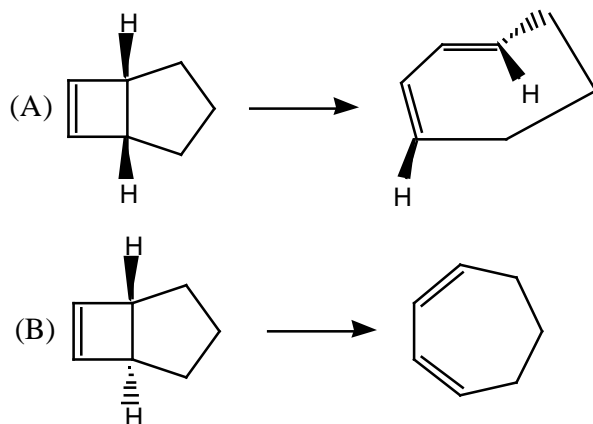
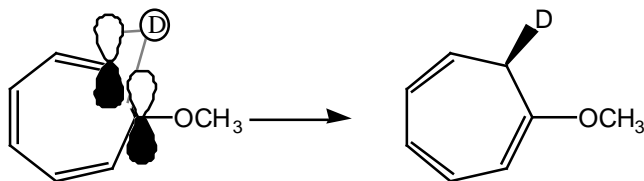


Answers to Problem Set #8
CH242-2002S

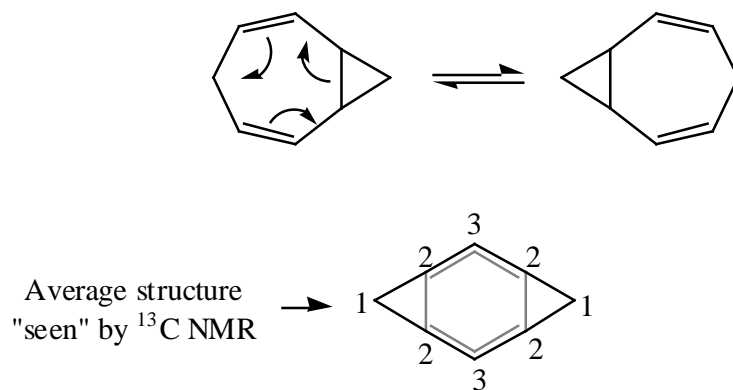
- (1) (a) Reaction A gives a strained diene containing a trans double bond in a seven-membered ring. This is because the 4e ring opening must occur in a conrotatory fashion under thermal conditions. Reaction B, on the other hand, leads to a more stable cyclic diene by conrotatory ring opening, and is therefore more favorable.



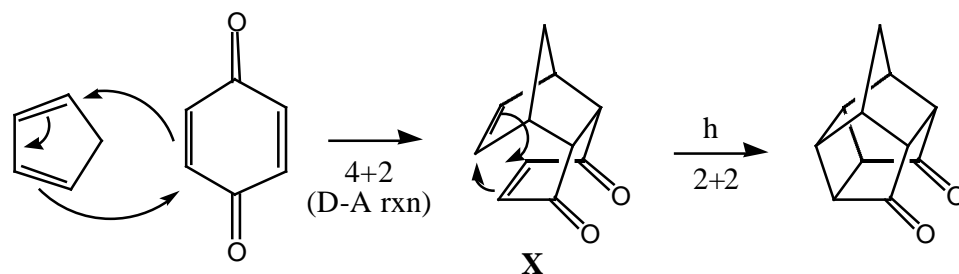
- (b) It is a 1,7-D shift that occurs suprafacially. It requires photochemical conditions.



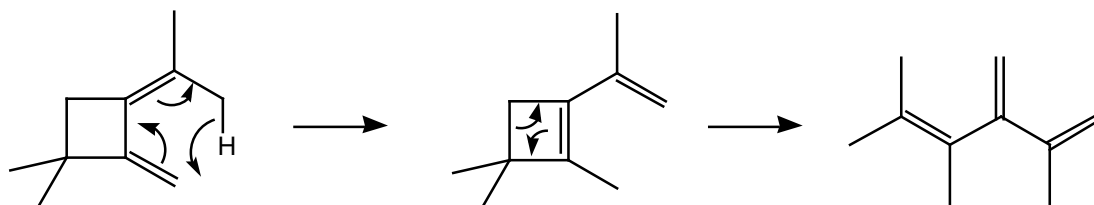
- (c) Degenerate Cope rearrangement (3,3-sigmatropic shift) can occur within homotropyliene. If this rearrangement is fast enough, what is seen by ¹³C NMR is an average structure that appears to have only three types of carbons.



- (2) (a) A thermally allowed 4+2 cycloaddition (Diels-Alder) gives the adduct **X**. In the next step, **X** is converted into the indicated product by a photochemically allowed 2+2 cycloaddition.



- (b) Lead off with a 1,5-H shift to get the cyclobutene ring system. Subsequent electrocyclic ring opening delivers the product.



- (c) A 3,3-sigmatropic shift directly gives the product. This reaction becomes a candidate once you notice that the two double bonds have a 1,5 relationship.

