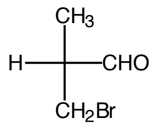
Chem 634
Pre-Problem Set
KEY

February 10, 2004
Prof. Fox

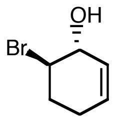
1. Assign all stereochemistry (R or S; E or Z)

a



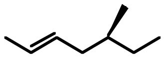
(2R)-3-bromo-2-methylpropanal

b



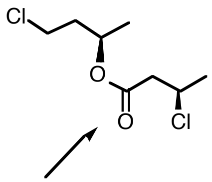
(1R,6R)-6-bromo-2-cyclohexenol

c



(2E, 5S)-5-methyl-2-heptene

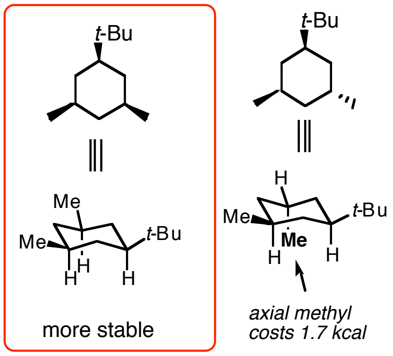
d



(1R)-3-chloro-1-methylpropyl (3R)-3-chlorobutanoate

2. For each pair, which is more stable?

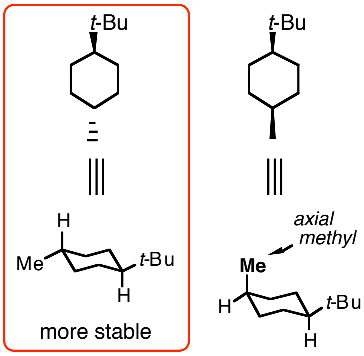
a



more stable

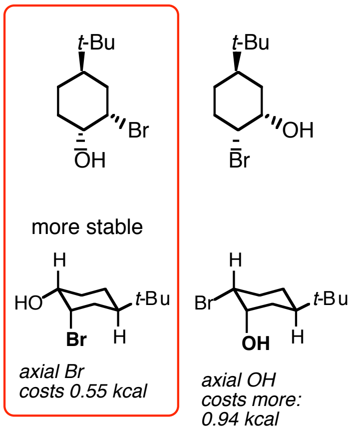
axial methyl costs 1.7 kcal

b



more stable

c



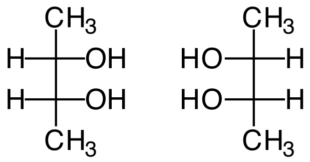
more stable

axial Br costs 0.55 kcal

axial OH costs more: 0.94 kcal

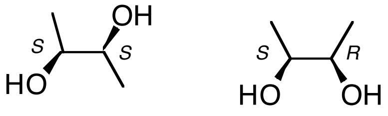
3. Indicate the relationship for each pair below: enantiomers, diastereomers, or meso

a



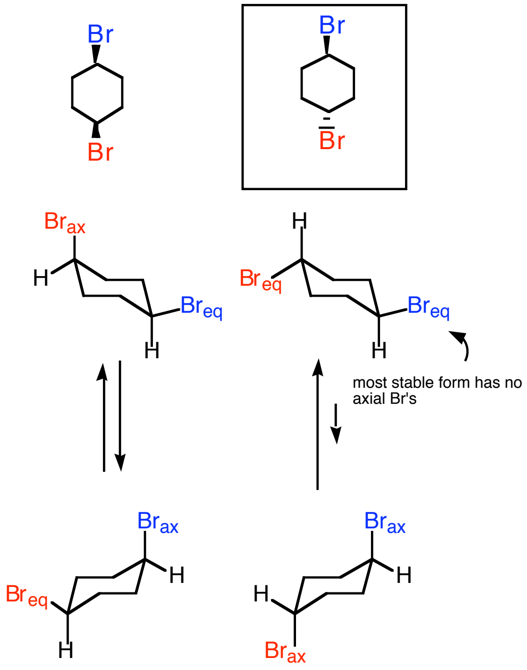
meso

b



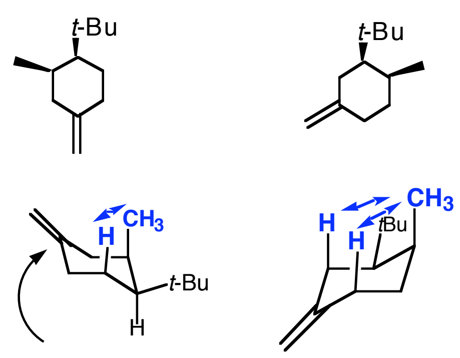
diastereomers

4) For each pair, indicate which is more stable. Use a clear picture to explain why



most stable form has no axial Br's

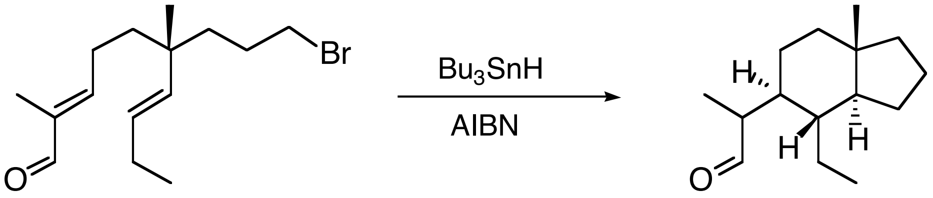
Both cyclohexanes are 'locked' with equatorial tBu's and axial methyl groups so the answer lies in the double bond



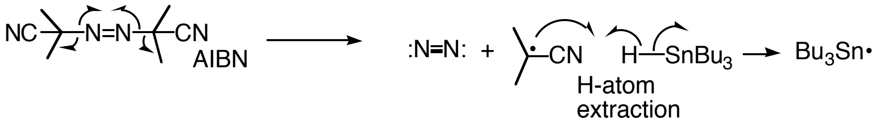
sp^2 center
There is no
axial group here,
and therefore there
is only one
1,3-diaxial interaction
make a model to
convince yourself!

two 1,3-diaxial
interactions

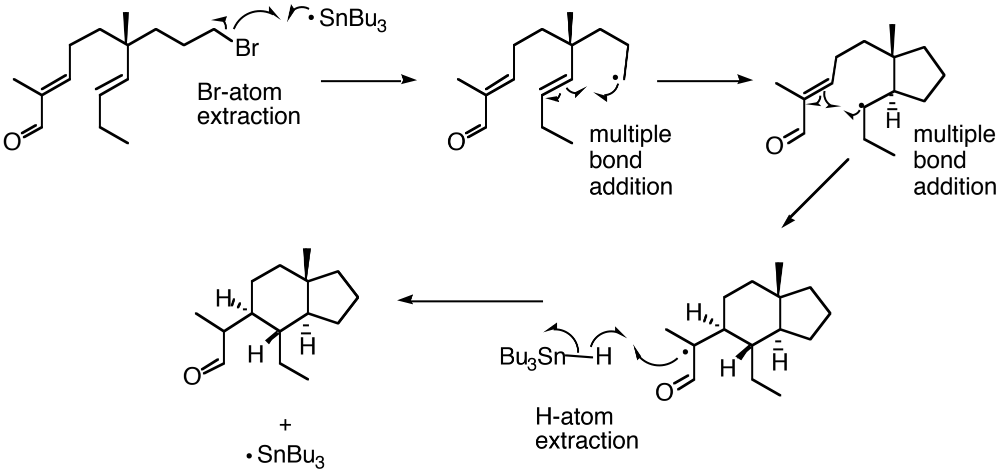
5. Provide a detailed arrow pushing mechanism for the following reaction



Initiation



H-atom
extraction



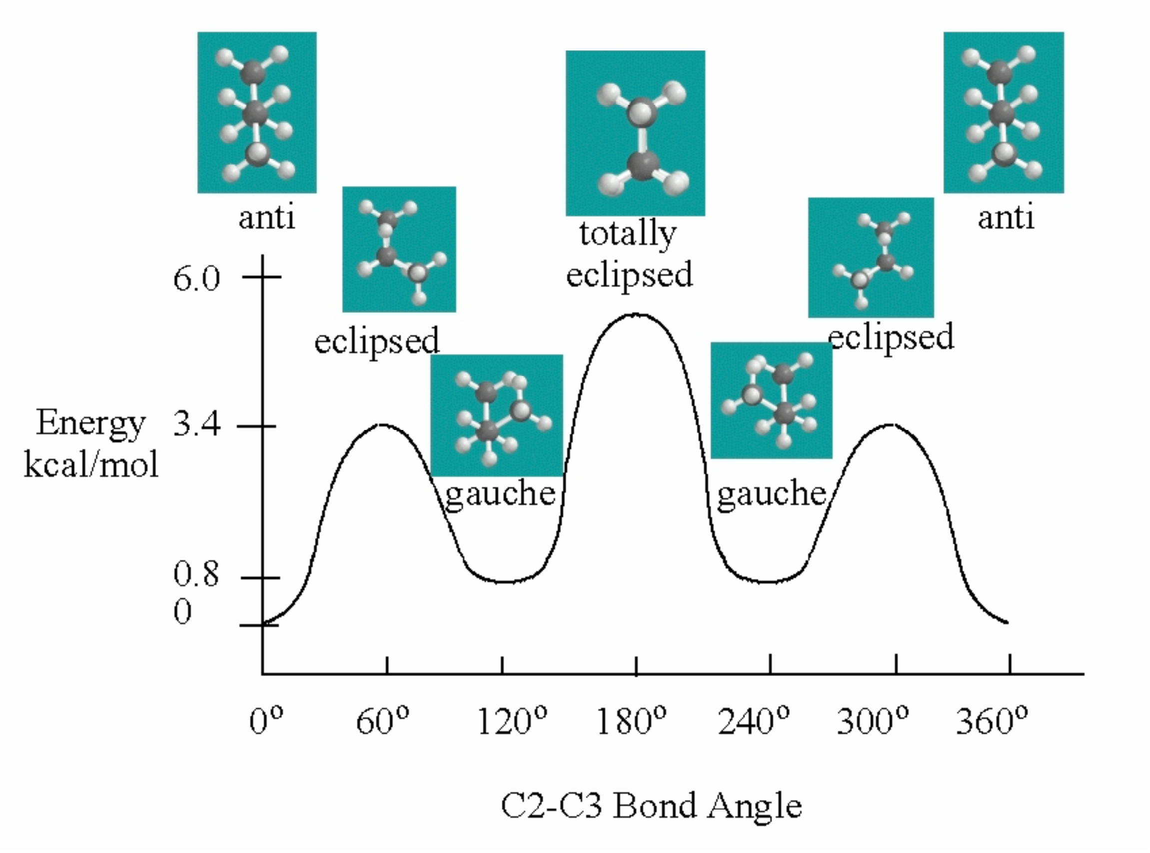
Br-atom
extraction

multiple
bond
addition

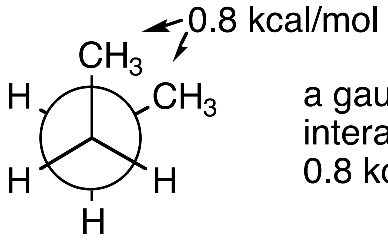
multiple
bond
addition

H-atom
extraction

6. Draw Newman projections for the staggered and eclipsed forms of n-butane. Give the relative energies of all of the eclipsed and staggered conformers.



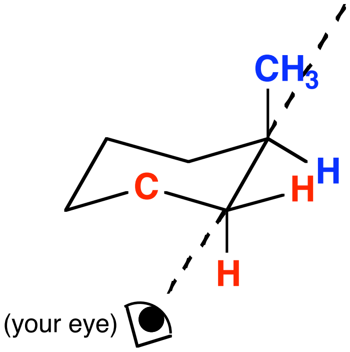
7. Gauche butane is ~ 0.8 kcal/mol higher in energy than anti butane. The A-strain of a methyl group on cyclohexane is ~1.7 kcal/mol. Use Newman projections to explain the relationship in detail.

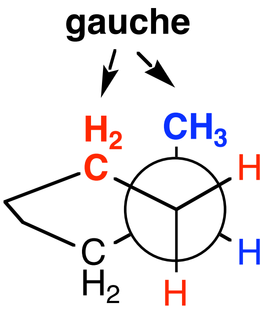


a gauche butane interaction costs 0.8 kcal/mol

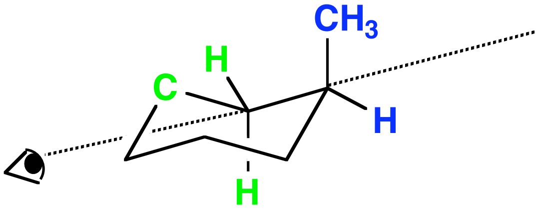
axial methylcyclohexane has two gauche butane type interactions

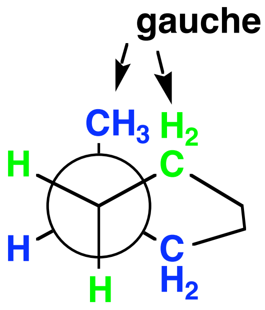
- the first can be seen from this projection





- the second can be seen from this projection

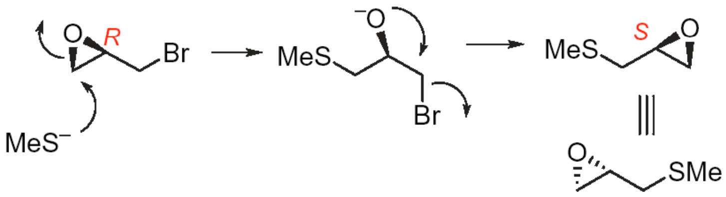




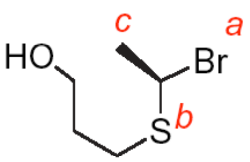
since each gauche interaction costs ~0.8 kcal.mol, 2 x 0.8 =1.6 kcal/mol. The actual value of 1.7 kcal/mol is a close fit.

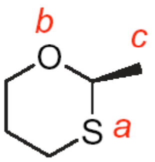
Use Models if you are having trouble seeing this!

8.



9.

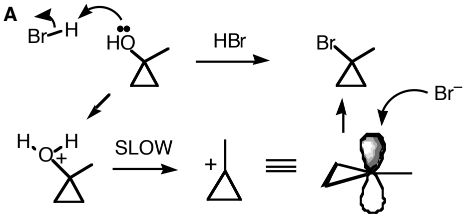




the 'trick' is in the assignments of stereochemistry. In the starting material, sulfur is the group of second highest priority. In the product, the sulfur has the highest priority. The apparent retention of stereochemistry is a result of a priority change, not a change in mechanism.

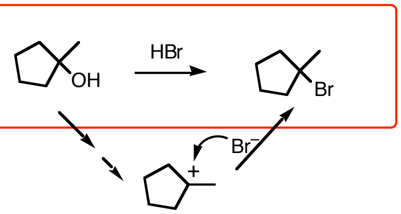
10) Which reaction is faster (**A** or **B**)? Why?

A



Remember: carbocation formation is rate determining!
The ideal geometry for a carbocation is planar with 120° angles.
Thus, the carbocation formation is slow because it is severly distorted by the 60 ° angle of the cyclopropane ring.

B

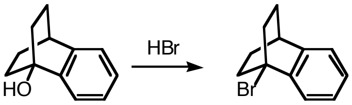


Severe distortions are *not* required in order to put a cyclopentane in a planar arrangement awith 120 ° angles.
This is the faster reaction

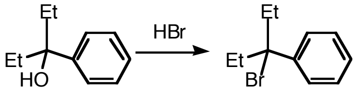
11) Which reaction is faster (**A** or **B**)? Why?

The arrow pushing is the same as for question 2. The rate differences again relate to carbocation stability.

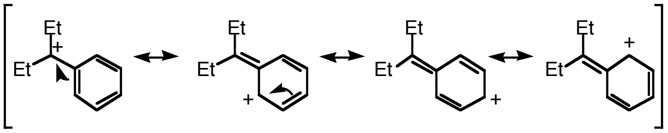
A



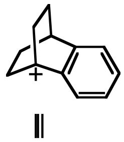
B



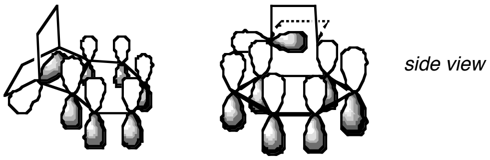
The carbocation intermediate is resonance stabilized (with the benzene ring— see below). This is the faster reaction



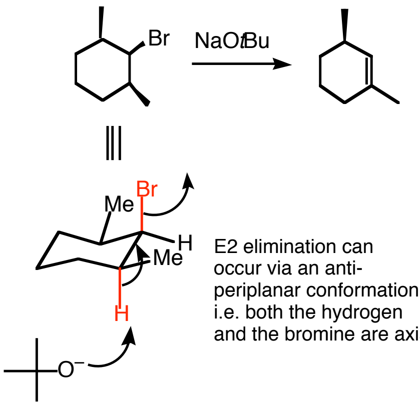
Such resonance structures do not apply for the cation below



the π orbital of the carbocation cannot overlap with the π system of the benzene ring.
No resonance stabilization

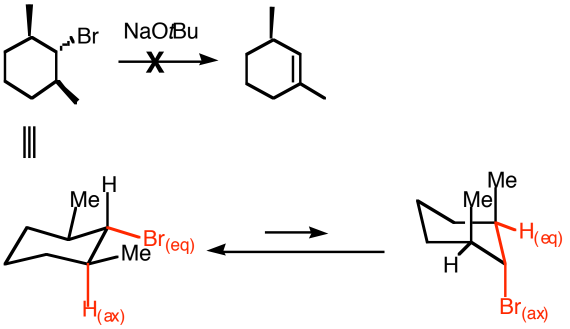


12) Provide a detailed explanation



E2 elimination can occur via an anti-periplanar conformation i.e. both the hydrogen and the bromine are axial

but



the molecule cannot adopt an conformation where Br and H are anti-periplanar. At least one group must be equatorial.

13) Provide a detailed arrow pushing mechanism.