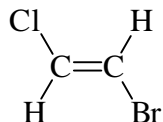
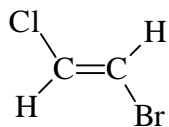
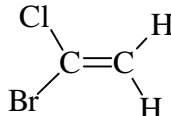


Exam # 3
Chemistry 2401 – March 23, 2007

(8) I. Draw all isomers with a molecular formula of C_2H_2BrCl . Indicate which ones are stereoisomers and which are constitutional isomers.



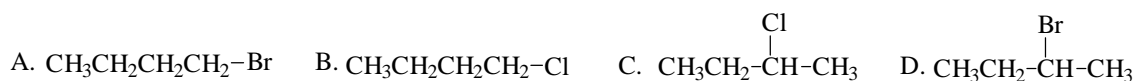
stereoisomers



constitutional isomer to the other two

(30) II. MULTIPLE CHOICE: Circle the letter corresponding to the correct response.

1. Which of the following would undergo an S_N2 reaction fastest with CN^- ?



A: least crowded with best leaving group.

2. Which of the following is the best nucleophile in an acetone solution?



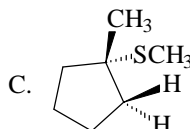
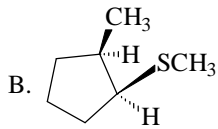
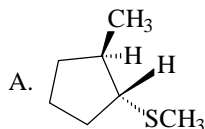
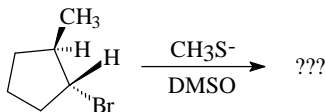
A: In polar aprotic solvents nucleophilicity parallels basicity

3. Which of the following is the best nucleophile in an ethanol solution?



D. It is larger and less solvated in the protic solvent.

B.4. Which of the following would result from the S_N2 reaction shown?

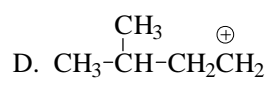
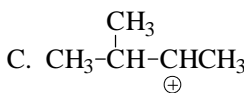
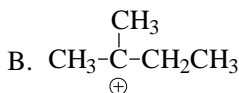
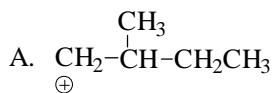


D. both A and B

E. A, B, and C

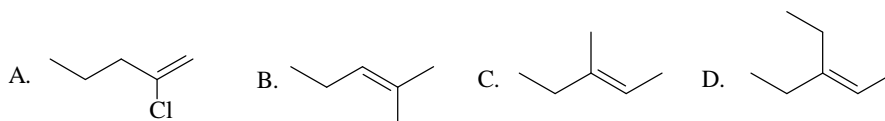
B. S_N2 reactions proceed with inversion.

5. Which of the following carbocations would be formed fastest from the corresponding alkyl bromide in an ethanol solution?



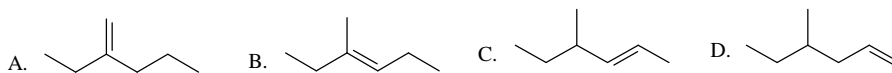
B. More stable 3° carbocation is formed faster.

6. Which of the following alkenes exists as stereoisomers?



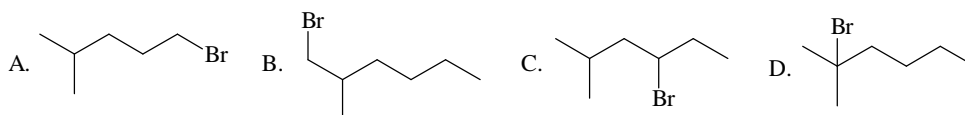
C. Only one with two different groups attached to each double bond carbon

7. If you burned each of the following alkenes, which one would produce the most heat?



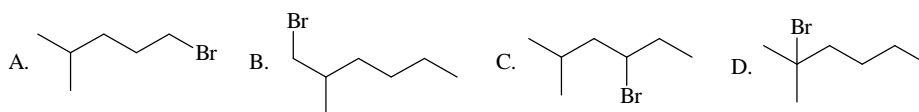
D. The least stable alkene produces the most heat when it is burned.

8. Which of the following alkyl halides would undergo an E2 reaction fastest?



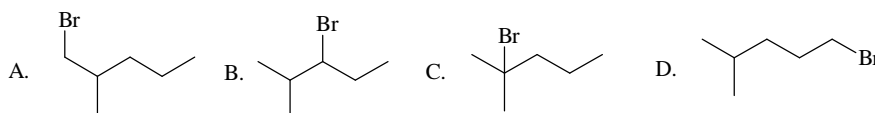
D. Order of reactivity for E2 is $3^\circ > 2^\circ > 1^\circ$ as we showed in lab

9. Which of the alkyl halides in # 8 would undergo an E1 reaction fastest?



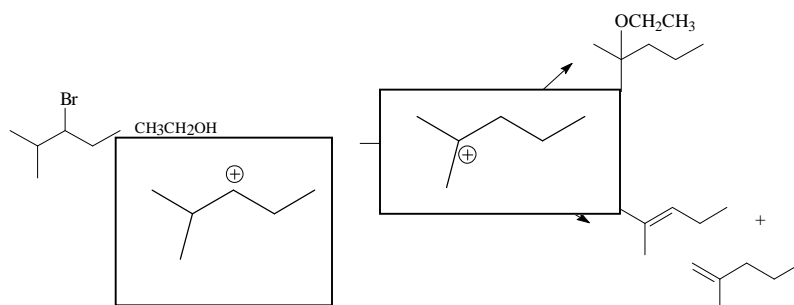
D. Order of reactivity parallels the stability of the carbocation generated.

10. Which of the alkyl halides would produce 3 different products when subjected to an E2 elimination reaction?



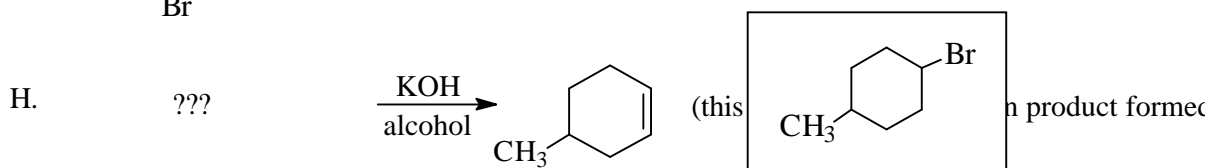
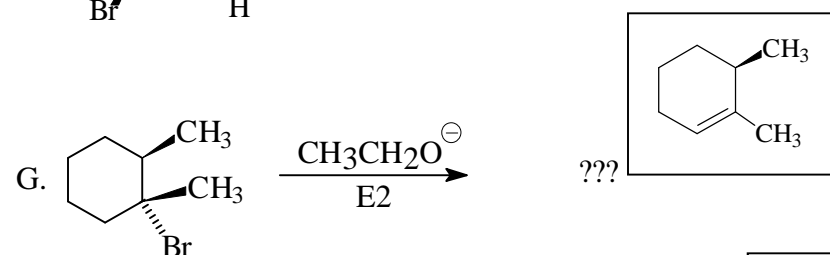
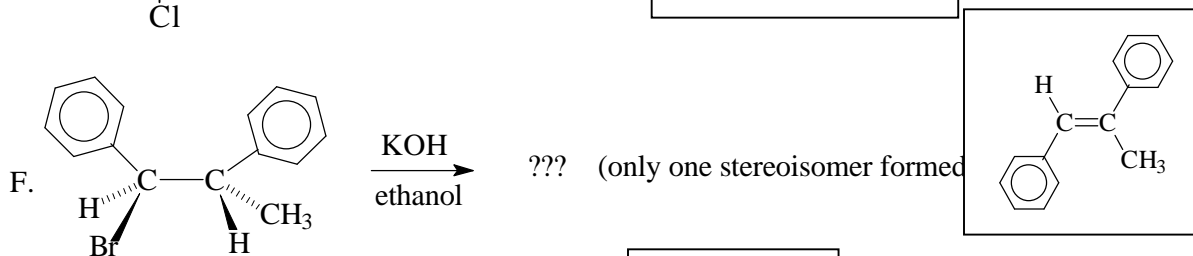
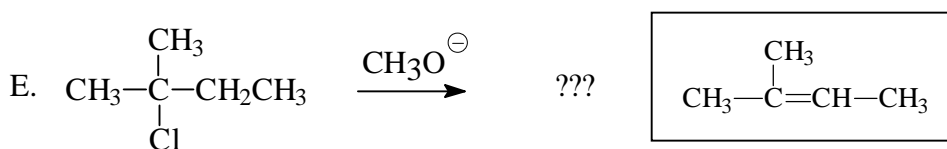
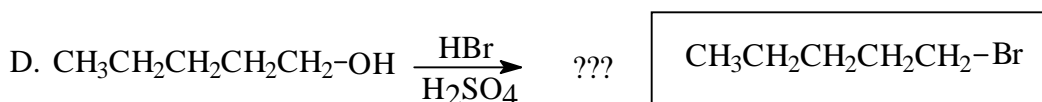
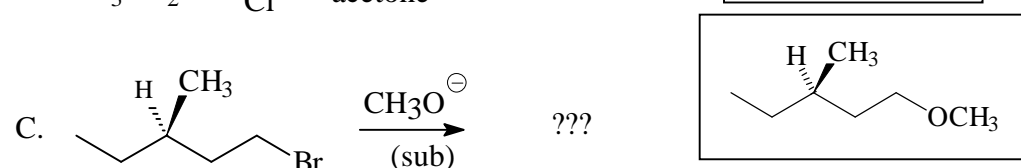
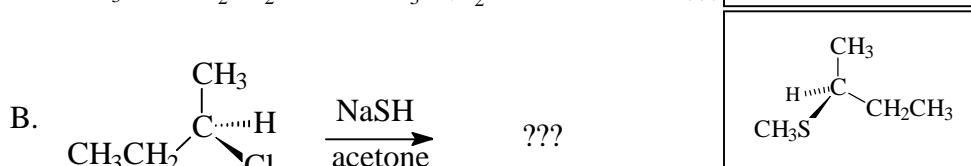
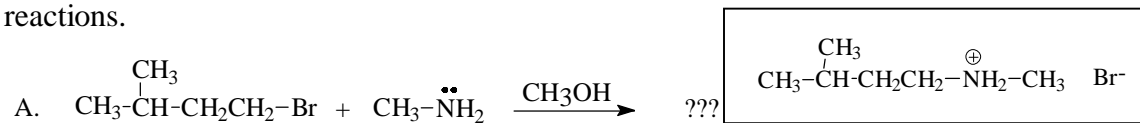
B. Produces 2-methyl-2-pentene and cis- and trans-4-methyl-2-pentene

(9) III. The rates of the reactions shown below depend only on the concentration of the alkyl halide. Fill in the structures of the missing reactive intermediates.



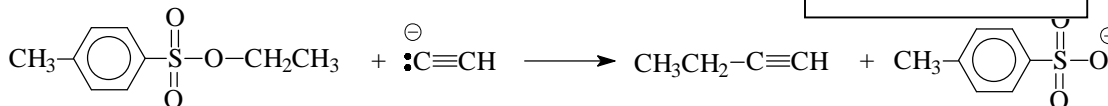
Rearrangement must occur to form the products observed.

(24) III. Write structural formulas for the products resulting from each of the following reactions.



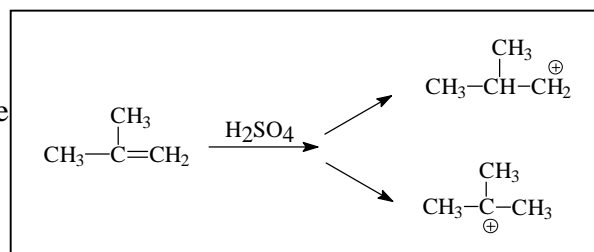
(12) IV. Explain briefly each of the following.

Given that the pK_a for p-toluenesulfonic acid (right) is -6.5 , what can you say about the rate of the reaction shown below. Explain your answer.



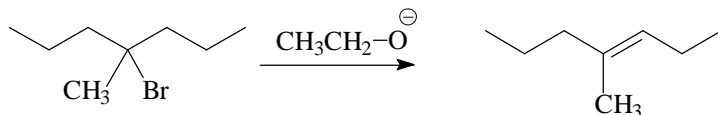
Since p-toluenesulfonic acid is a strong acid, its conjugate base is very weak which makes it an excellent leaving group. Therefore, this nucleophilic substitution reaction will be quite fast.

B. The transfer of a proton from a strong acid to isobutylene can occur in two ways as shown at the right. Use **Hammond's postulate** to explain why, in practice, the tert-butyl cation is formed much faster than the isobutyl cation.



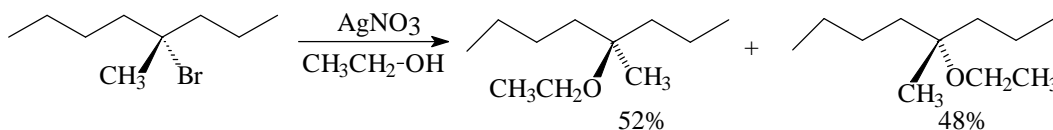
The formation of these carbocations are endothermic reactions. Hammond's postulate says that in an endothermic reaction the transition state will look like the product. In this case this means that the transition state leading to the more stable 3° carbocation will be lower in energy and that reaction will be faster.

C. Explain why the E2 reaction shown below occurs many times faster in DMSO solution than it does in methanol.



DMSO is a polar aprotic solvent which means that the ethoxide anion is poorly solvated and therefore more reactive.

D. The reaction of S-4-bromo-4-methyloctane with a solution of silver nitrate in ethanol yields the results shown.



1) Why are almost equal amounts of the two enantiomers formed?

The carbocation intermediate is planar and can be attacked equally well from either side.

2) Why is a slight excess of the R enantiomer formed?

The leaving group protects the front side while it is leaving providing a slight prejudice for backside attack.