

CHEM 633: Advanced Organic Chem: Physical
Problem Set 9
Due on THURS 11/19/09

1. When a mixture of 1,3-butadiene and ethylene are heated, cyclohexene is not formed. Instead, dimerization of 1,3-butadiene occurs.

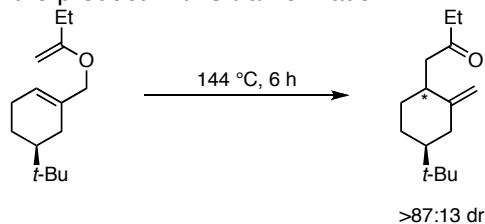
- (a) Predict the structure of the dimer of 1,3-butadiene.
 (b) Use FMO theory to show why 1,3-butadiene dimerizes more quickly than it reacts with ethylene.

2. Using FMO analysis, please illustrate why [1,5] hydrogen and alkyl shifts are allowed when suprafacial on the π component and proceeding with retention on the alkyl group.

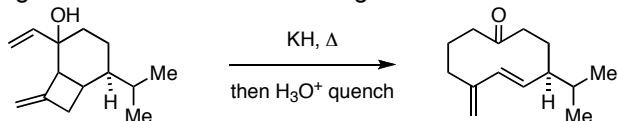
3. Please illustrate why the activation energy of the electrocyclic ring opening of **1** is much greater than that of **2**.



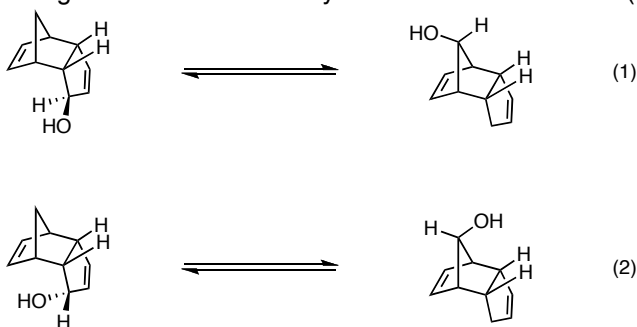
4. Predict the stereochemistry of the product in this transformation:



5. Propose an arrow-pushing mechanism for the following transformation.



6. Please consider the following isomerizations of tricyclic Diels–Alder adducts (eq 1 and 2).



- (a) Please propose **two** fundamentally different mechanisms for the transformation in eq 1. (Hint: Both mechanisms involve *only* pericyclic reactions as elementary steps.)
 (b) Within the limits of detection, only one stereoisomer is observed in each transformation (eq 1 and 2). On the basis of these results, evaluate the plausibility of each of your proposed mechanisms.

7. Please explain why Lewis acid catalysis *decreases* the regioselectivity of the following reaction.

