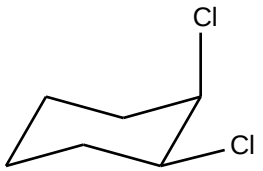
Exam 2 ***Chem 3045x*** ***Wednesday, November 5, 1997***

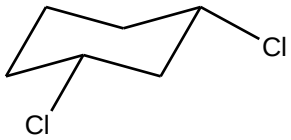
1. (10 Points) Draw the molecular structure corresponding to the most stable conformers of each of the following molecules. Which of these structures is chiral? Explain your reasoning.

cis-1,2-dichlorocyclohexane



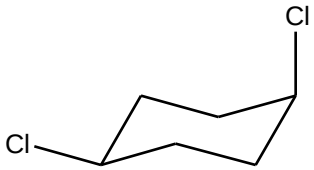
Chiral since there is no mirror plane in this molecule.

cis-1,3-dichlorocyclohexane



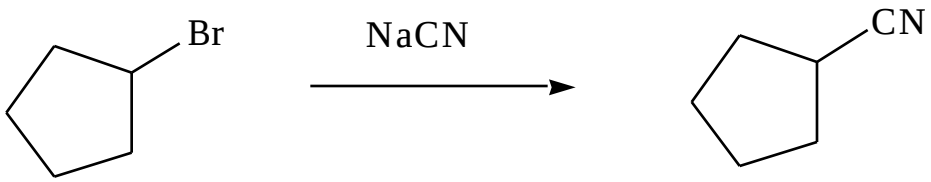
Achiral, mirror plane which passes between C2, C5

cis-1,4-dichlorocyclohexane



achiral, mirror plane between C1, C4

2. (10 Points) The reaction of cyclopentyl bromide with NaCN in acetone solvent yields cyclopentyl cyanide. The same reaction occurs when a small amount of NaI is added to an acetone solution containing cyclopentyl bromide and NaCN. However, the reaction occurs at a faster rate, i.e., the reaction is catalyzed by the addition of NaI. Suggest a reasonable explanation of the catalytic function of sodium iodide in the conversion of the bromide to the cyanide.

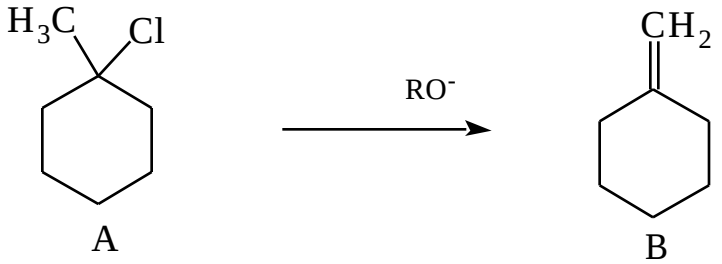


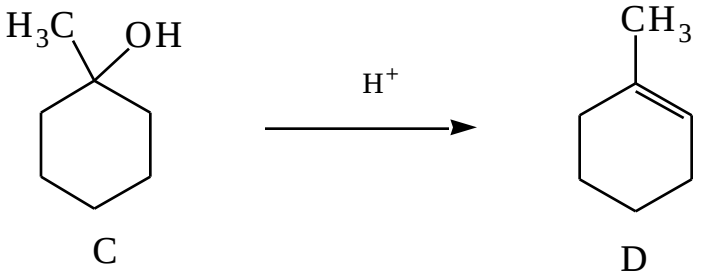
the cyclopentyl bromide reacts with the I- ion faster than the CN- nucleophile, which results in an intermediate cyclopentyl iodide. The intermediate cyclopentyl iodide reacts faster with the CN- than the cyclopentyl bromide, and the products of this reaction are the cyclopentyl cyanide and the I-. This frees the Iodide ion to catalyse another cycle of this reaction.

3. (10 Points) How many signals do you expect to see in the proton NMR of 2-pentanol? How many signals do you expect to see in the carbon 13 NMR of 2-pentanol? Explain your reasoning.

5- signals in H-NMR since there are 5 different types of H's in 2-pentanol.
5-signals in C-13 NMR since there a 5 different C's in 2-pentanol.

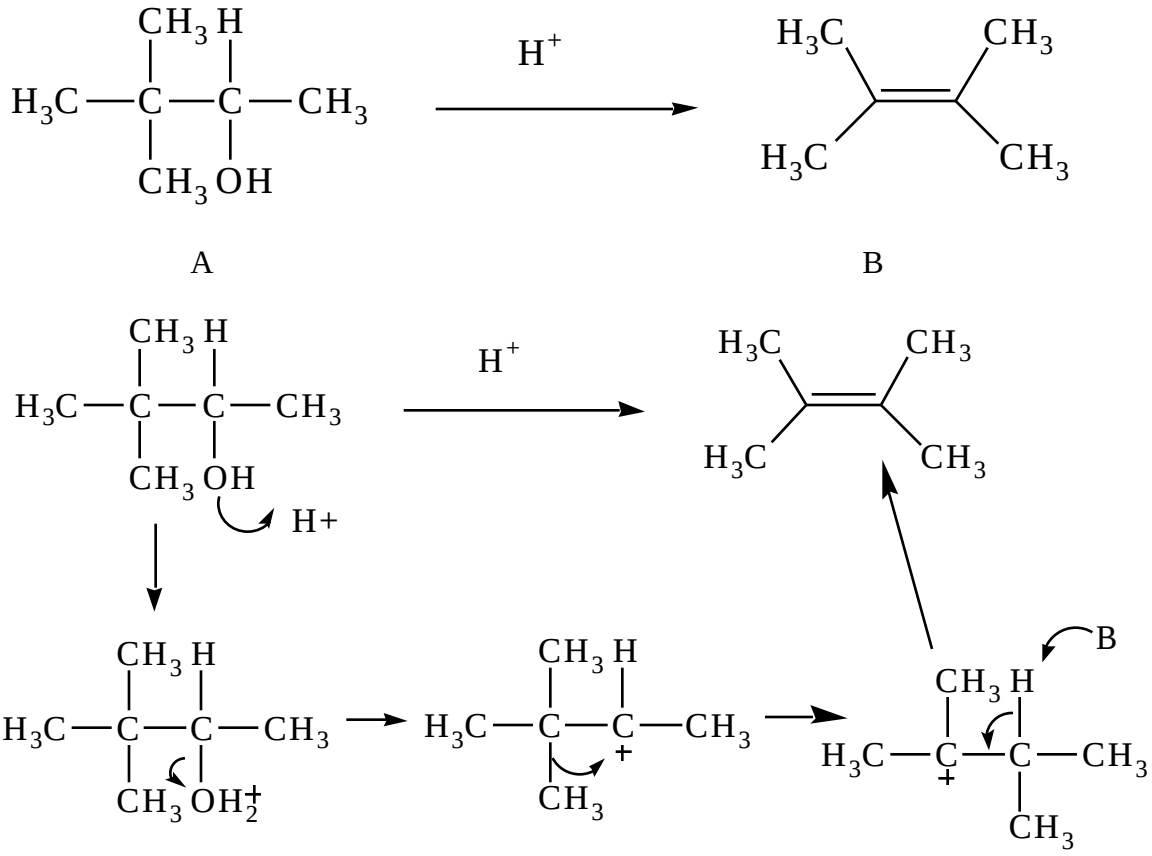
4. (10 Points) The chloride A yields the elimination product B upon treatment with base (RO^-), while the alcohol C yields the elimination product D upon treatment with acid. Explain why the eliminations yield different products.



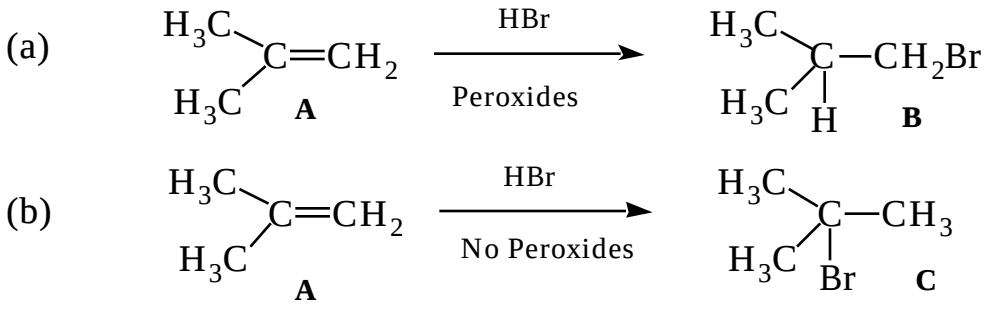


In the reaction C->D, we have acid catalysed dehydration of the alcohol to yield the most stable alkene (Zaitsev's rule).
In the reaction of A->B we generate the less stable alkene under basic conditions. Under basic condition we get E2 elimination. In this case we predict that the chloro-group will be in the axial position, so E2-eliminations are possible via deprotonation from the ring carbons as well as the methyl group (There are antiperi-planar hydrogens in the ring as well as on the methyl group). So we argue that steric effects would prevent the base from attacking the axial proton in the cyclohexane ring. The protons on the methyl group, which in not sterically hindered, will be deprotonated. This will result in the less substituted alkene (against Zaitsev's rule).

5. (10 Points) Treatment of the alcohol A leads to an ethylene with a rearranged carbon skeleton, B. Explain in terms of a mechanism.

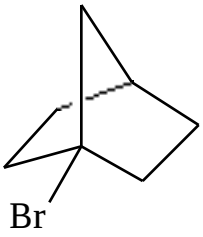


6. (10 Points) The ethylene A yields product B when treated with HBr and peroxides, but yields product C when treated with peroxide free HBr. Give a mechanistic interpretation of these results.

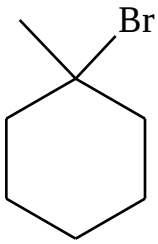


(a)In the presence of peroxides, get radical reaction (mxn p. 225 Carey) with Anti-Markovnikov regiochemistry.
(b)No peroxides, get an electrophilic addition of H-Br to the double bond, Markovnikov. (see p. 219 Carey)

7. (10 Points) Consider the two tertiary bromides, A and B. One of these bromides is very reactive to elimination under basic conditions and is also reactive to nucleophilic substitution under acidic conditions, while the other is completely inert to both elimination and substitution under the same conditions. Which bromide is inert and why?



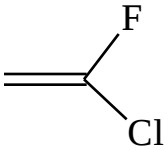
(A)



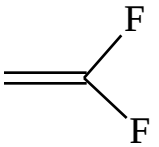
(B)

(A) is a tertiary alkyl bromide, so it should react via Sn1 mechanism (carbocation), but since it is tied up in a bicyclic ring, the carbocation formed on dissociation of Br- cannot become planar. For this reason, the carbonium ion will be extremely high energy, so it won't be formed. => compound is inert to substitution.

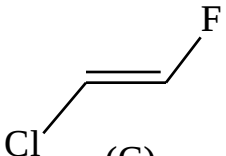
8. (10 Points) Imagine molecules that existed in "Flatland", that is two dimensional space. Translating the ideas of chirality in three dimensional space to two dimensional space, which, if any, of the following molecules are chiral in "Flatland"? Explain your reasoning.



(A)



(B)

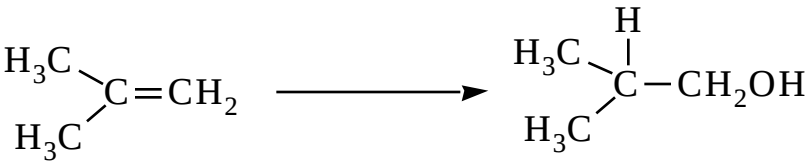


(C)

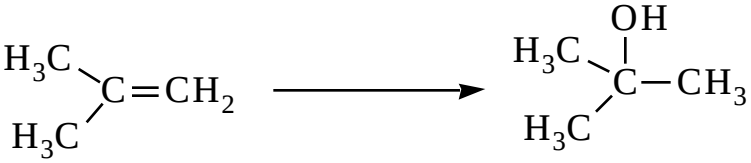
(D)

In "flatland" we are looking not for planes of symmetry but rather lines of symmetry. Any molecule with a line of symmetry will be achiral, without a line of symmetry will be chiral. A & C have no line of symmetry, they are chiral in flatland. B & C are achiral.

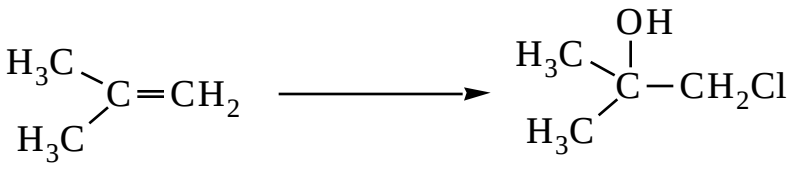
9. (20 Points) Indicate how you would achieve the following syntheses. Do not write mechanisms, just indicate the steps and reagents required to achieve the reactions indicated.

(a) 

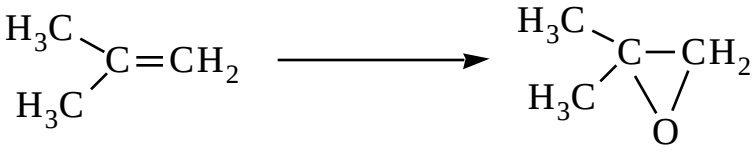
1)B2H6
2) H2O2 / Base

(b) 

H+, H2O

(c) 

Cl2, H2O

(d) 

RC(O)OOH