CHEMISTRY 230/232

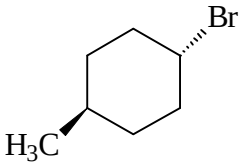
Final Examination December 1991

1. Fill in the blank in the following equations with the correct structural formula. If stereochemical details are important, make sure your drawing shows these. Show any required catalysts over the arrow. [33 points]

(a)

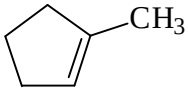
$(CH_3)_2C{=}CHCH_2CH_3$ + _____ → $(CH_3)_2CHCHCH_2CH_3$ (OH)

(b)



+ CN^- → _____

(c)



+ Br_2 $\xrightarrow[\text{solvent}]{CCl_4}$ _____

(d)

$CH_3CH_2CHCH{=}O$ (CH_3) + CH_3CH_2OH (excess) → _____

(e)

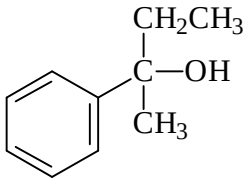
$CH_2{=}CCH_2CH_2CH_2Br$ (Br) + OH^- → _____

(f)

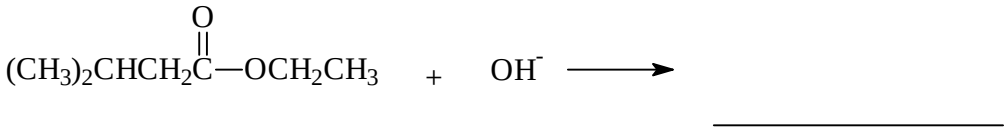
$CH_3CH_2C(=O)-OH$ + _____ → $CH_3CH_2C(=O)-Cl$

(g)

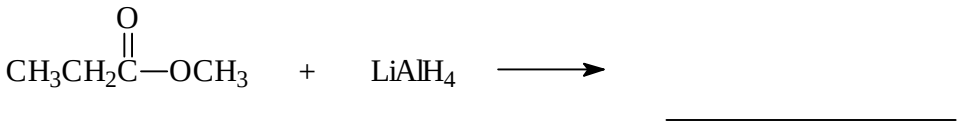
$CH_3C(=O)CH_2CH_3$ + _____ →



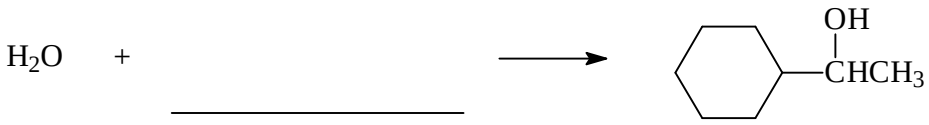
(h)



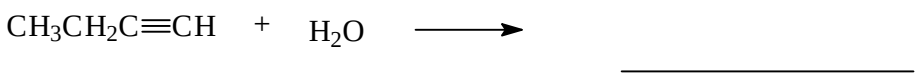
(i)



(j)



(k)



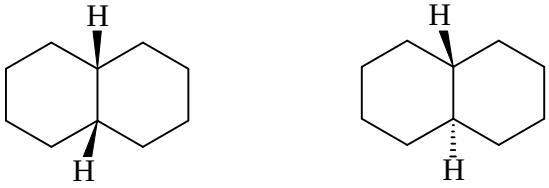
2(a). Draw the NEWMAN PROJECTION of the more stable chair conformation of the less stable configuration of 3-methylcyclohexanol. Label the substituents as being axial (a) or equatorial (e) [4 points]

(b) Draw the three dimensional perspective structure of trans 4-chloro-1-methylcyclohexane in its more stable chair conformation. Label the substituents as being axial or equatorial. [4 points]

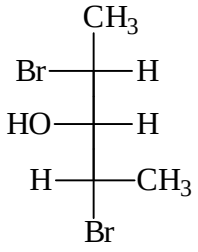
3. (a) Pick the word from the following list (enantiomers, diastereomers, identical, positional isomers) which correctly describes the relationship between the following pairs of compounds. [8 points]

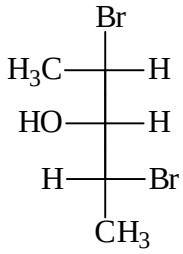
(i)

(ii)

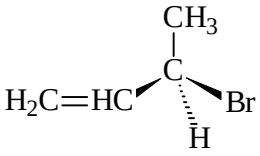


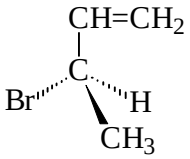
(iii)





(iv)





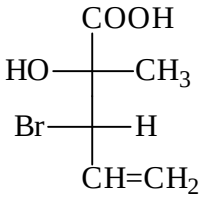
(b) Circle the compounds in the following list [which refers to part (a) of this question] which are MESO FORMS. [3 points]

(i) right drawing (i) left drawing
(ii) right drawing (ii) left drawing
(iii) right drawing (iii) left drawing
(iv) right drawing (iv) left drawing

(c) Indicate (by circling the appropriate entry below) which (if any) of the pairs of compounds shown in part (a) when mixed in a 1:1 ratio would NOT show optical activity. [2 points]

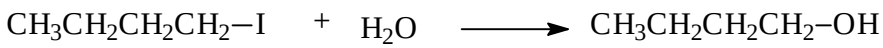
(i) (ii) (iii) (iv)

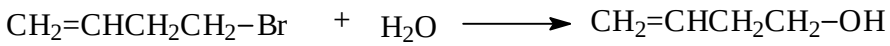
(d) For the drawing below, determine the configuration (R or S) for each of the chiral centres. Show the priorities you determine for each group as well as your final answer. [4 points]



4. For each of the pairs of reactions shown below, answer the question asked and give a brief explanation for your choice. [3 points each]

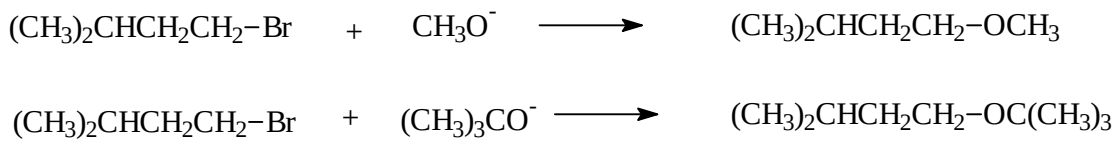
(a)





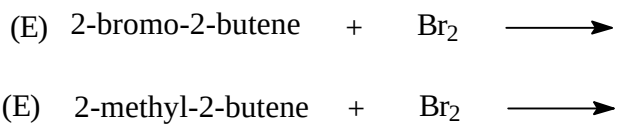
Which reaction is more likely to proceed via a Sn2 mechanism?

(b)



Which reaction will proceed faster?

(c)



Which reaction will proceed faster?

5. DO EITHER PART A OR PART B, NOT BOTH!! [10 points]

PART A
Draw the complete MECHANISM of the acid-catalyzed reaction of 2-methylpropanal with excess methanol. Show all steps and intermediates and make sure you indicate whch steps are reversible. Also, draw the equation of the overall reaction.

PART B
Draw the complete MECHANISM of the acid-catalyzed reaction of ethyl 2-methylpropanoate with water. Show all steps and intermediates and make sure you indicate which steps are reversible. Also draw the equation of the overall reaction.

6. (a) When (R) 2-methylbutanal reacts with methylmagnesium bromide, how many stereoisomers are formed and how are they related? [3 points]

(b) When a racemic mixture of 2-methylpropanal reacts with methylmagnesium bromide, how many stereoisomers are formed and how are they related? [3 points]

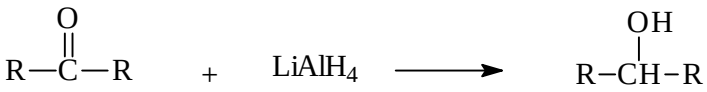
7. [2 points each] You are given two bottles, each of which contains a pure compound and two labels. Indicate how you would decide which label should be attached to each bottle on the basis of a visual test. Describe what you would do and what would be observed in each case if the labels read:
(a) 2-butanol and methyl ethyl ether

(b) 2-methyl-2-hexene and methylcyclohexane

(c) 2-methylpentanal and 2-methyl-3-pentanone.

8. Show by equation five (5) ways you could prepare 3-methyl-2-pentanol, each of which starts with a different starting material. [5 points]

9. When a ketone is reacted with $LiAlH_4$ and the reaction mixture is then treated with acid (e.g. HCl), the product is an alcohol.



The atom deuterium (symbol ^2H, commonly written as D) is an isotope of hydrogen. Draw the structure of the product which would be obtained from this reaction if:
(a) The reaction was carried out with $LiAlD_4$ and then treated with HCl [2 points]

(b) The reaction was carried out with $LiAlH_4$ and then treated with DCl [2 points]

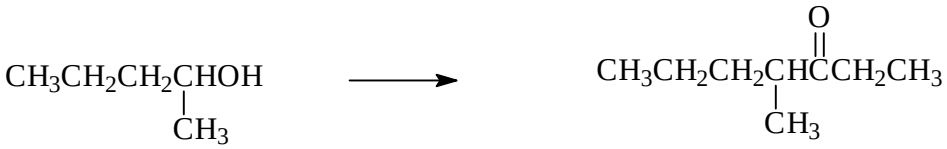
(c) The reaction was carried out with $LiAlD_4$ on an ester (RCO_2CH_3) and then was treated with DCl [2 points]

BONUS QUESTION

DO EITHER PART A OR PART B, NOT BOTH!!

10. [5 points] Show by equation how you could convert the given starting material into the requested product. Show all the reqgtents you would use and the structure of teh product obtained from each step.

PART A



PART B