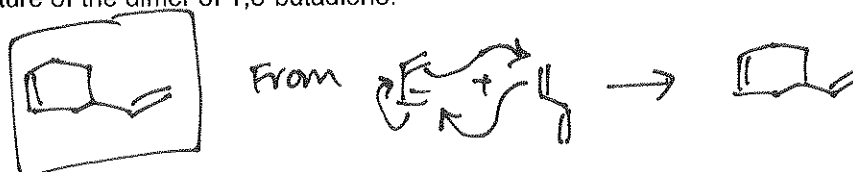


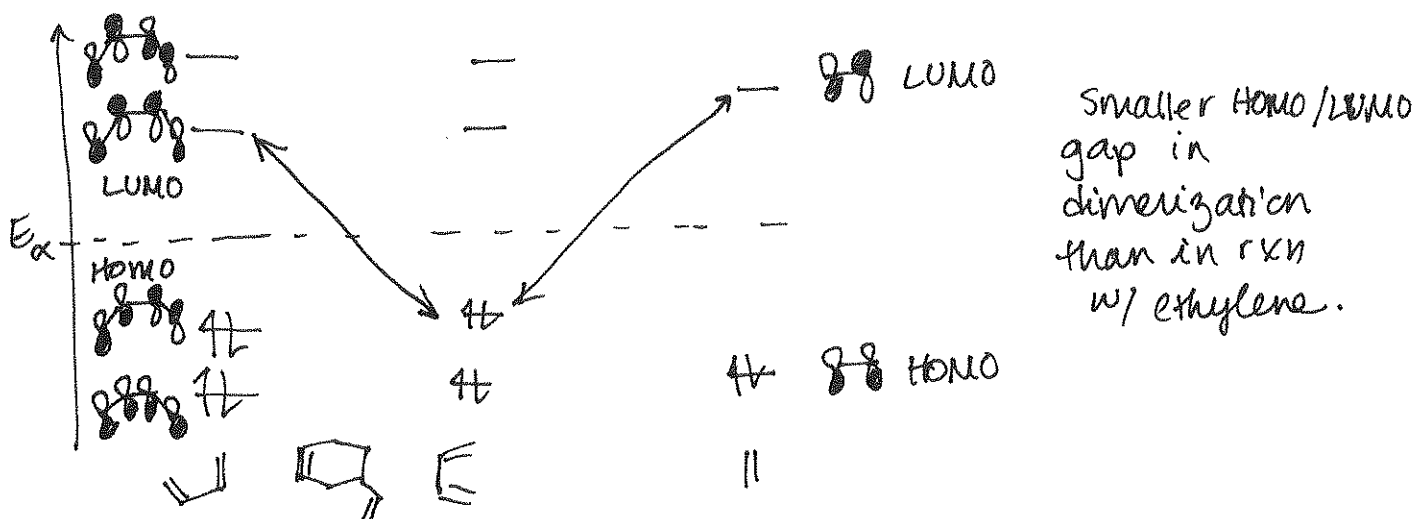
CHEM 633: Advanced Organic Chem: Physical
 Problem Set 9 ANSWER KEY
 Due on THURS 11/19/09

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

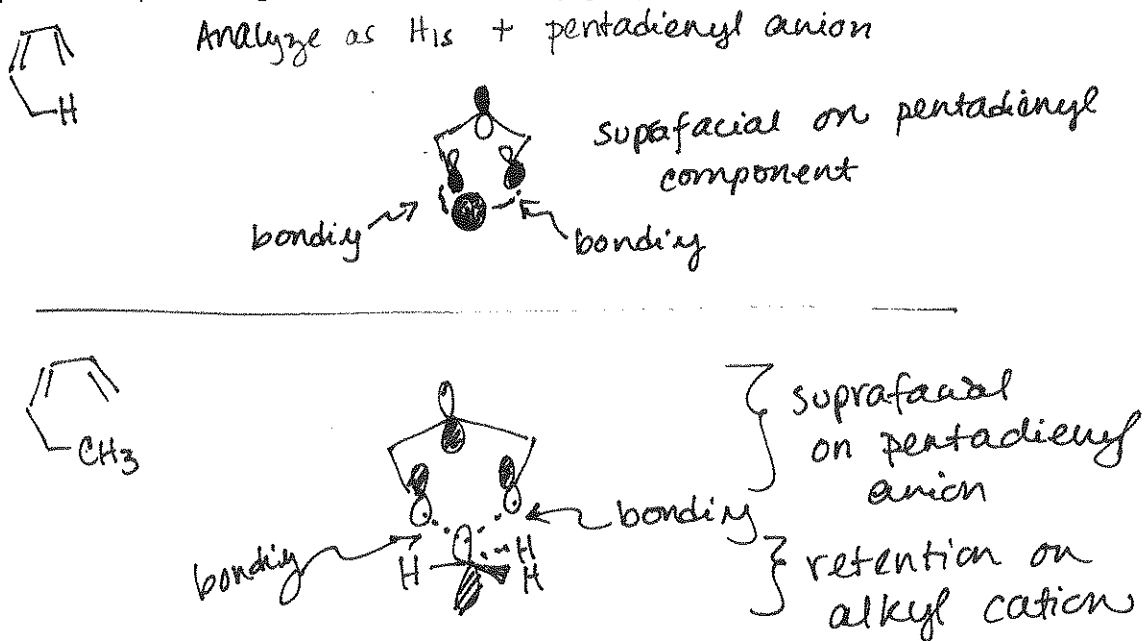
(a) Predict the structure of the dimer of 1,3-butadiene.



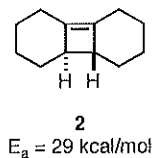
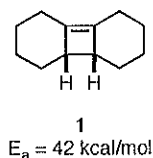
(b) Use FMO theory to show why 1,3-butadiene dimerizes more quickly than it reacts with ethylene.



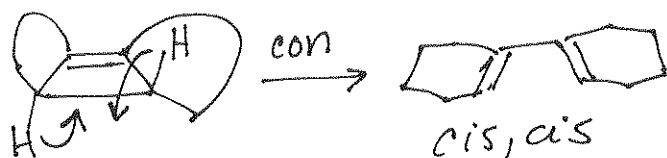
2. Using FMO analysis, please illustrate why [1,5] hydrogen and alkyl shifts are allowed when suprafacial on the π component and proceeding with retention on the alkyl group.



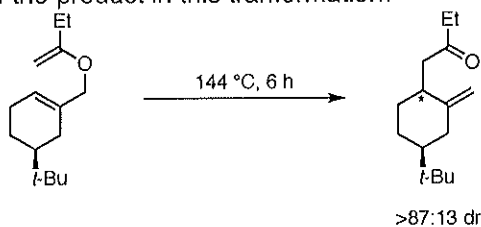
3. Please illustrate why the activation energy of the electrocyclic ring opening of 1 is much greater than that of 2.



trans olefin in cyclohexene is very strained \rightarrow build-up of strain raises TS energy.

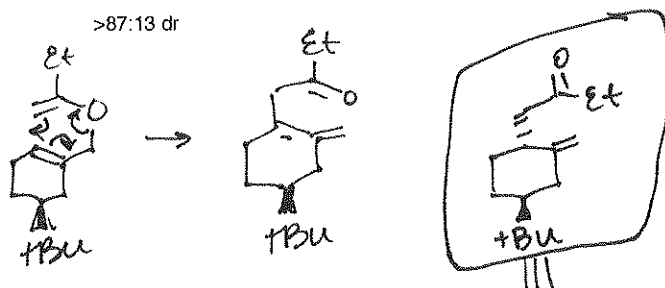


4. Predict the stereochemistry of the product in this transformation:

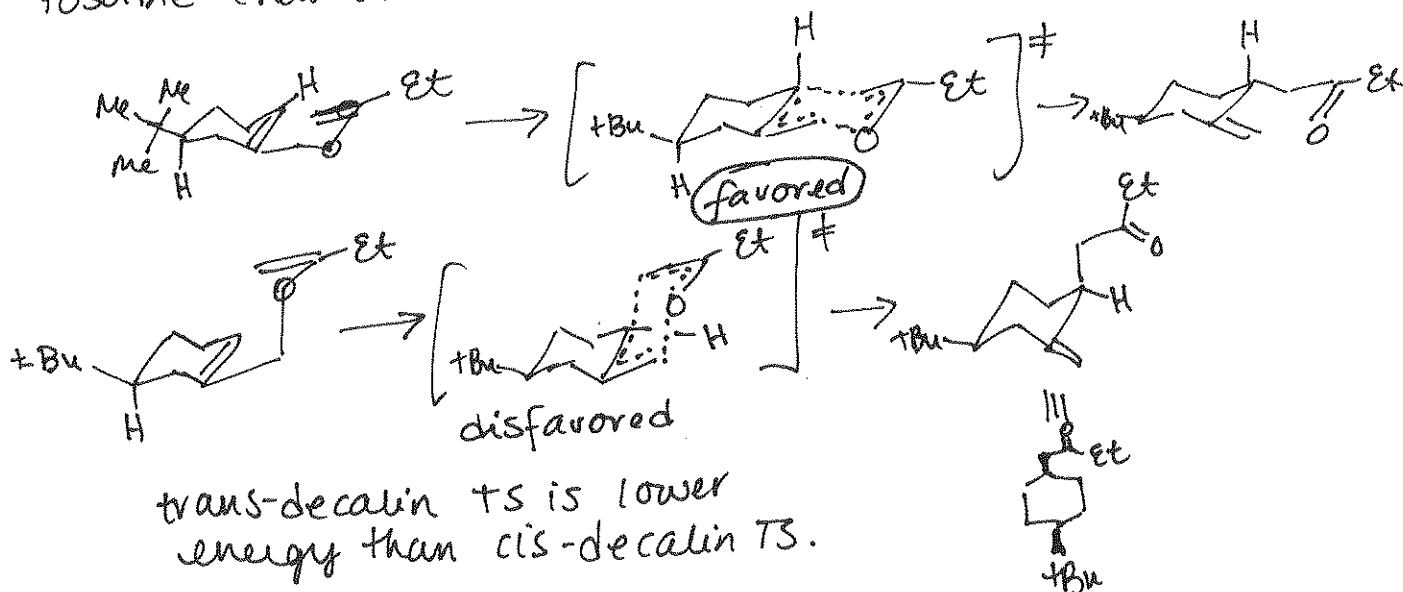


Ireland. JOC 1983, 48, 1829.

Claisen Rearrangement:

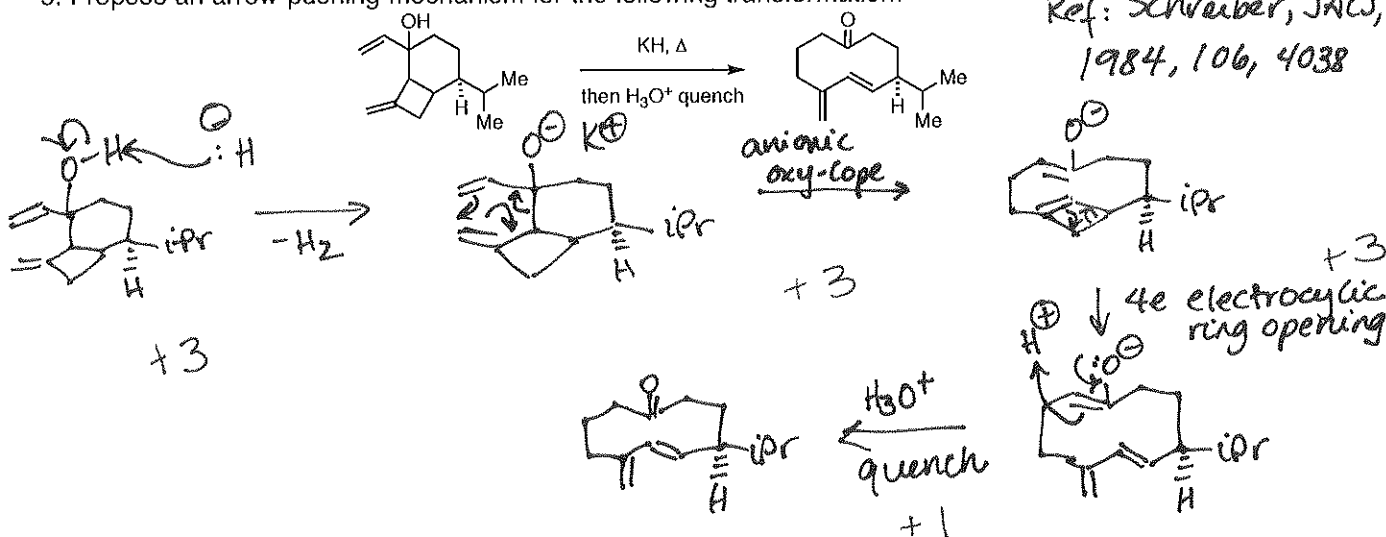


Possible Chair-like TS's:

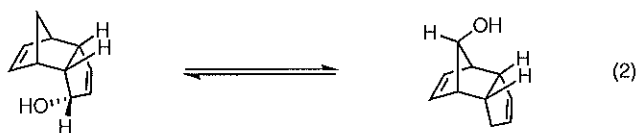
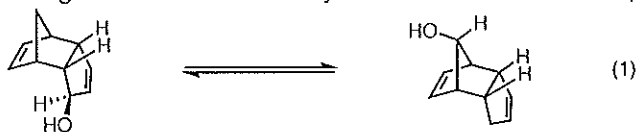


5. Propose an arrow-pushing mechanism for the following transformation.

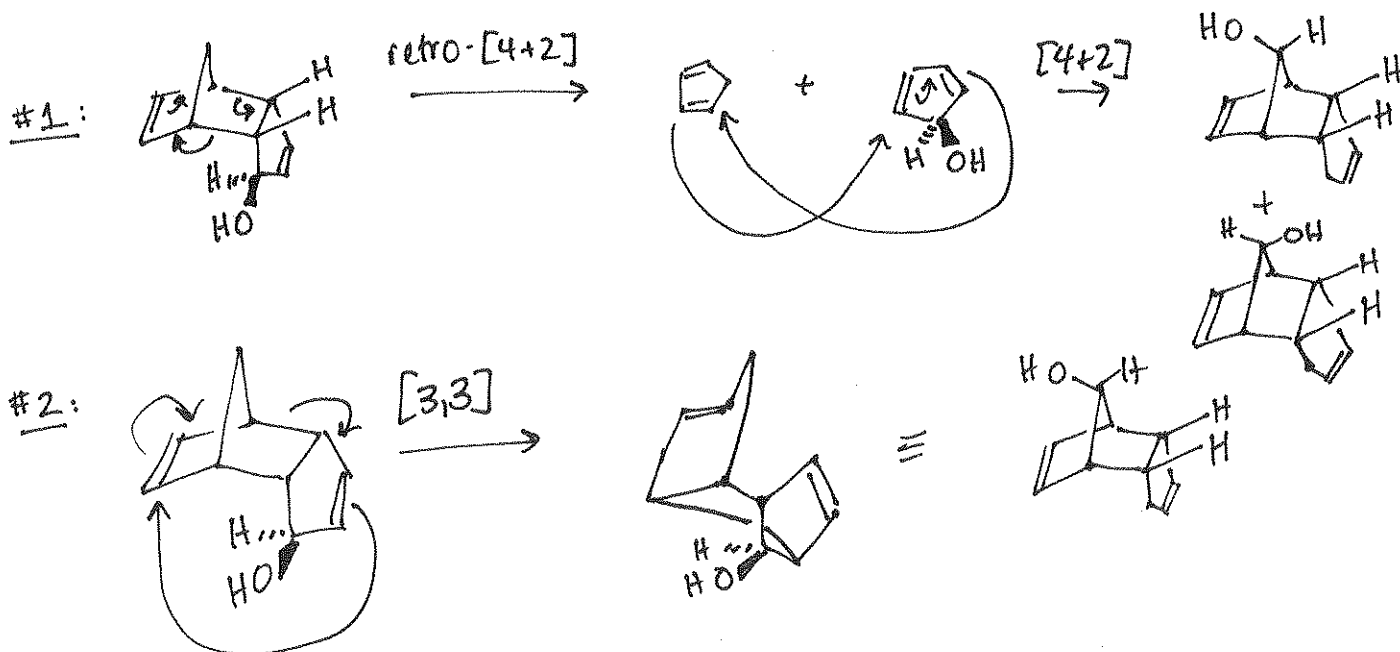
Ref: Schweiber, JACS, 1984, 106, 4038



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.)

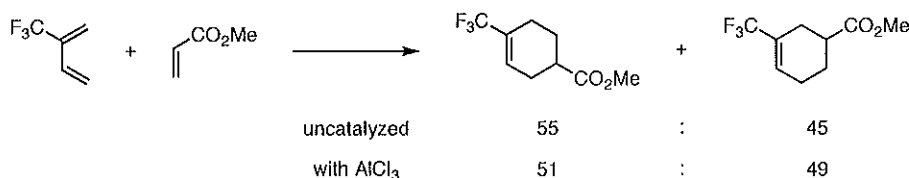


(b) Within the limits of detection, only one stereoisomer is observed in each transformation (eq 1 and 2). On the basis of these results, evaluate the plausibility of each of your proposed mechanisms.

#1 is not stereospecific. Both isomers would be observed. } RULED OUT.

#2 is stereospecific ← MORE LIKELY

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



We know in normal electron demand, Lewis acids increase regioselectivity.

Maybe this is inverse electron demand...

