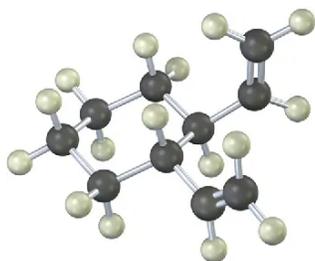


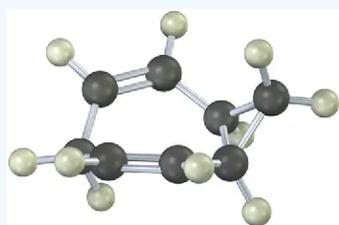
15.11: Additional Problems

Visualizing Chemistry

Predict the product obtained when the following substance is heated:

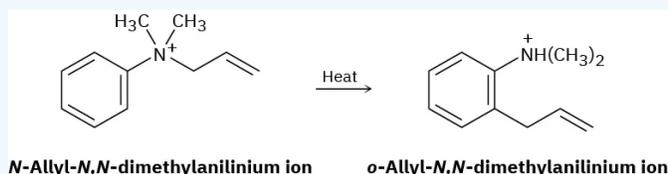


The ^{13}C NMR spectrum of homotropilidene taken at room temperature shows only three peaks. Explain.

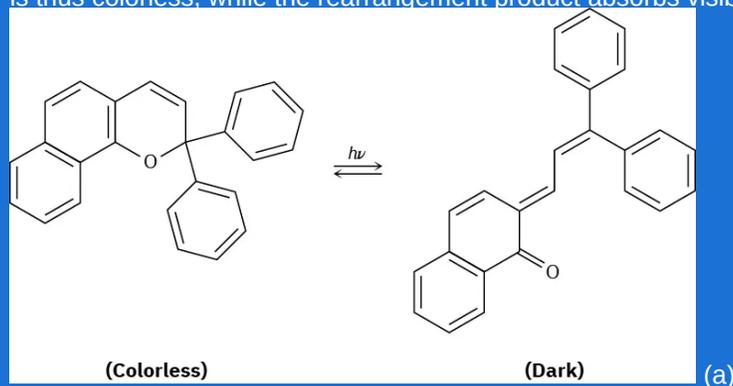


Mechanism Problems

The following rearrangement of *N*-allyl-*N,N*-dimethylanilinium ion has been observed. Propose a mechanism.



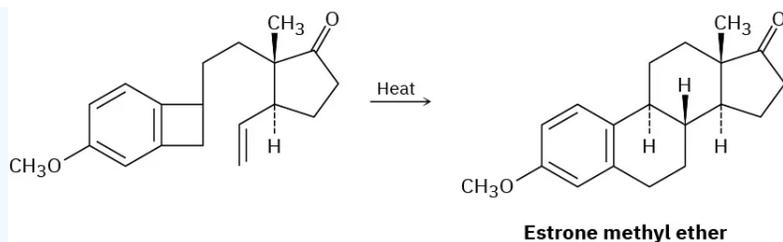
Plastic photochromic sunglasses are based on the following reversible rearrangement of a dye inside the lenses that occurs when the lenses are exposed to sunlight. The original dye absorbs UV light but not visible light and is thus colorless, while the rearrangement product absorbs visible light and is thus darkened.



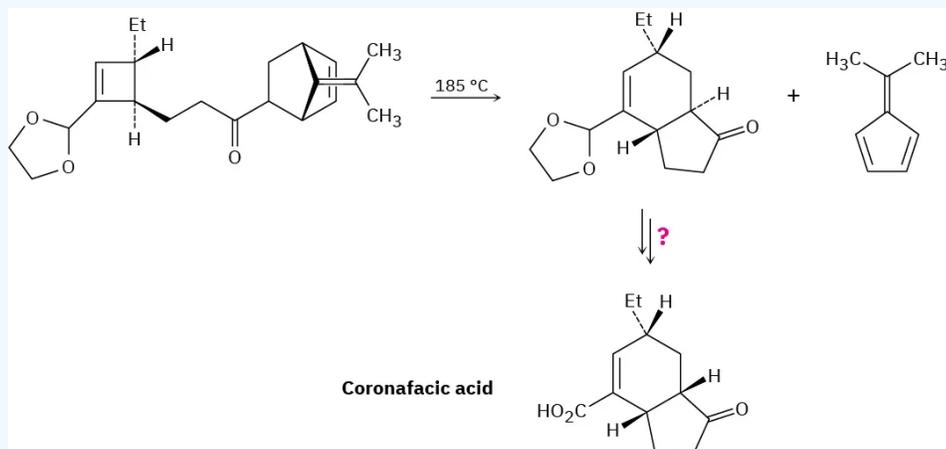
Show the mechanism of the rearrangement.

(b) Why does the rearrangement product absorb at a longer wavelength (visible light) than the original dye (UV)?

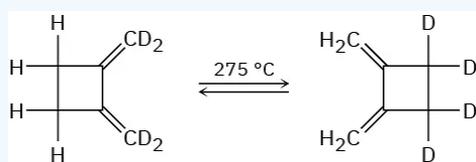
The sex hormone estrone has been synthesized by a route that involves the following step. Identify the pericyclic reactions involved, and propose a mechanism.



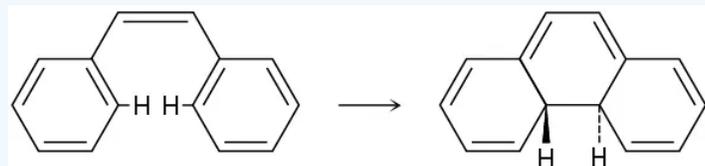
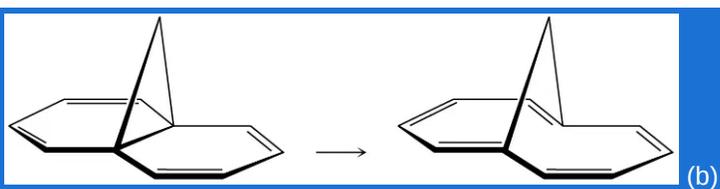
Coronafacic acid, a bacterial toxin, was synthesized using a key step that involves three sequential pericyclic reactions. Identify them, and propose a mechanism for the overall transformation. How would you complete the synthesis?



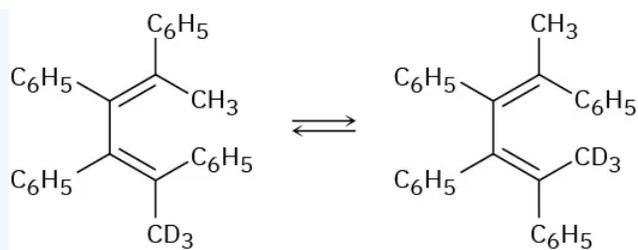
The following thermal rearrangement involves two pericyclic reactions in sequence. Identify them, and propose a mechanism to account for the observed result.



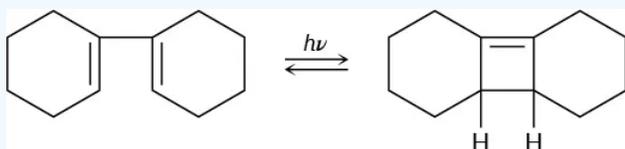
Electrocyclic Reactions



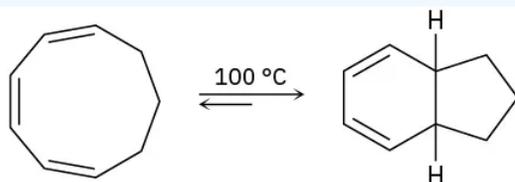
The following thermal isomerization occurs under relatively mild conditions. Identify the pericyclic reactions involved, and show how the rearrangement occurs.



Would you expect the following reaction to proceed in a conrotatory or disrotatory manner? Show the stereochemistry of the cyclobutene product, and explain your answer.



Heating (1Z,3Z,5Z)-1,3,5-cyclononatriene to 100 °C causes cyclization and formation of a bicyclic product. Is the reaction conrotatory or disrotatory? What is the stereochemical relationship of the two hydrogens at the ring junctions, cis or trans?

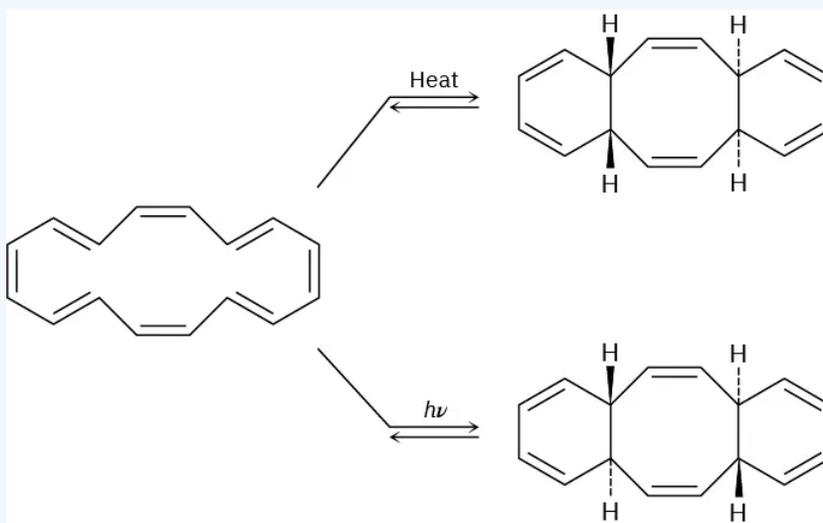


(1Z,3Z,5Z)-1,3,5-Cyclononatriene

(2E,4Z,6Z,8E)-2,4,6,8-Decatetraene has been cyclized to give 7,8-dimethyl-1,3,5-cyclooctatriene. Predict the manner of ring-closure—conrotatory or disrotatory—for both thermal and photochemical reactions, and predict the stereochemistry of the product in each case.

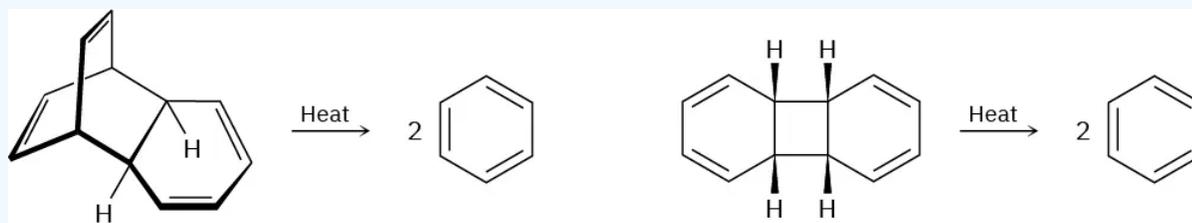
Answer Problem 30-24 for the thermal and photochemical cyclizations of (2E,4Z,6Z,8Z)-2,4,6,8-decatetraene.

The cyclohexadecaoctaene shown isomerizes to two different isomers, depending on reaction conditions. Explain the observed results, and indicate whether each reaction is conrotatory or disrotatory.

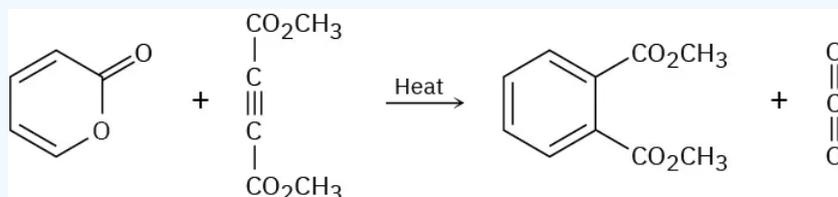


Cycloaddition Reactions

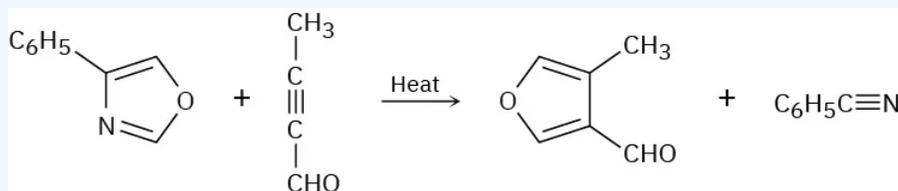
Which of the following reactions is more likely to occur? Explain.



The following reaction takes place in two steps, one of which is a cycloaddition while the other is a *reverse* cycloaddition. Identify the two pericyclic reactions, and show how they occur.

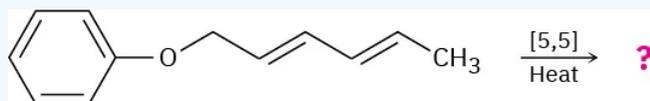


Two sequential pericyclic reactions are involved in the following furan synthesis. Identify them, and propose a mechanism for the transformation.

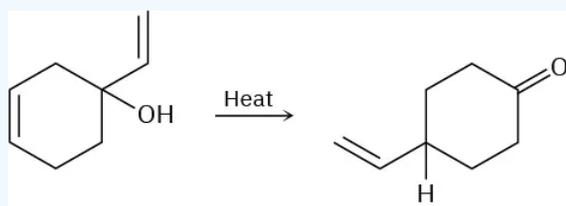


Sigmatropic Rearrangements

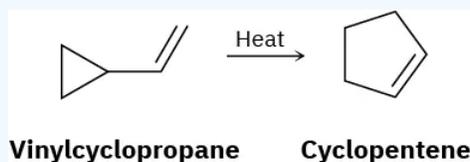
Predict the product of the following pericyclic reaction. Is this [5,5] shift a suprafacial or an antarafacial process?



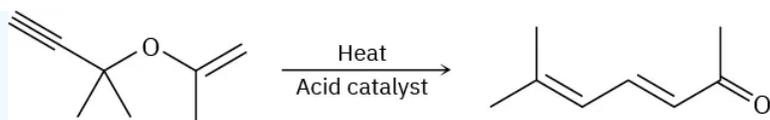
Propose a pericyclic mechanism to account for the following transformation:



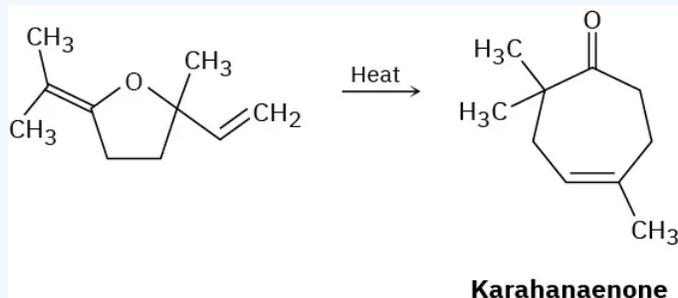
Vinyl-substituted cyclopropanes undergo thermal rearrangement to yield cyclopentenes. Propose a mechanism for the reaction, and identify the pericyclic process involved.



The following synthesis of dienones occurs readily. Propose a mechanism to account for the results, and identify the kind of pericyclic reaction involved.



Karahanaenone, a terpenoid isolated from oil of hops, has been synthesized by the thermal reaction shown. Identify the kind of pericyclic reaction, and explain how karahanaenone is formed.

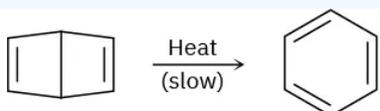


General Problems

(a) A photochemical [1,5] sigmatropic rearrangement

(b) A thermal [4 + 6] cycloaddition (c) A thermal [1,7] sigmatropic rearrangement (d) A photochemical [2 + 6] cycloaddition

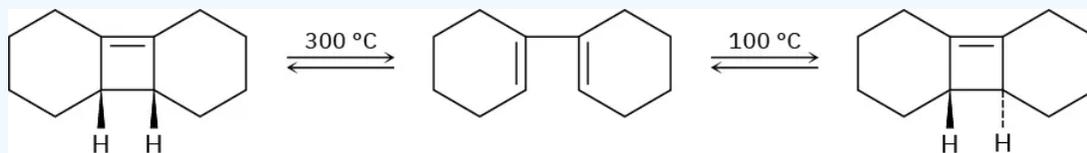
Bicyclohexadiene, also known as *Dewar benzene*, is extremely stable despite the fact that its rearrangement to benzene is energetically favored. Explain why the rearrangement is so slow.



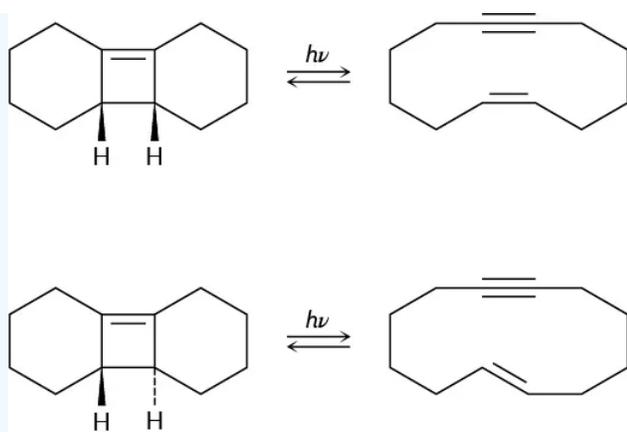
Dewar benzene

Benzene

Ring-opening of the *trans*-cyclobutene isomer shown takes place at much lower temperature than a similar ring-opening of the *cis*-cyclobutene isomer. Explain the temperature effect, and identify the stereochemistry of each reaction as either conrotatory or disrotatory.



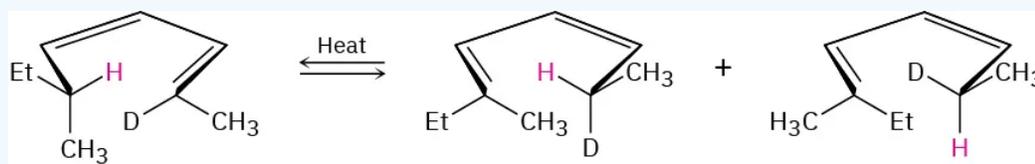
Photolysis of the *cis*-cyclobutene isomer in Problem 30-37 yields *cis*-cyclododecaen-7-yne, but photolysis of the *trans* isomer yields *trans*-cyclododecaen-7-yne. Explain these results, and identify the type and stereochemistry of the pericyclic reaction.



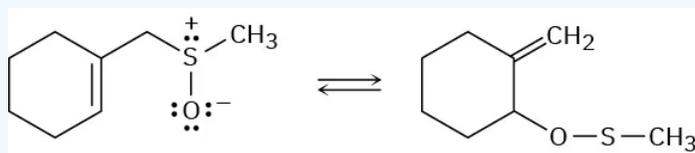
The ^1H NMR spectrum of bullvalene at $100\text{ }^\circ\text{C}$ consists only of a single peak at $4.22\ \delta$. Explain.



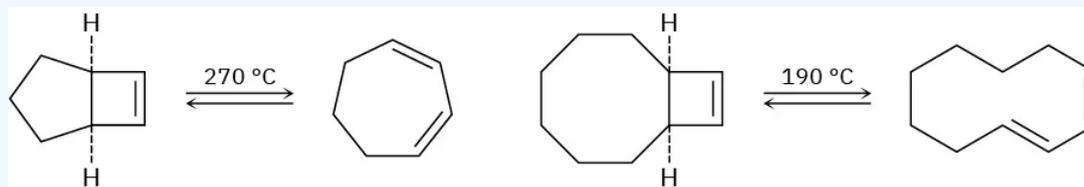
The following rearrangement was devised and carried out to prove the stereochemistry of [1,5] sigmatropic hydrogen shifts. Explain how the observed result confirms the predictions of orbital symmetry.



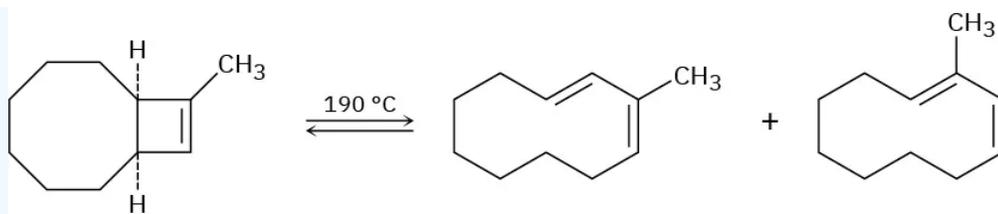
The following reaction is an example of a [2,3] sigmatropic rearrangement. Would you expect the reaction to be suprafacial or antarafacial? Explain.



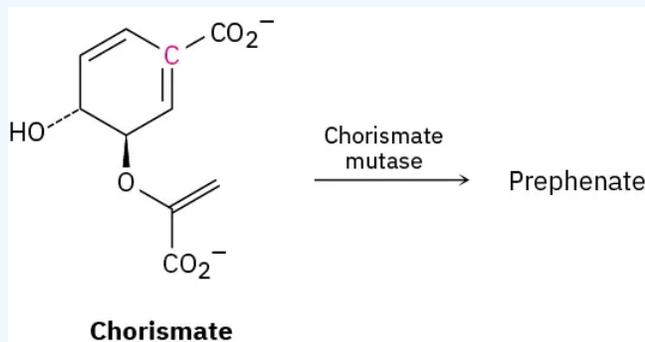
When the compound having a cyclobutene fused to a five-membered ring is heated, (1*Z*,3*Z*)-1,3-cycloheptadiene is formed. When the related compound having a cyclobutene fused to an eight-membered ring is heated, however, (1*E*,3*Z*)-1,3-cyclodecadiene is formed. Explain these results, and suggest a reason why opening of the eight-membered ring occurs at a lower temperature.



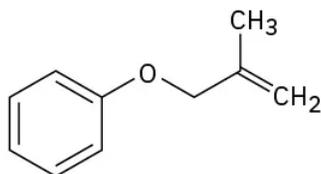
In light of your answer to Problem 30-42, explain why a mixture of products occurs in the following reaction:



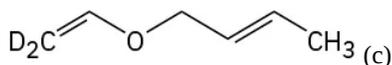
In nature, the enzyme chorismate mutase catalyzes a Claisen rearrangement of chorismate that involves both the terminal double bond and the double bond with the highlighted carbon. What is the structure of prephenate, the biological precursor to the amino acids phenylalanine and tyrosine?



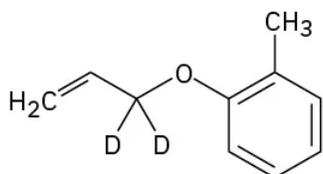
Problem 30-45 Predict the product(s) if the starting materials underwent a Claisen rearrangement. Draw arrows to illustrate the rearrangement of electrons. (a)



(b)



(c)



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