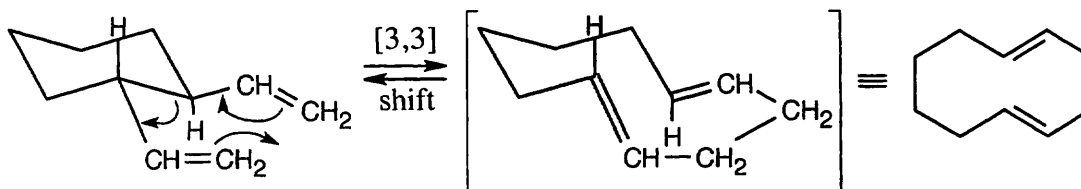


30.10

| Type of reaction | Number of electron pairs | Stereochemistry |
|---|--------------------------|-----------------|
| (a) Thermal electrocyclic | four | conrotatory |
| (b) Photochemical electrocyclic | four | disrotatory |
| (c) Photochemical cycloaddition | four | suprafacial |
| (d) Thermal cycloaddition | four | antarafacial |
| (e) Photochemical sigmatropic rearrangement | four | suprafacial |

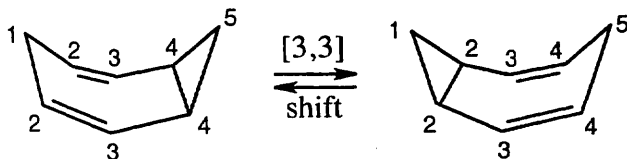
Visualizing Chemistry

30.11



This reaction is a [3,3] sigmatropic rearrangement that yields 1,5-cyclodecadiene as a product.

30.12

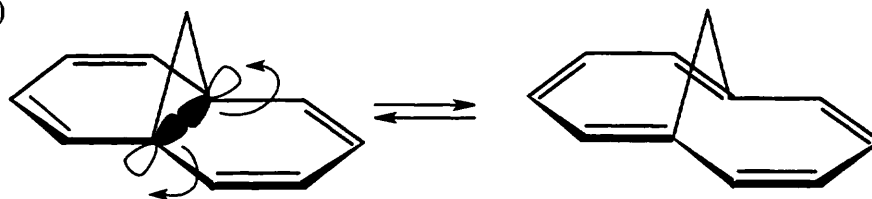


The ^{13}C NMR spectrum of homotropilidene would show five peaks if rearrangement were slow. In fact, rearrangement occurs at a rate that is too fast for NMR to detect. The ^{13}C NMR spectrum taken at room temperature is an average of the two equilibrating forms, in which positions 1 and 5 are equivalent, as are positions 2 and 4. Thus, only three distinct types of carbons are visible in the ^{13}C NMR spectrum of homotropilidene.

Additional Problems

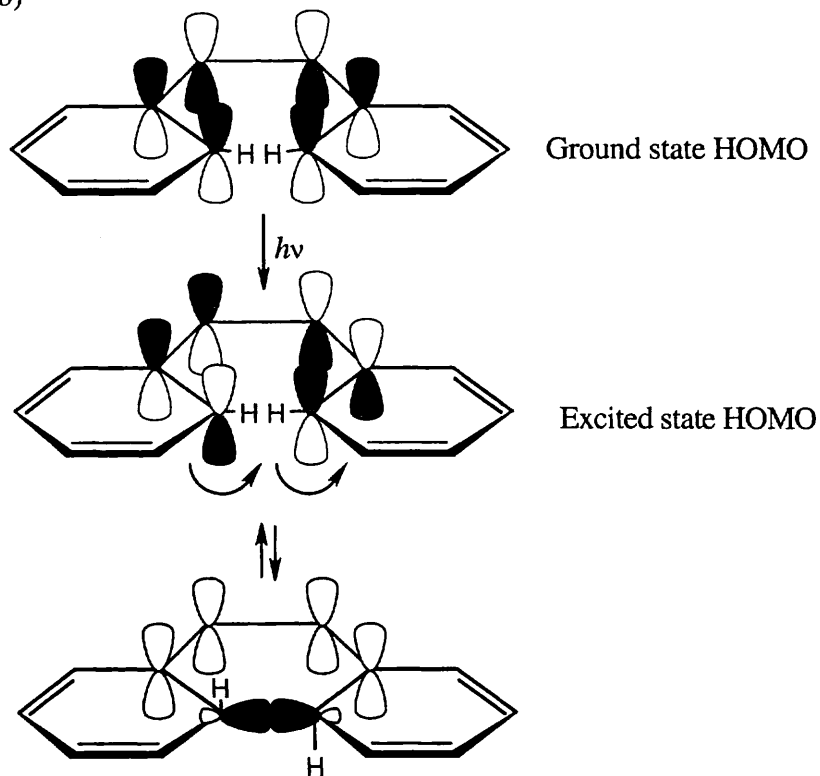
30.13

(a)



Rotation of the orbitals in the 6π electron system occurs in a disrotatory fashion. According to the rules in Table 30.1, the reaction should be carried out under thermal conditions.

(b)

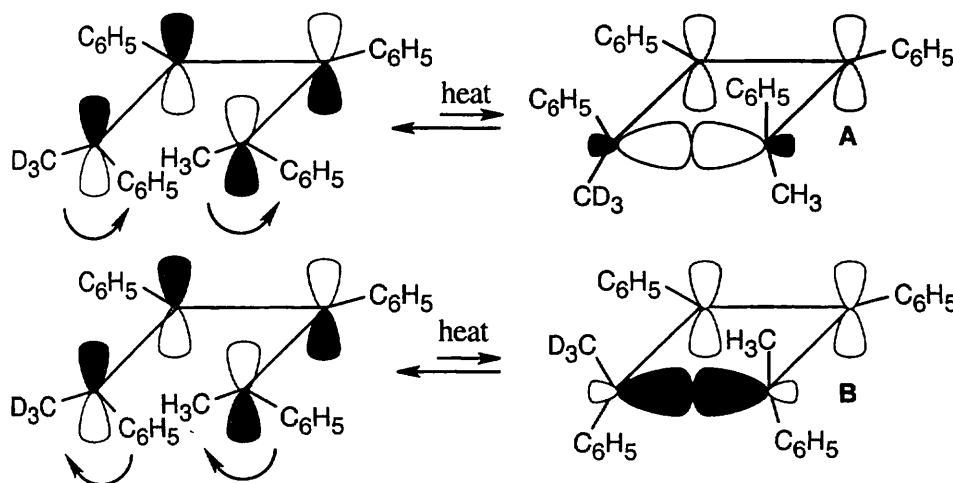


For the hydrogens to be *trans* in the product, rotation must occur in a conrotatory manner. This can happen only if the HOMO has the symmetry pictured. For a 6π electron system, this HOMO must arise from photochemical excitation of a π electron. To obtain a product having the correct stereochemistry, the reaction must be carried out under photochemical conditions.

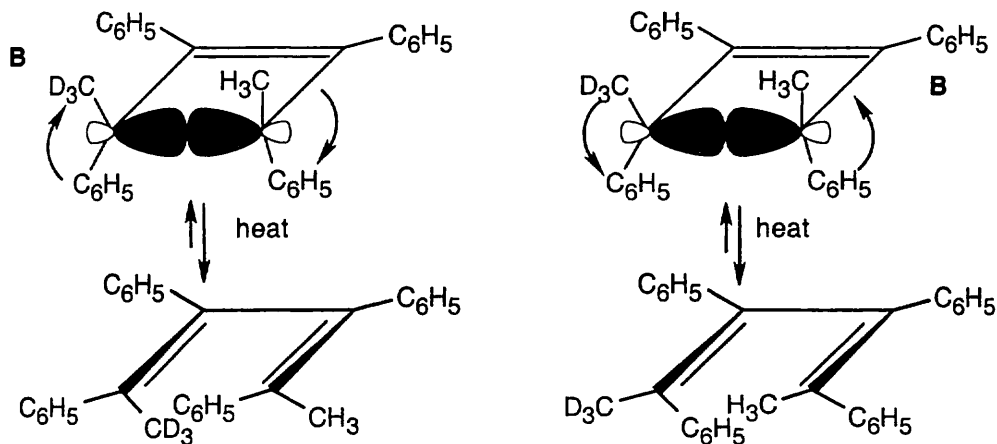
30.14 Tables 30.1 – 30.3 may be helpful. The first step is always to find the number of electron pairs involved in the reaction.

| Type of reaction | Number of electron pairs | Stereochemistry |
|---|--------------------------|-----------------|
| (a) Photochemical [1,5] sigmatropic rearrangement | 3 | antarafacial |
| (b) Thermal [4 + 6] cycloaddition | 5 | suprafacial |
| (c) Thermal [1,7] sigmatropic rearrangement | 4 | antarafacial |
| (d) Photochemical [2 + 6] cycloaddition | 4 | suprafacial |

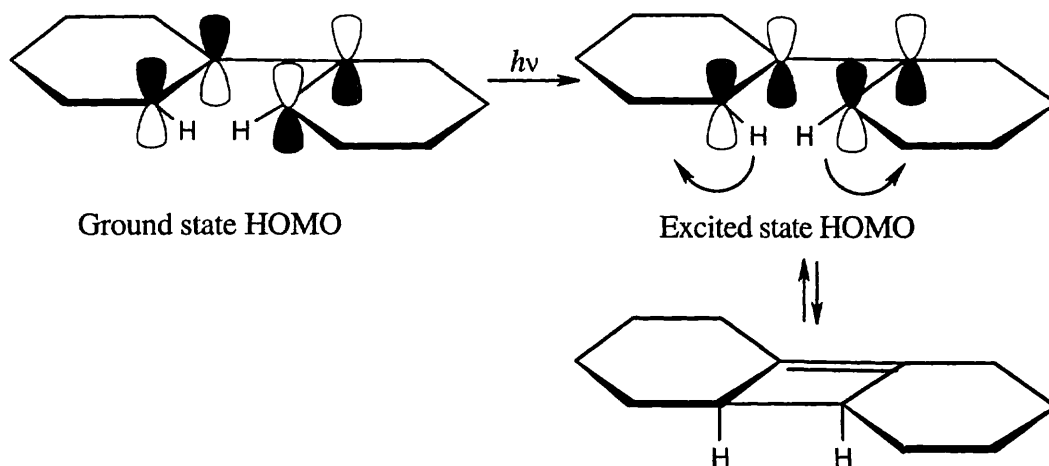
30.15 The diene can cyclize by either of two conrotatory paths to form cyclobutenes **A** and **B**.



Opening of each cyclobutene ring can occur by either of two conrotatory routes to yield the isomeric dienes. Using **B** as an example:

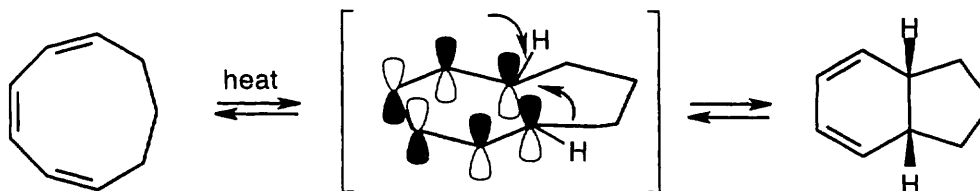


- 30.16** A photochemical electrocyclic reaction involving two electron pairs proceeds in a *disrotatory* manner (Table 30.1).

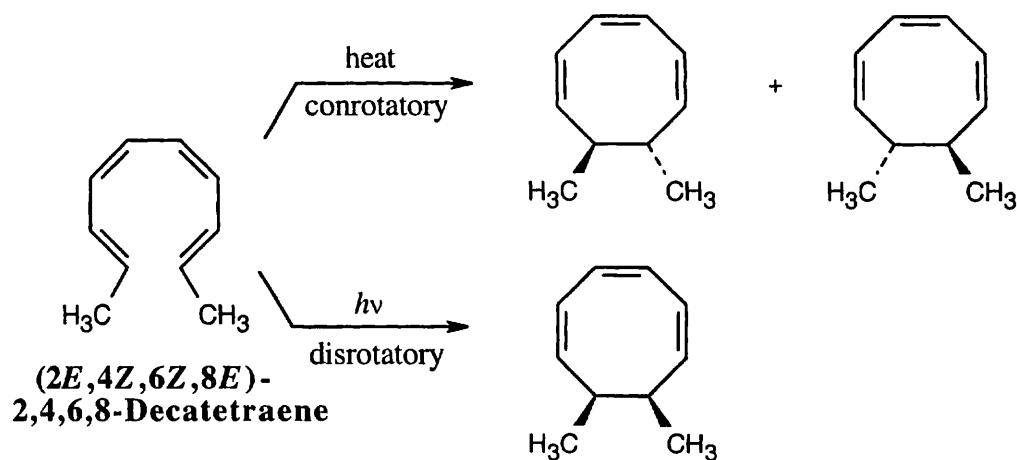


The two hydrogen atoms in the four-membered ring are *cis* to each other in the cyclobutene product.

- 30.17** The cyclononatriene is a 6π electron system that cyclizes by a disrotatory route under thermal conditions. The two hydrogens at the ring junction have a *cis* relationship.

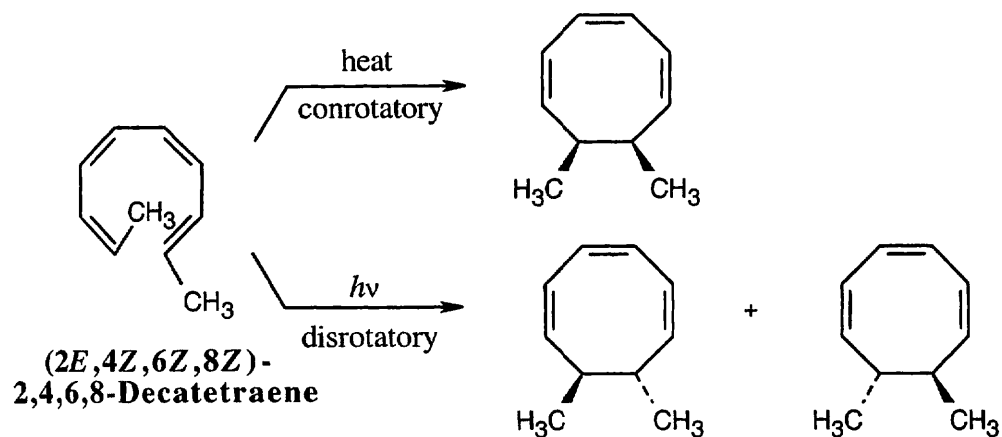


30.18



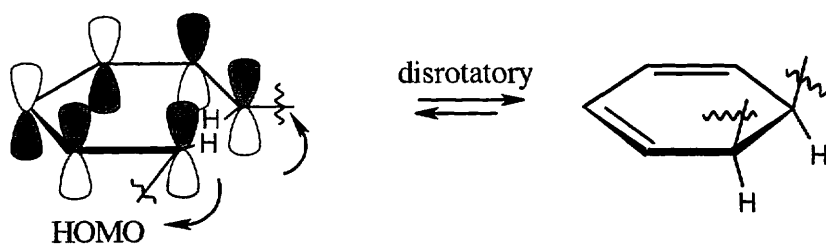
Four electron pairs undergo reorganization in this electrocyclic reaction. The thermal reaction occurs with conrotatory motion to yield a pair of enantiomeric *trans*-7,8-dimethyl-1,3,5-cyclooctatrienes. The photochemical cyclization occurs with disrotatory motion to yield the *cis*-7,8-dimethyl isomer.

30.19

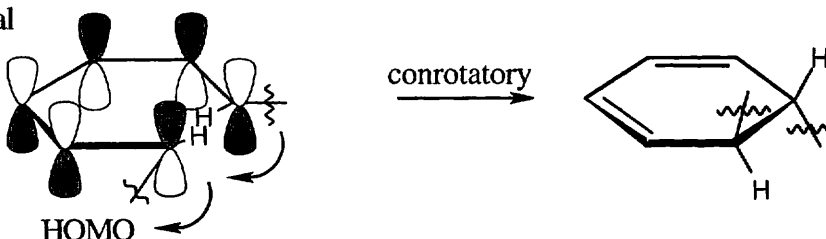


30.20

Thermal reaction:

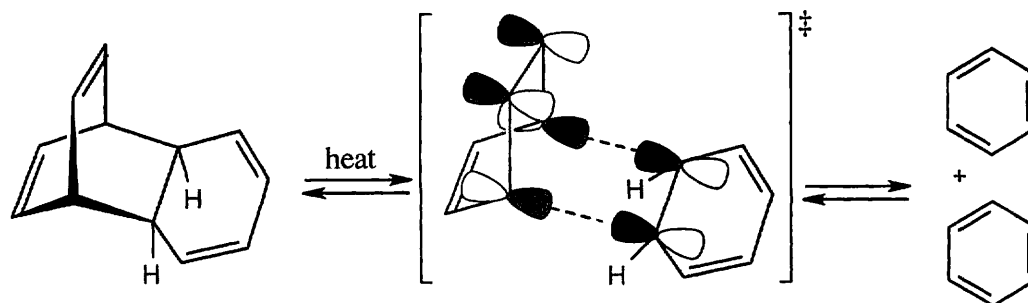


Photochemical reaction:

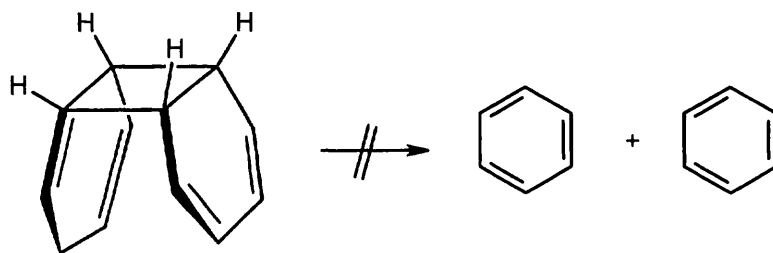


Two electrocyclic reactions, involving three electron pairs each, occur in this isomerization. The thermal reaction is a disrotatory process that yields two *cis*-fused six-membered rings. The photochemical reaction yields the *trans*-fused isomer. The two pairs of π electrons in the eight-membered ring do not take part in the electrocyclic reaction.

30.21



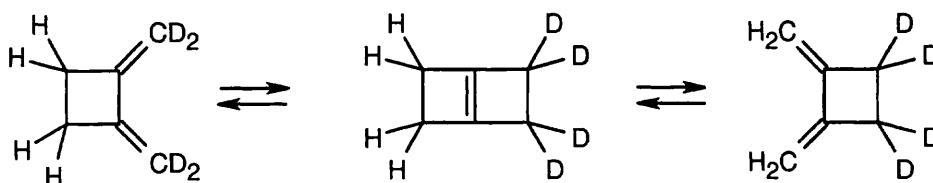
This reaction is a reverse $[4 + 2]$ cycloaddition. The reacting orbitals have the correct symmetry for the reaction to take place by a favorable suprafacial process.



This $[2 + 2]$ reverse cycloaddition is not likely to occur as a concerted process because the antarafacial geometry required for the thermal reaction is not possible for a four π -electron system.

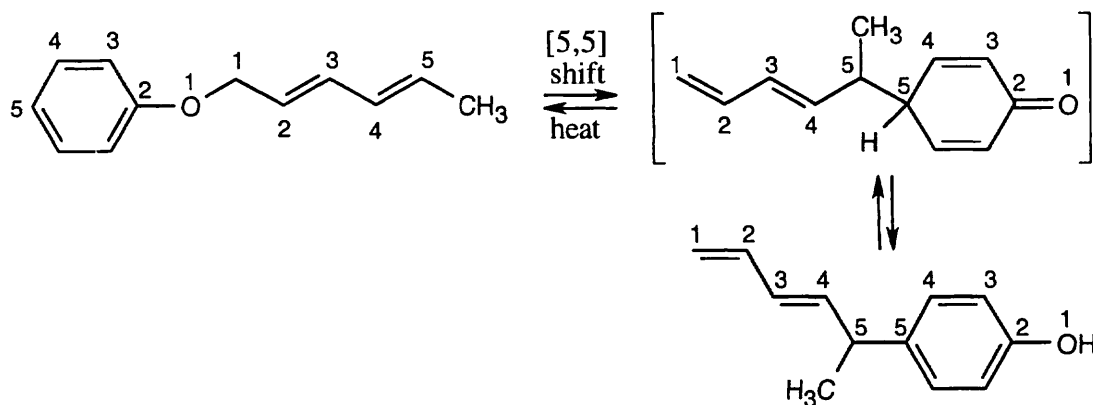
30.22 Ring opening of Dewar benzene is a process involving two electron pairs and, according to Table 30.1, should occur by a conrotatory pathway. However, if you look back to other ring openings of cis-fused cyclobutenes, you will see that conrotatory ring opening produces a diene in which one of the double bonds is trans. Since a trans double bond in a six-membered ring is not likely to be formed, ring opening occurs by a different, higher energy, nonconcerted pathway.

30.23



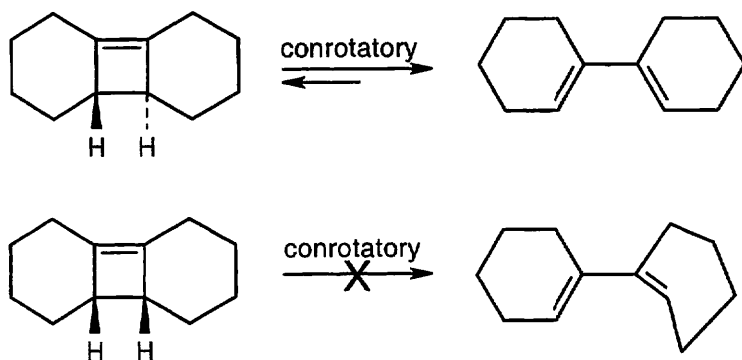
Each electrocyclic reaction involves two pairs of electrons and proceeds in a conrotatory manner.

30.24



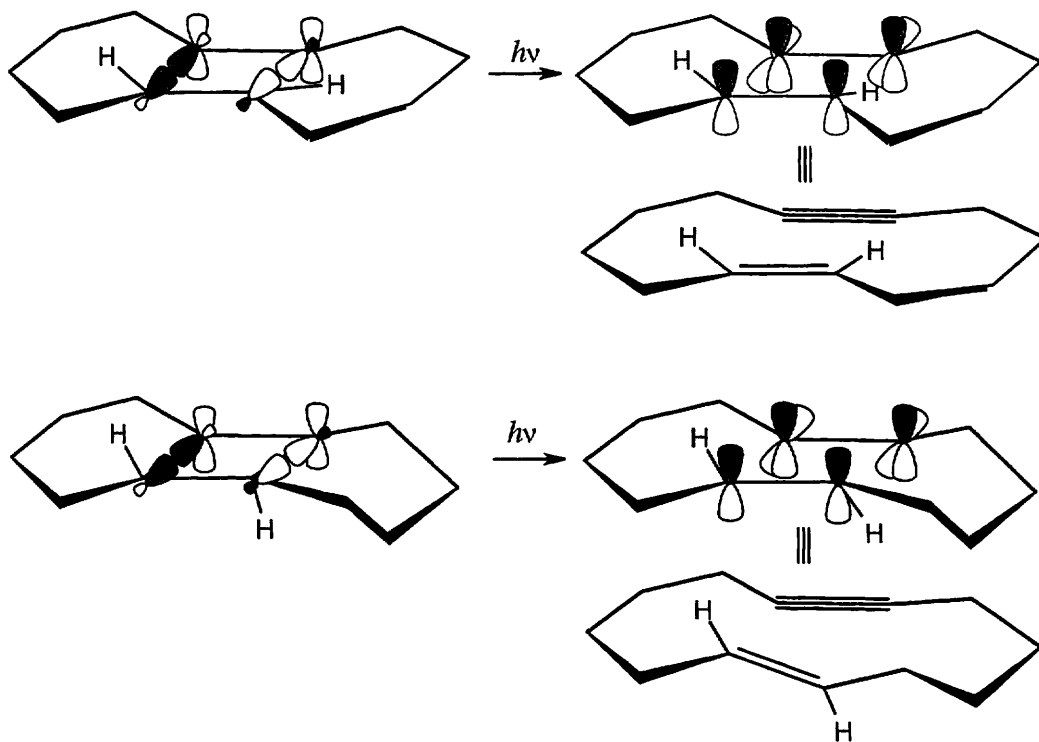
This thermal sigmatropic rearrangement is a suprafacial process since five electron pairs are involved in the reaction.

30.25



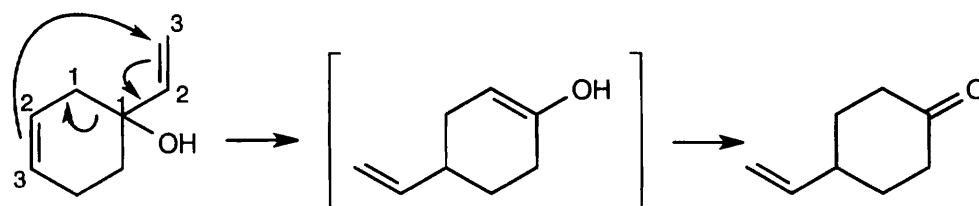
Ring opening of the *trans*-cyclobutene isomer proceeds by the expected conrotatory route to form the observed product. For the *cis*-cyclobutene isomer, the observed product can be formed by a four-electron *pericyclic* process only if the four-membered ring geometry is *trans*. Ring opening of the *cis* isomer by a concerted process would form a severely strained six-membered ring containing a *trans* double bond. Reaction of the *cis* isomer to yield the observed product occurs instead by a higher energy, nonconcerted path.

30.26

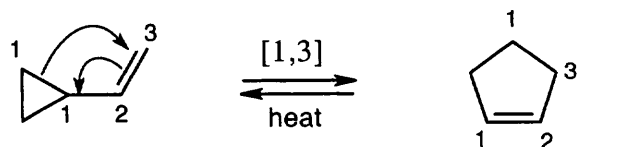


Both reactions are [2 + 2] photochemical electrocyclic reactions, which occur with disrotatory motion.

30.27 The product of this [3,3] sigmatropic rearrangement is an enol that tautomerizes to a ketone.



30.28

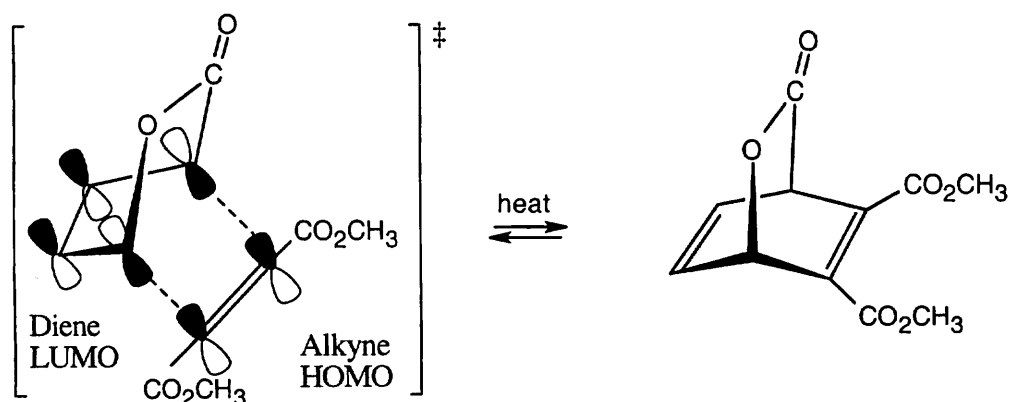


Vinylcyclopropane

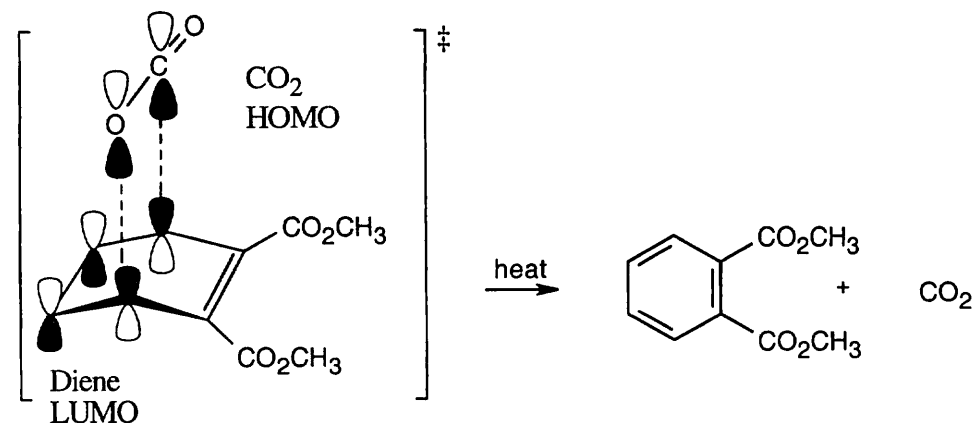
Cyclopentene

This reaction is a [1,3] sigmatropic rearrangement.

30.29

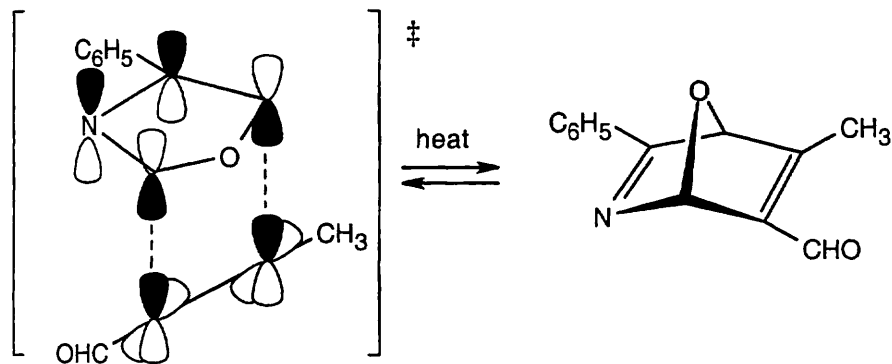


Formation of the bicyclic ring system occurs by a suprafacial [4 + 2] Diels–Alder cycloaddition process. Only one pair of π electrons from the alkyne is involved in the reaction; the carbonyl π electrons are not involved.

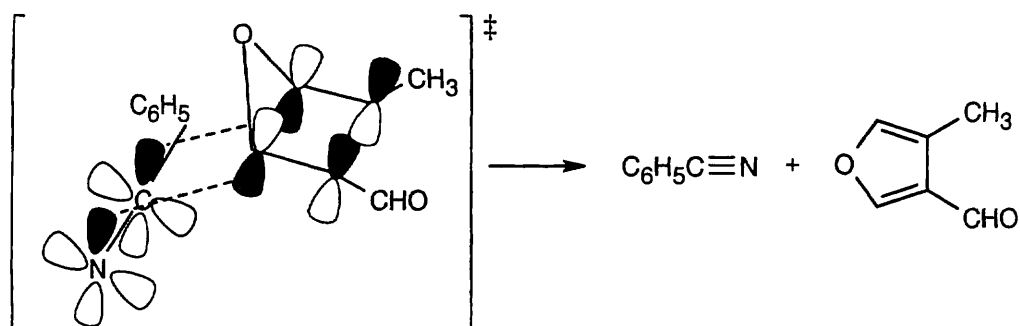


Loss of CO_2 is a reverse Diels–Alder [4 + 2] cycloaddition reaction.

30.30

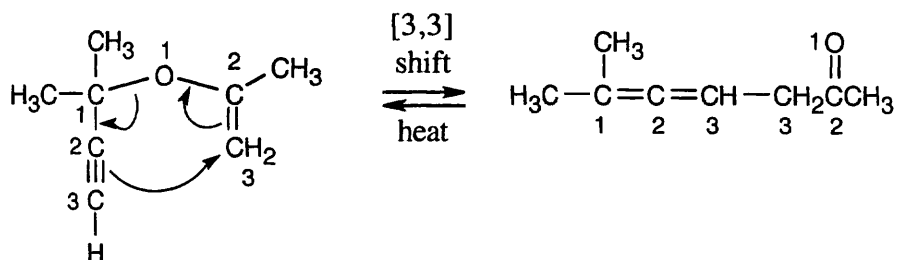


The first reaction is a Diels–Alder [4 + 2] cycloaddition, which proceeds with suprafacial geometry.

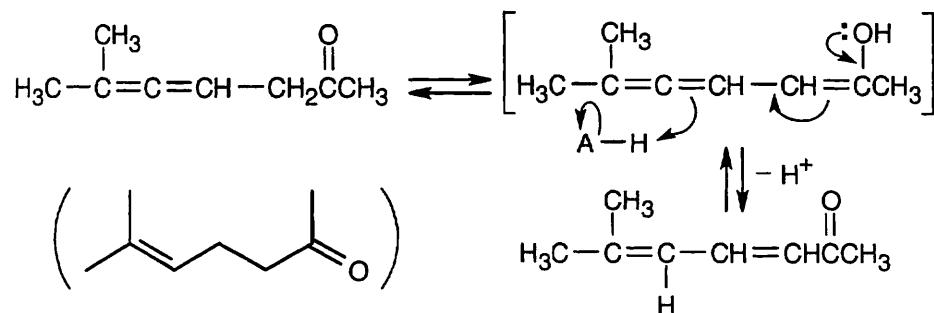


The second reaction is a reverse Diels–Alder [4 + 2] cycloaddition.

30.31

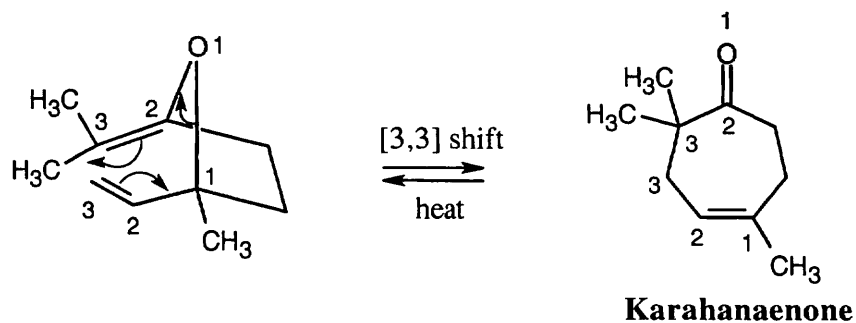


An allene is formed by a [3,3] sigmatropic rearrangement.



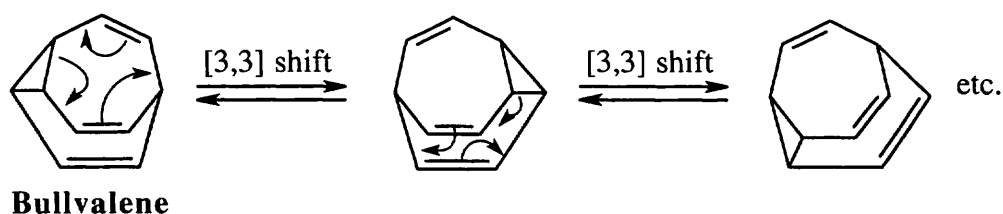
Acid catalyzes isomerization of the allene to a conjugated dienone *via* an intermediate enol.

30.32



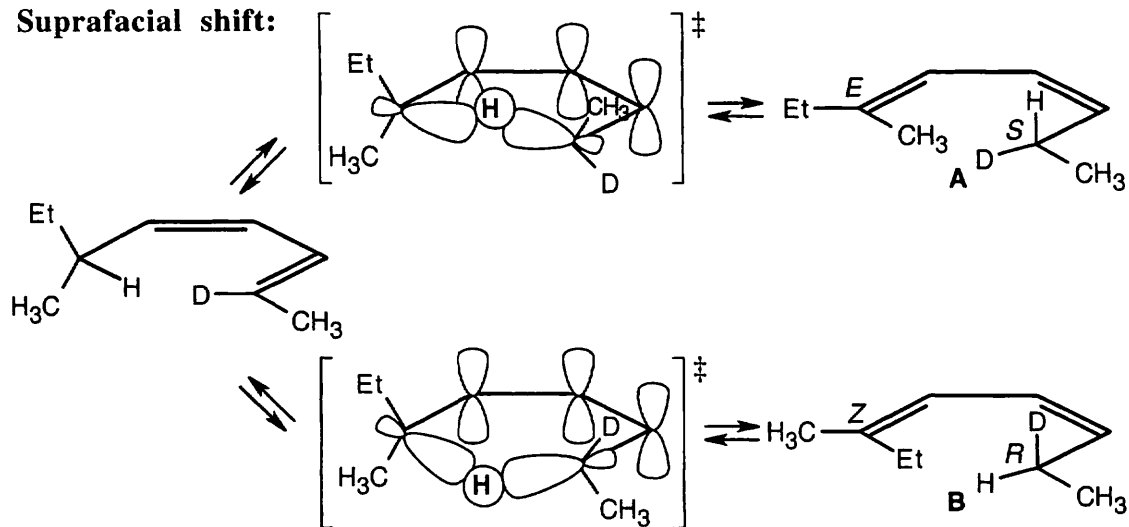
Karahanaenone is formed by a [3,3] sigmatropic rearrangement (Claisen rearrangement).

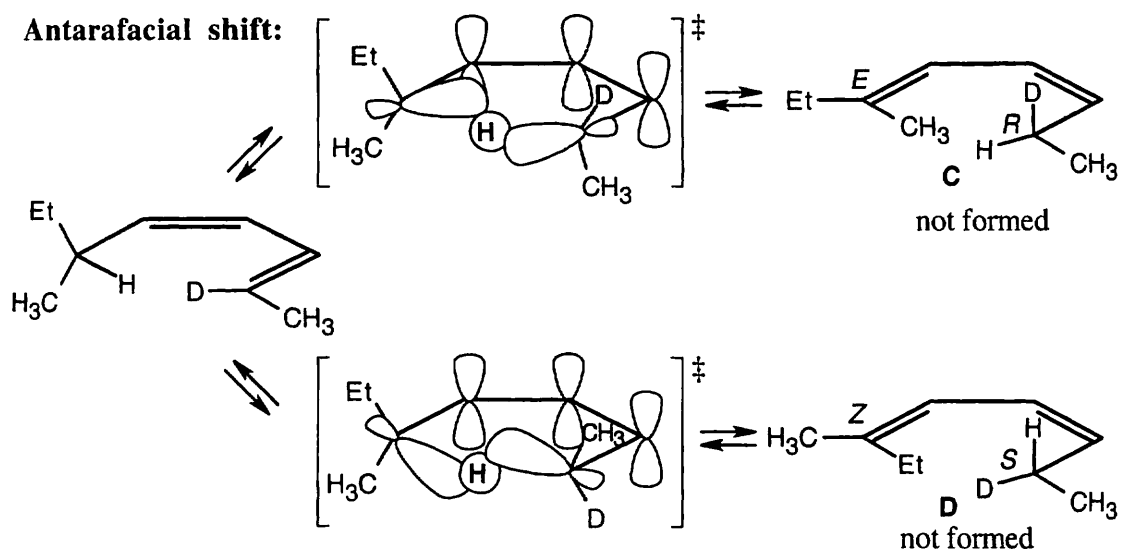
30.33



Bullvalene can undergo [3,3] sigmatropic rearrangements in all directions. At 100°, the rate of rearrangement is fast enough to make all hydrogen atoms equivalent, and only one signal is seen in the ^1H NMR spectrum.

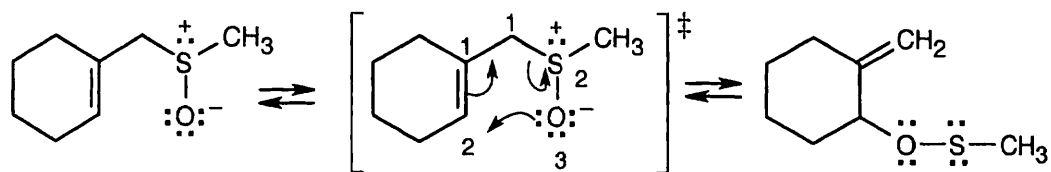
30.34

Suprafacial shift:



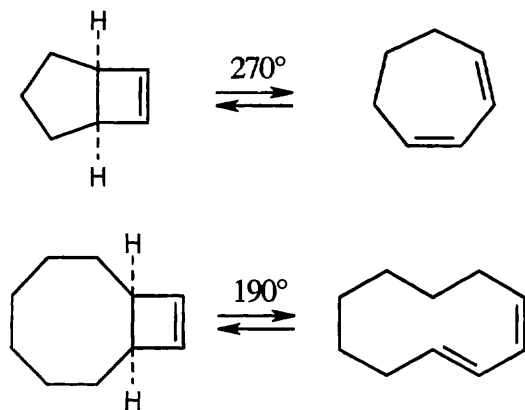
The observed products **A** and **B** result from a [1,5] sigmatropic hydrogen shift with suprafacial geometry, and they confirm the predictions of orbital symmetry. **C** and **D** are not formed.

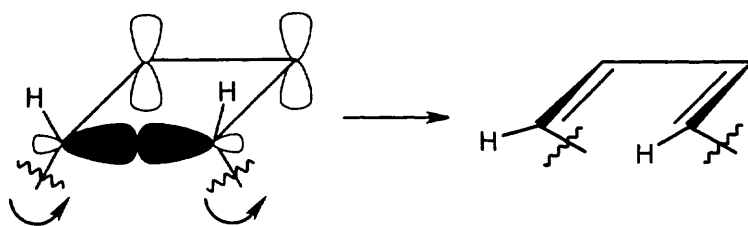
30.35



This [2,3] sigmatropic rearrangement involves three electron pairs and should occur with suprafacial geometry.

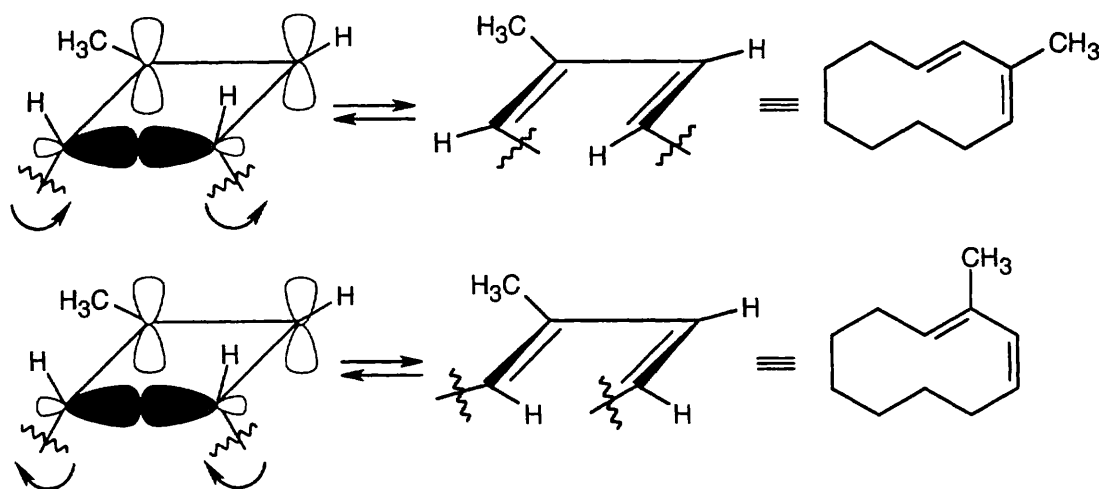
30.36





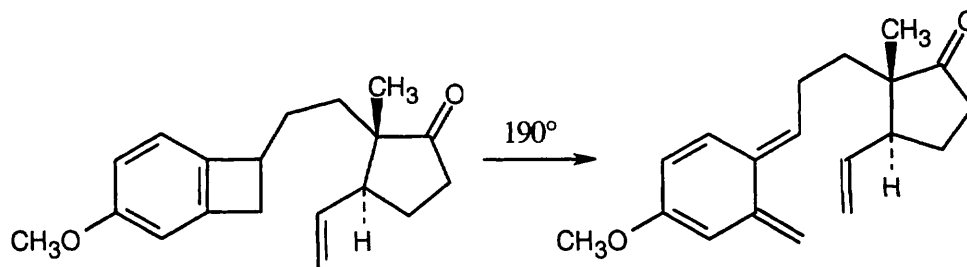
Concerted thermal ring opening of a cis-fused cyclobutene ring yields a product having one cis and one trans double bond. The ten-membered ring product of reaction 2 is large enough to accommodate a trans double bond, but a seven-membered ring containing a trans double bond is highly strained. Opening of the cyclobutene ring in reaction 1 occurs by a higher energy nonconcerted process to yield a seven-membered ring having two cis double bonds.

30.37

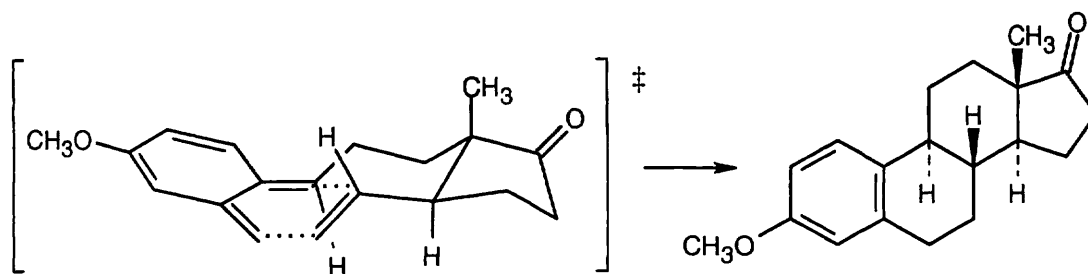


Thermal ring opening of the methylcyclobutene ring can occur by either of two symmetry-allowed conrotatory paths to yield the observed product mixture.

30.38

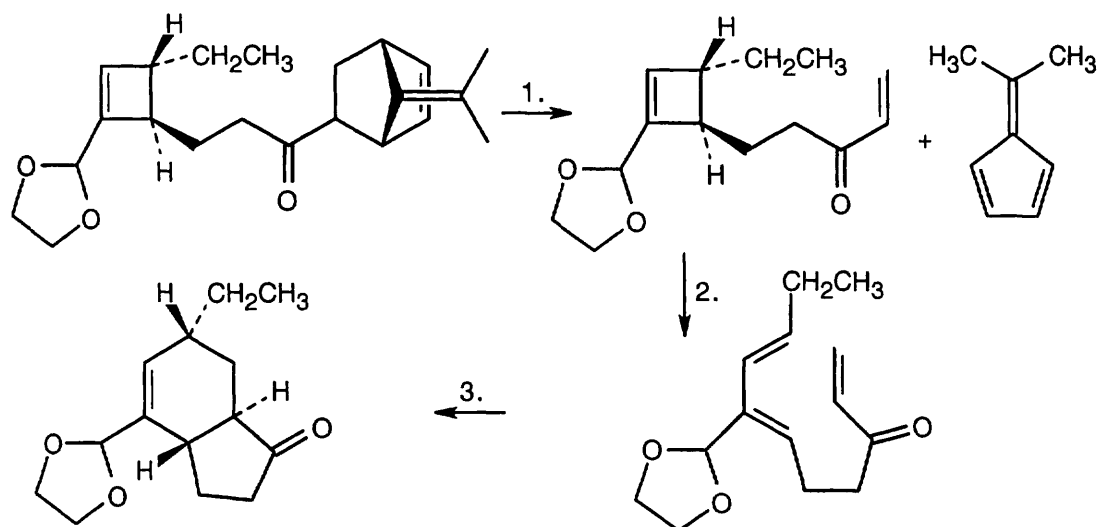


The first reaction is an electrocyclic opening of a cyclobutene ring.



Formation of estrone methyl ether occurs by a Diels–Alder [4 + 2] cycloaddition.

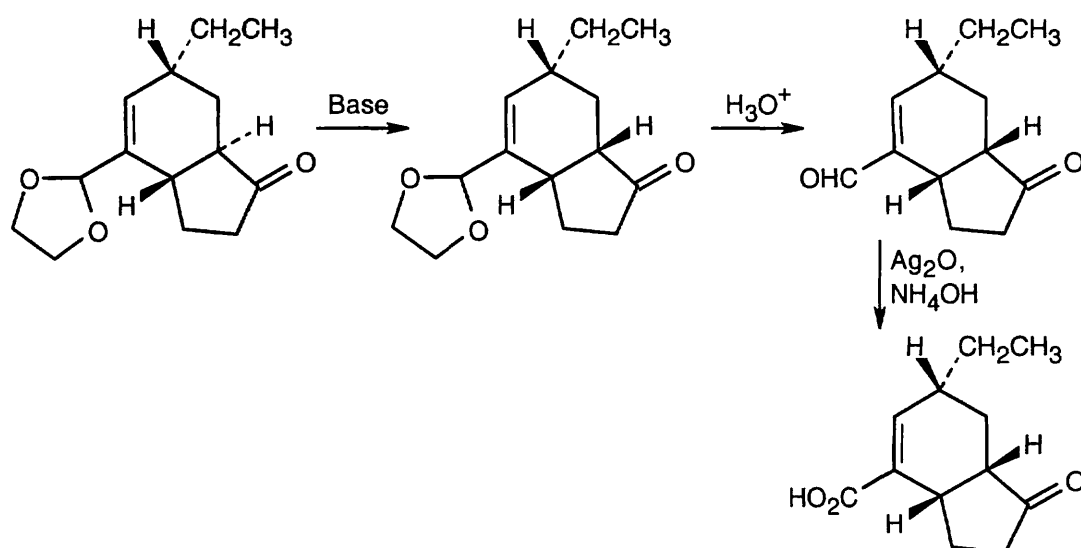
30.39



Reaction 1: Reverse Diels–Alder [4 + 2] cycloaddition;

Reaction 2: Conrotatory electrocyclic opening of a cyclobutene ring;

Reaction 3: Diels–Alder [4 + 2] cycloaddition.

**Coronafacic acid**

Treatment with base enolizes the ketone and changes the ring junction from *trans* to *cis*. A *cis* ring fusion is less strained when a six-membered ring is fused to a five-membered ring.

30.40