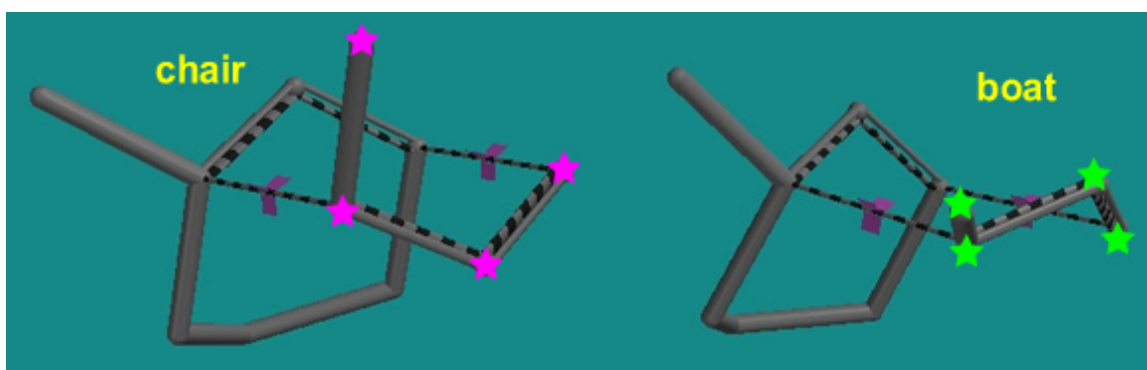


SELECTED ANSWERS

2. The first molecule, a butenylcyclohexene, rearranges by a [3,3] bond shift or Cope mechanism. Since the stereochemistry of the reactant and product are indicated, you can use this information to determine whether a *chair* or *boat* transition state is involved. I needed models to settle this in my own mind. To build a *chair* pseudo-transition state (an exact transition state is not needed), I constructed a bicyclic structure in which 1) all of the carbons were tetrahedral with four neighbors, 2) all of the bonds were single, 3) the skeleton matched that of a Cope transition state, i.e., partial bonds were treated as single bonds. Then I changed the bond types, and removed one H from the “middle” C of each allyl group, constrained the partial *single* bond distances to 2.1 Å and minimized. The results for the *chair* and *boat* look remarkably good (I have omitted hydrogens so that you can see the skeletons more clearly):



I added colored stars to the exocyclic C-C=C-C group. As (I hope) you can see, the *chair* transition state would yield a *cis* product, while the *boat* would yield a *trans* product, so the correct answer is *boat*.

No stereochemistry has been specified for the second reaction. Therefore, the observed product might result from either a *chair* or *boat* transition state. Come see me if you would like to discuss this further or play with models.

3. To answer this problem, I built the following models:

- *E chair* pseudo-TS
- Product derived from *E chair* TS
- *E boat* pseudo-TS
- Product derived from *E boat* TS
- Another four models based on *Z* starting material

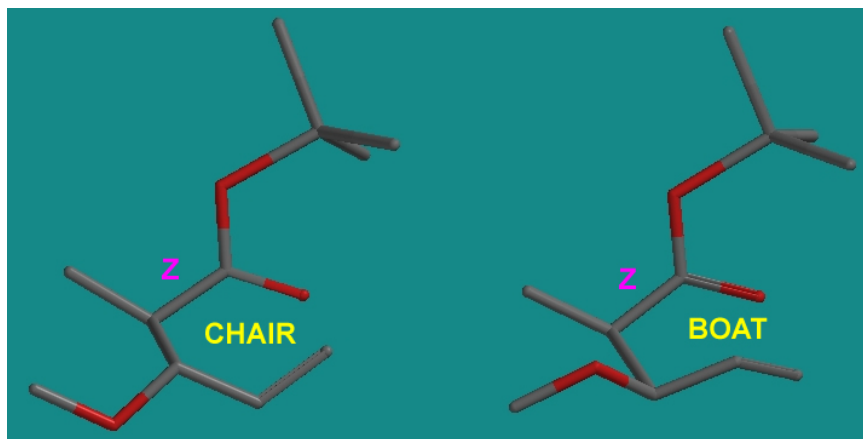
I went a little farther in my modeling here than I did in the previous problem, but the model-building was still remarkably easy. Here are outlines of my procedures:

- ***E chair* pseudo-TS.** Start with cyclohexane. Replace one C with O. Replace single bonds with partial single and partial double bonds as needed. Constrain distances of partial single bonds (I chose 2.1 and 1.9 Å for the CC and CO bonds, respectively, but any value near 2 would be ok). Remove equatorial H from the “middle” C of each allyl group. Add

remaining substituents (OMe, Me, OTMS) with proper stereochemistry. Calculate equilibrium geometry using semi-empirical AM1 with constraints.

- **Product derived from *E chair* TS.** Start with previous model. Freeze all atoms. Replace partial bonds with full bonds as needed.
- ***E boat* pseudo-TS.** Built bicyclo[2.2.2]octane and minimized. This generates a bicyclic structure containing boat cyclohexane rings. Deleted one CH₂CH₂ bridge leaving boat-like cyclohexane. The rest of the procedure was identical to ***E chair* pseudo-TS**, i.e., replaced atoms, replaced bonds, constrained two bonds, removed two H, added substituents, and calculated equilibrium geometry using semi-empirical AM1 with constraints.
- **Product derived from *E boat* TS.** Start with previous model. Freeze atoms and replace bonds.
- **Pseudo-TS and Product based on *Z* starting material.** Used **Save As** to make copies of the 4 *E* models. Switched position of Me substituent in each model (delete Me then add Me in new position).

Notice that I didn't actually do any transition state calculations. It wasn't necessary to do these calculations because the only information that I cared about was product stereochemistry. The following image shows models of the products derived from the *Z chair* and *boat* pseudo-transition states (hydrogens have been omitted for clarity). As you can see, changing from chair to boat affects stereo-chemistry at the OMe-substituted position only. And, I think it is possible to see that changing from *Z* to *E* starting material affects only the Me-substituted position.



After doing this, I found that rotating my models and comparing them to the formulas given in the problem produced these conclusions:

- The major product from each starting material was produced by a *chair* transition state.
- The minor product was produced by a *boat* transition state.

I did run into one small complication. Depending on how I put my models together, I sometimes produced a model that was the *enantiomer* of the formula shown in the homework assignment. However, it doesn't matter in this case because the starting materials are achiral and the products are racemic (enantiomers are present, but not drawn).