

CHEMISTRY 412/512

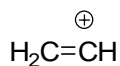
Final exam

May 03, 2007

Name

The total number of points is 35. The total exam time is 120 min (2 h).

1. (4 pts) Consider the vinyl carbocation (see below). Use the group orbitals for CH₂ and CH to construct the orbital mixing diagram for the carbocation. Occupy the resultant orbitals with the appropriate number of electrons.



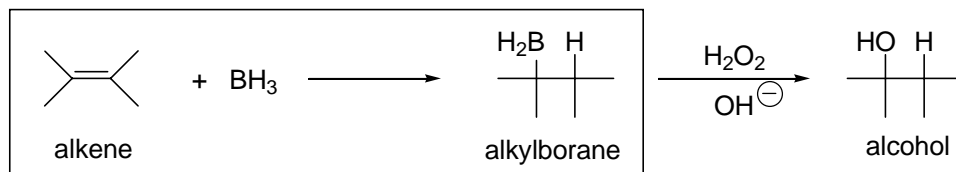
2. (4 pts) Provide structures for two odd-alternant hydrocarbons and two nonalternant hydrocarbons.

3. (4 pts) In cyclic amines, such as piperidine (see below), there is a substantial difference in the properties of the axial C – H bonds at C2 and C6 and the equatorial ones at the same centers. One particular aspect is bond strength: The axial C – H bonds are weaker than the equatorial ones (evidenced by their IR frequencies). Provide a structural rationalization for this result.



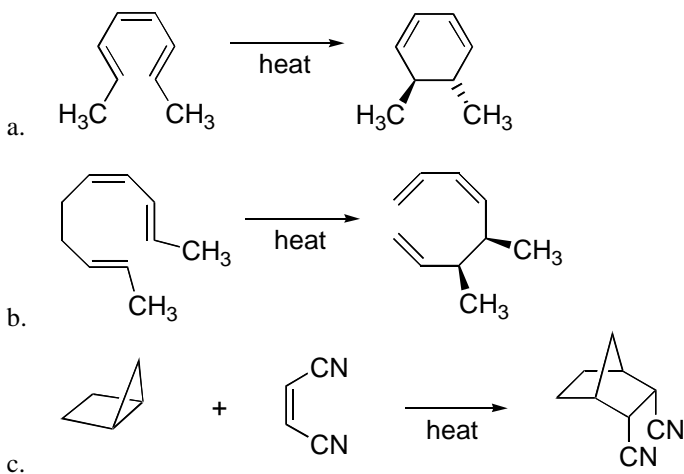
piperidine

4. (4 pts) One of the most useful methodologies to convert alkenes to alcohols is the hydroboration – oxidation procedure, which is depicted below. The first part is the hydroboration, which is a concerted addition of borane (BH_3) to the carbon – carbon double bond to form an alkylborane. It can be viewed as a cycloaddition process. Analyze hydroboration using a) the *Möbius/Hückel* TS protocol and b) the FMO theory. Show explicitly the allowed transition state geometry. Indicate whether the process is *supra* or *antara* with respect to each of the components.

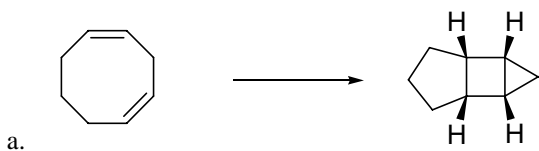


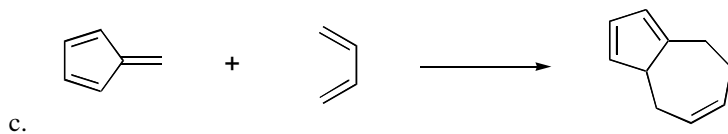
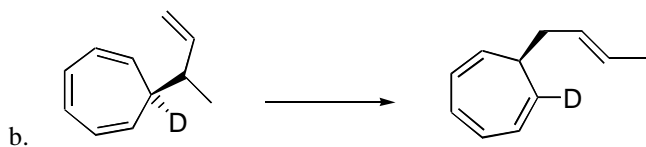
Hydroboration - Oxidation

5. (6 pts) Determine whether each of the following reactions is allowed or forbidden as suggested.

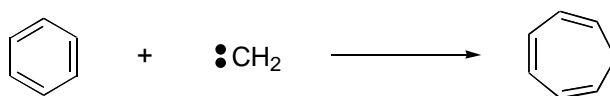


6. (6 pts) Classify each of the following reactions as electrocyclic, $[m + n]$ cycloaddition or an $[i, j]$ sigmatropic rearrangement. Predict if it is allowed or forbidden.





7. (3 pts) The addition of carbene (:CH_2) to benzene leads to a product with a seven-membered ring. Mechanistically, this conversion is a sequence of pericyclic reactions. Provide the detailed mechanism and specifically indicate the nature of each step.



8. (4 pts) Provide plausible mechanisms for the following transformations:

