The bicyclo[2.2.0]hexa-2,5-diene system is a valence isomer of the benzene ring and is often referred to as Dewar benzene. Propose a reasonable mechanism that accounts for the formation of this product under photochemical conditions.

Note: Part of the stability of this particular derivative can be attributed to steric factors. The t-butyl groups are farther apart in the Dewar benzene structure than in the aromatic structure. Subsequently Dewar benzene was synthesized by the following scheme:

However, the thermal conversion of Dewar benzene to benzene is slow. Can you provide an explanation for this?
A particularly interesting case involves the bicyclo[2.2.0]hexa-2,5-diene system. This ring system is a valence isomer of the benzene ring and is often referred to as Dewar benzene. Attempts prior to 1960 to prepare Dewar benzene derivatives failed, and the pessimistic opinion was that such efforts would be fruitless because Dewar benzene would be so unstable as to immediately revert to benzene. Then in 1962, van Tamelen and Pappas isolated a stable Dewar benzene derivative 9 by photolysis of 1,2,4-tri-(t-butyl)benzene. The compound was reasonably stable, reverting to the aromatic starting material only on heating. Part of the stability of this particular derivative can be attributed to steric factors. The t-butyl groups are farther apart in the Dewar benzene structure than in the aromatic structure.

The unsubstituted Dewar benzene 10 was successfully prepared in 1963.

This compound is less stable than 9 and reverts to benzene with a half-life of about 2 days at 25°C, with $\Delta H^\ddagger = 23$ kcal/mol. Nevertheless, the relative kinetic stability of Dewar benzene is surprisingly high when one considers that its conversion to benzene is exothermic by 71 kcal/mol. Furthermore, the central bond is not only strained but also bis-allylic. The kinetic stability of Dewar benzene is related to the orbital symmetry requirements for concerted electrocyclic transformations. The concerted thermal pathway would be conrotatory, since the reaction is the ring opening of a cyclobutene and therefore leads not to benzene, but to a highly strained Z,Z,E-cyclohexatriene. A disrotatory process, which would lead directly to benzene, is forbidden.
(a) On being heated to 320–340°C, compound 4-B produces 1,4-dimethoxynaphthalene and 1-acetoxybutadiene. Furthermore, deuterium labeling has shown that the reaction is stereospecific as indicated. Can you provide a reasonable explanation for this? (952, C&S)

(b) The following compound is reported to equilibrate with another compound at elevated temperatures. Can you identify this compound?

(c) Z,Z,Z,Z-1,3,5,7-cyclononatetraene undergoes a spontaneous electrocyclic ring closure at 25°C. Predict the most likely structure for this cyclization product A. Although another product B of electrocyclization is allowed, this product is not formed. Can you identify this compound and explain why this product is less favored?
10.3. The observed product results from a disrotatory six-electron electrocyclization.

A conrotatory eight-electron electrocyclization is also allowed but this would lead to a more strained trans ring junction with a three-membered ring.

3. Propose a reasonable mechanism for the following reaction

\[ \text{Propyne} \overset{\text{Trifluoroacetic acid (catalytic)}}{\longrightarrow} \text{H-C=CH}_2 \]


(147, Challenging problems)

4. Propose a reasonable mechanism for the following reaction

\[ \text{X} \overset{\text{AIBN, Bu}_3\text{SnH, Heat}}{\longrightarrow} \text{H-C=CH}_2 \]


(242)
During the Osmium tetroxide mediated dihydroxylation reaction given below, the product given below is produced. In order to access the stereochemical option, a two-step reaction sequence was followed i.e. iodine/AgOAc followed by saponification. Draw out suitable structures (in chair conformation) to explain the outcome of the two reactions. (127)
Top face shielded by axial methyl

Pseudo-axial ring opening (chair T.S.)

Saponification