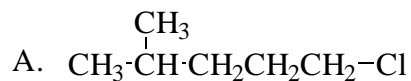
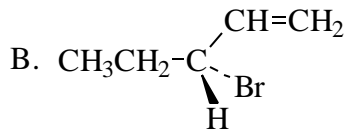


CHEMISTRY 2401  
Exam # 4 - December 10, 1999

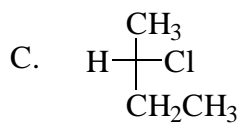
(12) I. Name each of the following including stereochemical designations (R & S) where appropriate.



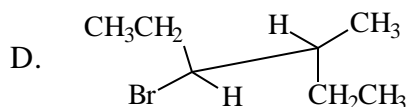
1-chloro-1-methylpentane



R-3-bromo-1-pentene



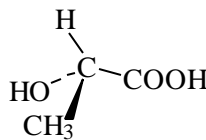
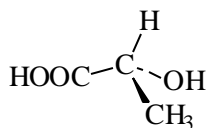
S-2-chlorobutane



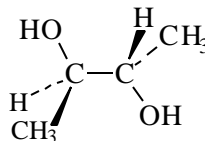
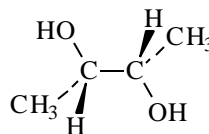
(3R,4S)-3-bromo-4-methylhexane

(6) II. Draw structural formulas for each of the following:

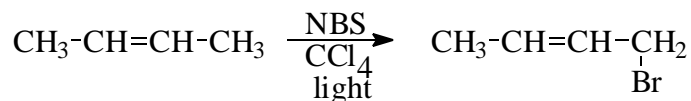
A. (-)-Lactic acid has the structure shown below:  
Draw the structure of (+)-lactic acid.



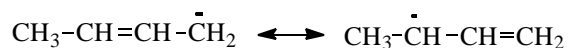
B. Draw a diastereomer of the compound shown below.



(6) III. 2-Butene undergoes the allylic bromination shown below:



A. Draw resonance structures for the free radical intermediate in this reaction.

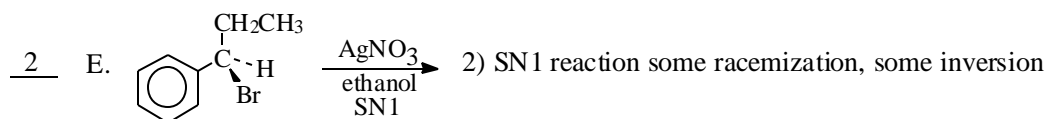
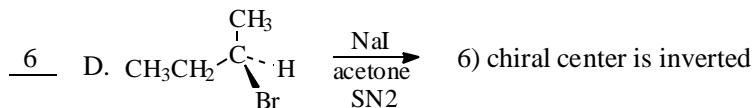
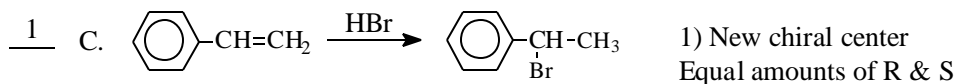
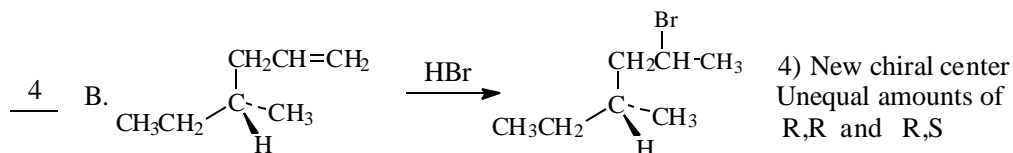
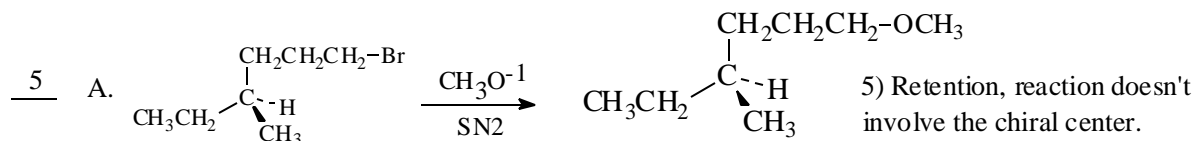


B. Actually a second product is also formed by the reaction. Draw it.



(18) IV. What are the stereochemical consequences of each of the following reactions. I've listed the possible answers below. Choose the right one and place its number in the space provided. Use each answer only once.

1. Equal amounts of two enantiomers are formed.
- 2) Two enantiomers are formed in unequal amounts.
- 3) Two diastereomers are formed in equal amounts.
- 4) Two diastereomers are formed in unequal amounts.
- 5) Only one enantiomer is formed and the absolute configuration of the chiral center is retained.
- 6) Only one enantiomer is formed and the absolute configuration of the chiral center is inverted.



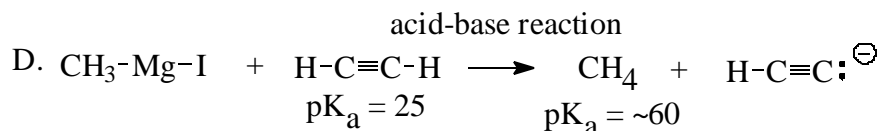
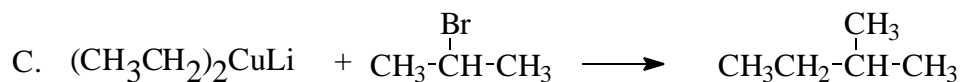
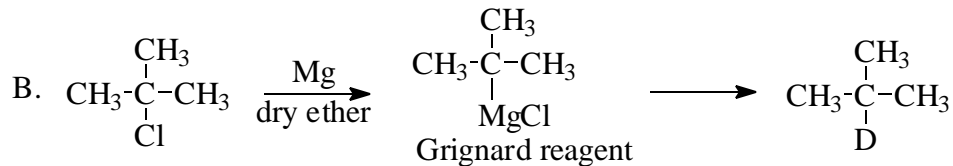
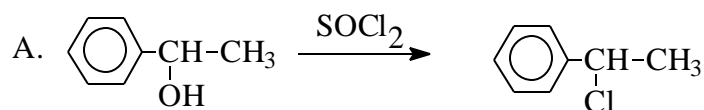
(9) V. Answer each of the following:

A. Name of the enantiomer of (2R,3S)-dichlorohexane? (2S,3R)-dichlorohexane

B. Name of a diastereomer of (2R,3S)-dichlorohexane? (2R,3R)-dichlorohexane

C. What would be the absolute configuration of the chiral centers in meso-3,4-dichlorohexane?  
R and S

(12) VI. Complete each of the reactions shown below.

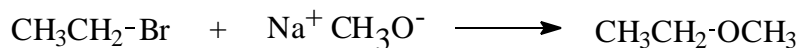


(18) VII. Explain each of the following observations in molecular terms. While being brief, you should demonstrate that you understand the principles involved. For example, in response to the first question it is not sufficient to say that tertiary halides undergo  $\text{S}_{\text{N}}1$  reactions faster than primary halides. You must also explain why this is true.

A. When mixed with  $\text{AgNO}_3$  in ethanol, 2-chloro-2-methylpropane produces a white precipitate of  $\text{AgCl}$  almost immediately, but it takes days for the precipitate to form when the halide used is 1-chlorobutane.

*This is an  $\text{S}_{\text{N}}1$  reaction and the rate determining step in  $\text{S}_{\text{N}}1$  reactions is the formation of a carbocation. Since the transition state looks very much like the carbocation, more stable carbocations will have lower energies of activation for their formation. Since the tertiary carbocation formed from 2-chloro-2-methylpropane is more stable than the primary carbocation formed from 1-chlorobutane, that reaction occurs faster.*

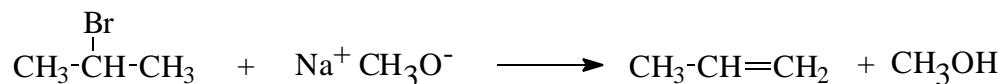
B. The reaction of ethyl bromide with sodium methoxide (below) occurs much more rapidly in acetone than it does in ethanol.



*In ethanol the methoxide ion is solvated by ethanol molecules and must break through this solvation sphere to react. In the polar aprotic solvent, acetone, the methoxide ion is not solvated and this unsolvated ion is more reactive in  $\text{S}_{\text{N}}2$  reactions such as the one shown.*

C. 2-Bromopropane also reacts rapidly with sodium methoxide in acetone (see part B), but the reaction does not produce the expected ether.

Since the alkyl halide is secondary and the methoxide ion is a strong base, the reaction that occurs here is not the SN2 reaction shown, but is instead the E2 reaction below:

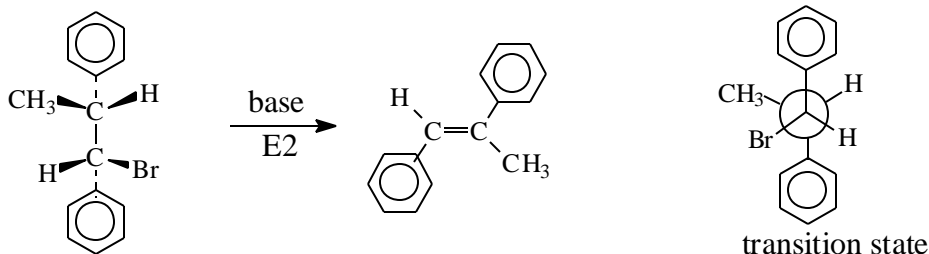


D. In our laboratory experiment allyl chloride, CH<sub>2</sub>=CH-CH<sub>2</sub>-Cl reacted well with both NaI/acetone (SN2) and AgNO<sub>3</sub>/ethanol (SN1).

*Allyl chloride undergoes SN2 reactions readily because it is uncrowded (primary).*

*Allyl chloride undergoes SN1 reactions readily because it forms a low energy (resonance stabilized) carbocation.*

E. The stereoisomer of 1-bromo-2,3-diphenylpropane shown below undergoes E2 elimination in base to form only the E-isomer of the product alkene. (Draw the transition state for this reaction as part of the answer)



*In order for the compound to undergo an E2 reaction, the -H and the -Br must be anti-periplanar. Placing these groups anti-planar also requires that the two benzene rings be anti which results in the formation of only the E-isomer.*

F. 2-Bromobutane reacts faster than 2-chlorobutane in both SN1 reactions (AgNO<sub>3</sub>, ethanol) and SN2 reactions (NaI, acetone).

*Anyone who does not get the right answer to this question deserves a good, swift kick in the pants.*