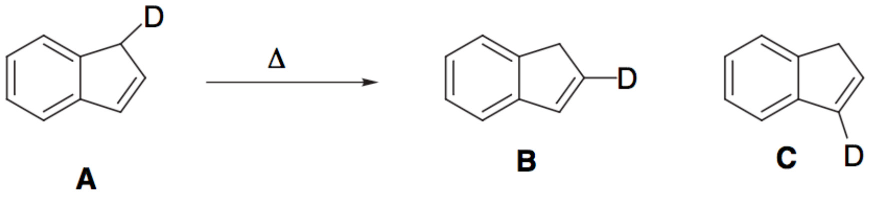
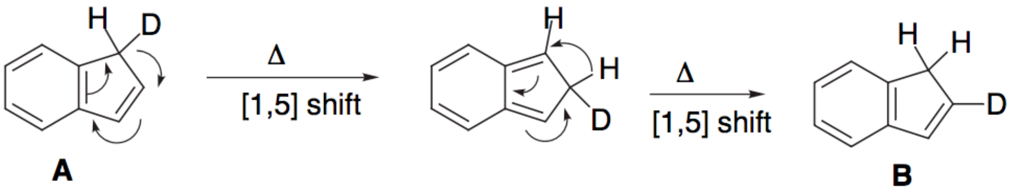
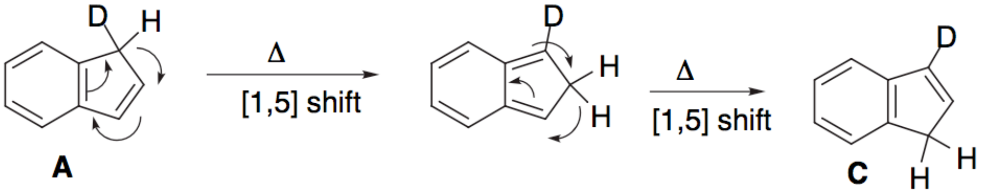
PS 5, 2005
CHEM 332

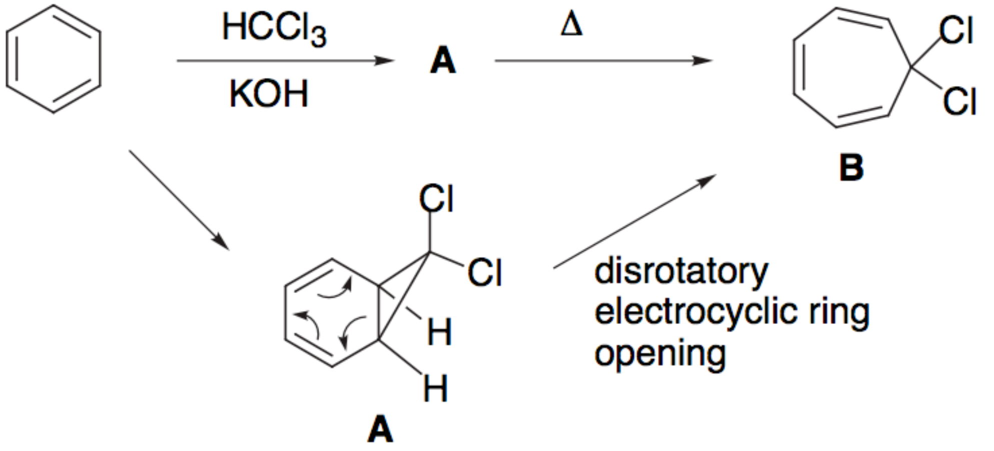
1. Provide a mechanism





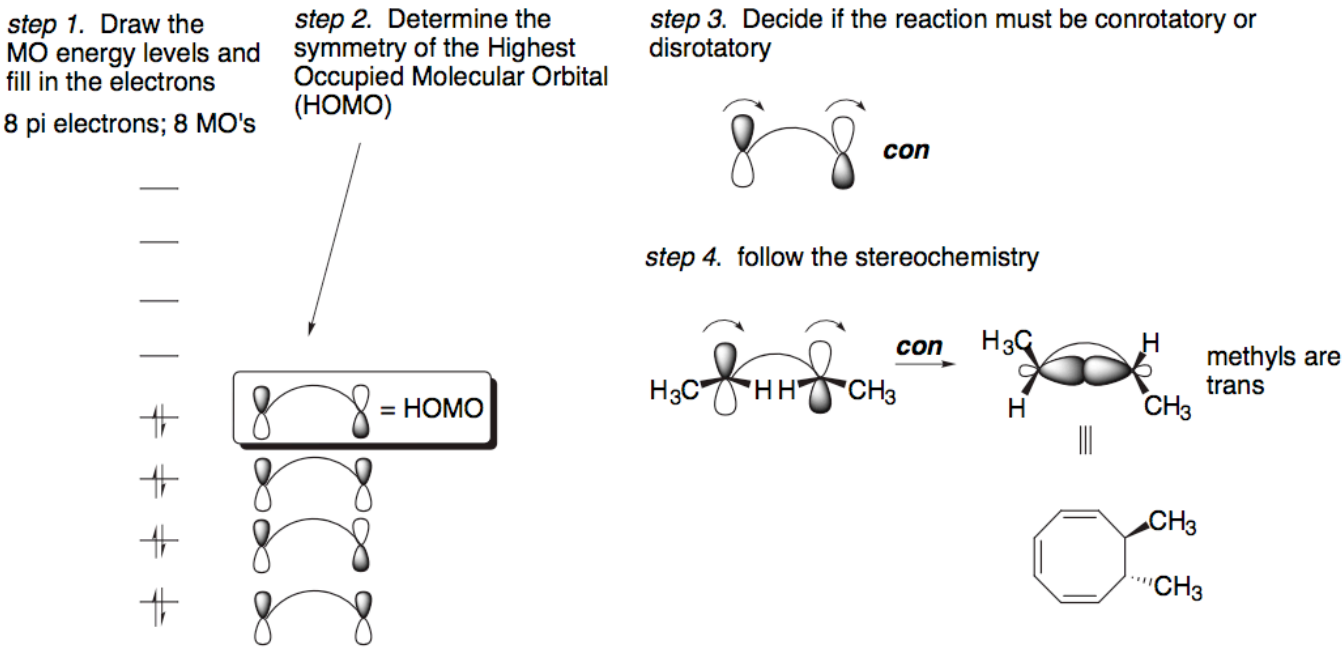


2. Provide a structure for **A** and a mechanism for the conversion to **B**



disrotatory
electrocyclic ring
opening

3.



*step 1.* Draw the MO energy levels and fill in the electrons

8 pi electrons; 8 MO's

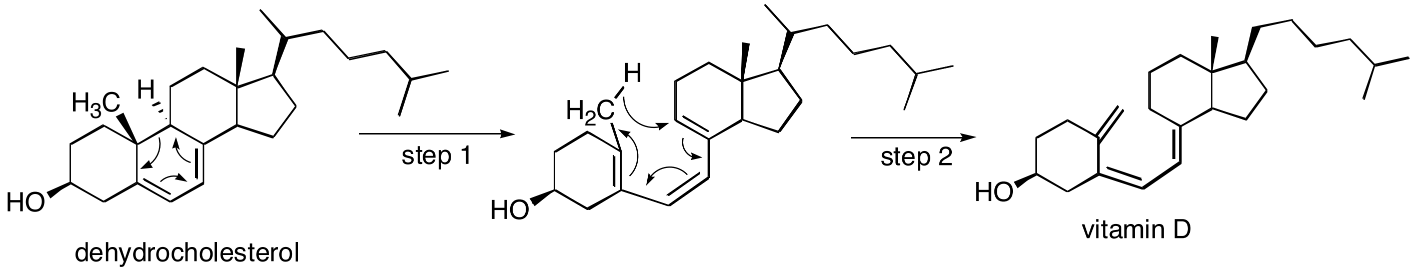
*step 2.* Determine the symmetry of the Highest Occupied Molecular Orbital (HOMO)

*step 3.* Decide if the reaction must be conrotatory or disrotatory

*step 4.* follow the stereochemistry

methyls are trans

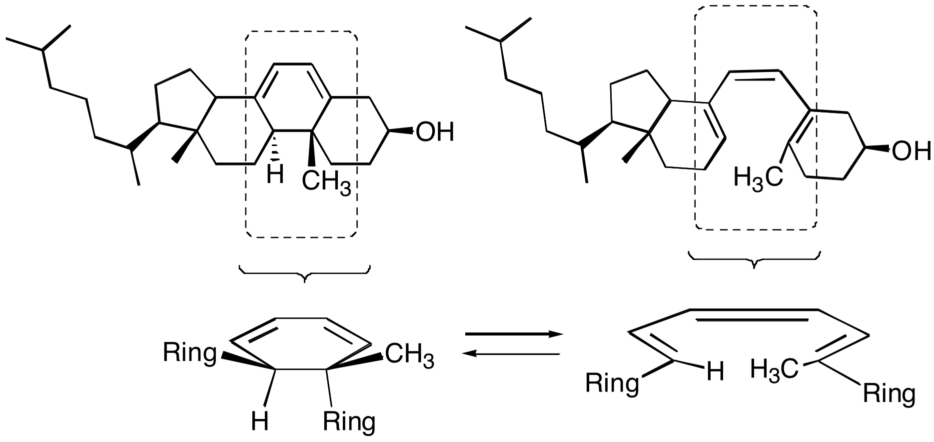
4. Biochemically, vitamin D is made from dehydrocholesterol by sequential electrocyclic ring opening and a 1,7-sigmatropic shift as shown below.



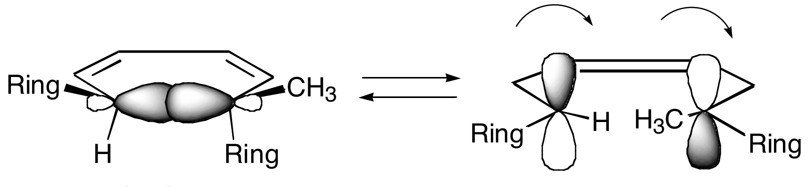
a. Is step 1 photochemical or thermal? Explain in detail using molecular orbital arguments.
b. We discussed in class that 1,5 sigmatropic hydride shifts are allowed, but that 1,3 hydride shifts are not allowed. Step 2 is a 1,7 sigmatropic hydride shift. Explain why this step is allowed (this is a challenging question)

**part a**

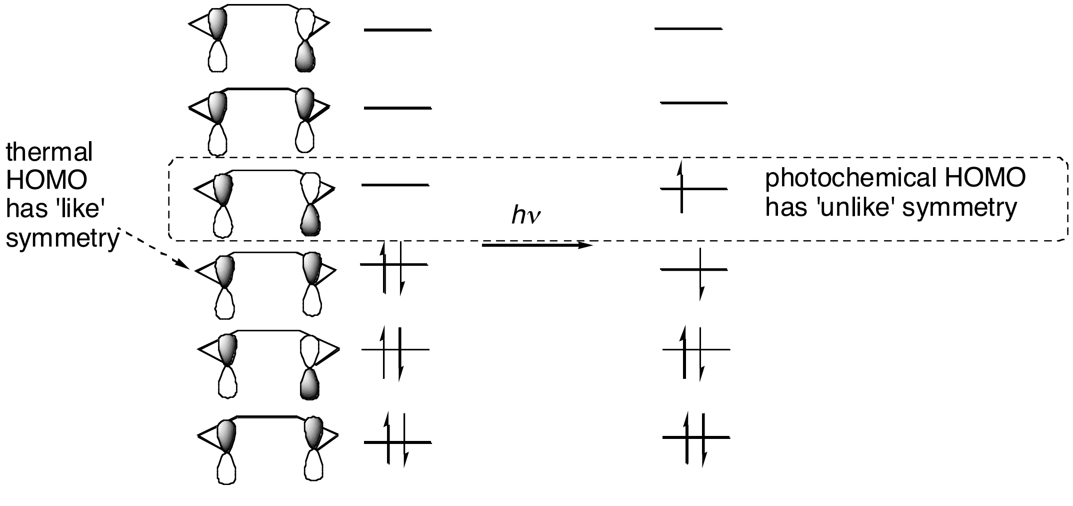
begin by simplfy the structure of dehydrocholesterol and the ring opened product:



now we can see that the first part is a conrotatory ring opening



therefore, the HOMO has 'unlike' symmetry at the ends. For hexadiene, this is the photochemical homo.

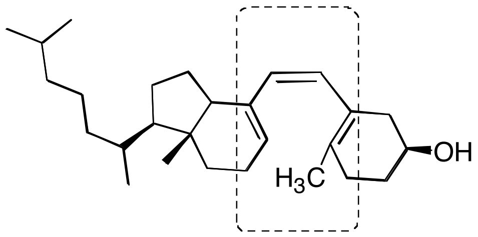


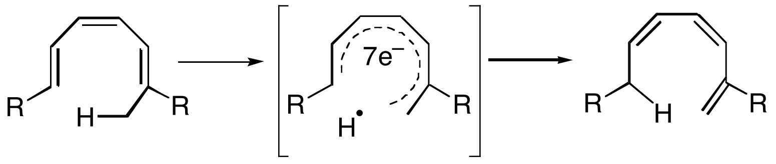
thermal HOMO has 'like' symmetry

photochemical HOMO has 'unlike' symmetry

**part b**

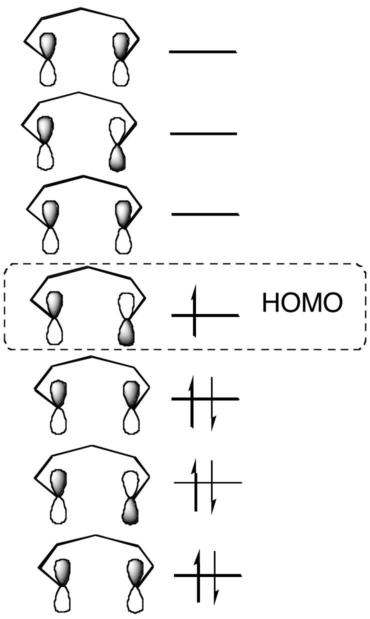
again, consider only the business end of the molecule. Draw the transition state

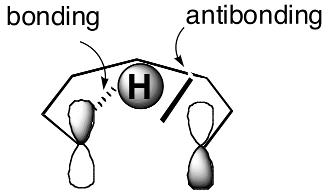




Thus, we have a 7 carbon,
7 electron pi system.
The HOMO has 'unlike' symmetry

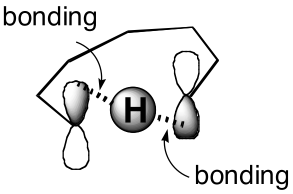
Here is the tricky part. The 1,7 shift cannot take place on the top face of the molecule as we observed for the 1,5 shift. This would result in an unfavorable anti-bonding interaction as shown below:





'Top face' delivery is not allowed
for a 1,7-shift.

We are saved (literally, because we need vitamin D!) by the flexibility of the 7 carbon bridge. Distortion of the bridge can put the like ends of the HOMO within reach of the hydrogen s-orbital. Thus the concerted [1,7]- shift can occur by an 'over-under mechanism'.



'over/under' delivery is allowed
for a 1,7-shift.

Note that this over/under mechanism cannot occur for a 1,3 shift because a 3 carbon tether is not flexible enough!