Chemistry 3351: Organic Chemistry/3rd Exam/HLMS 201
Thursday: Nov. 18th from **7:00pm → 9:00pm**

Name: Key (please print, 5 points)

Page	Possible Points	Score
1	5	
2	9	
3	9	
4	10	
5	9	
6	12	
7	10	
8	10	
9	10	
10	10	
11	10	
12	10	
TOTAL	114	

1. Clickers in Action (3 pts each):

1) How many constitutional isomers of C_4H_9Br are possible? How many of these are primary alkyl bromides?

(A) 3, 1
(B) 4, 1
(C) 4, 2
(D) 5, 1
(E) 5, 2

2) Identify the equilibria that favor the formation of alkoxides and mercaptides. The pK_a values of C_2H_5SH and H_2 are 10.5 and 37, respectively.

(I) $C_2H_5OH + {}^{\ominus}OH \rightleftharpoons C_2H_5O^{\ominus} + H_2O$
(II) $C_2H_5SH + {}^{\ominus}OH \rightleftharpoons C_2H_5S^{\ominus} + H_2O$
(III) $C_2H_5SH + {}^{\ominus}OC_2H_5 \rightleftharpoons C_2H_5S^{\ominus} + C_2H_5OH$
(IV) $C_2H_5OH + NaH \rightleftharpoons C_2H_5ONa + H_2$

(A) I, II and III
(B) II, III and IV
(C) I, II and IV
(D) I, III and IV

3) Which alcohol is the relatively strongest acid?

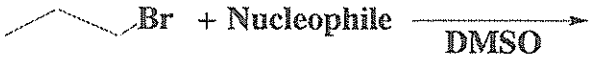
(A) CH_3CH_2OH
(B) CF_3CH_2OH
(C) $CF_3CH_2CH_2OH$
(D) $CF_3CH_2CH_2CH_2OH$

4) Arrange these Grignard reagents in order of decreasing basicity.

(I) CH_3CH_2MgBr
(II) $HC{\equiv}CMgBr$
(III) CH_3CH_2OMgBr

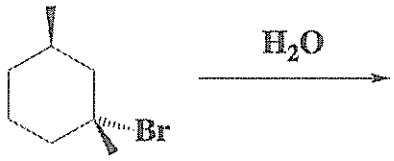
A) I > II > III
B) I > III > II
C) III > II > I
D) II > I > III

5) Which nucleophile would react at the fastest rate in this reaction?



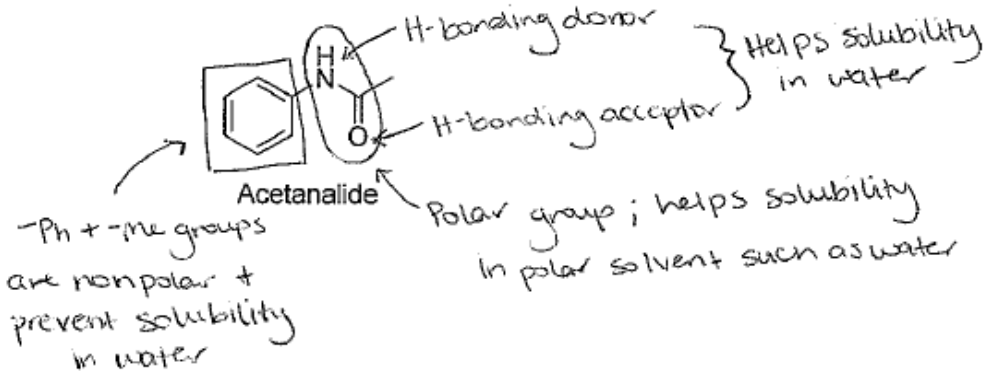
(A) Nucleophile = CH_3OH
(B) Nucleophile = $CH_3O^{\ominus}$
(C) Nucleophile = $CH_3S^{\ominus}$
(D) Nucleophile = $CH_3CO_2^{\ominus}$

6) Predict the relationship between the major substitution products in this reaction.

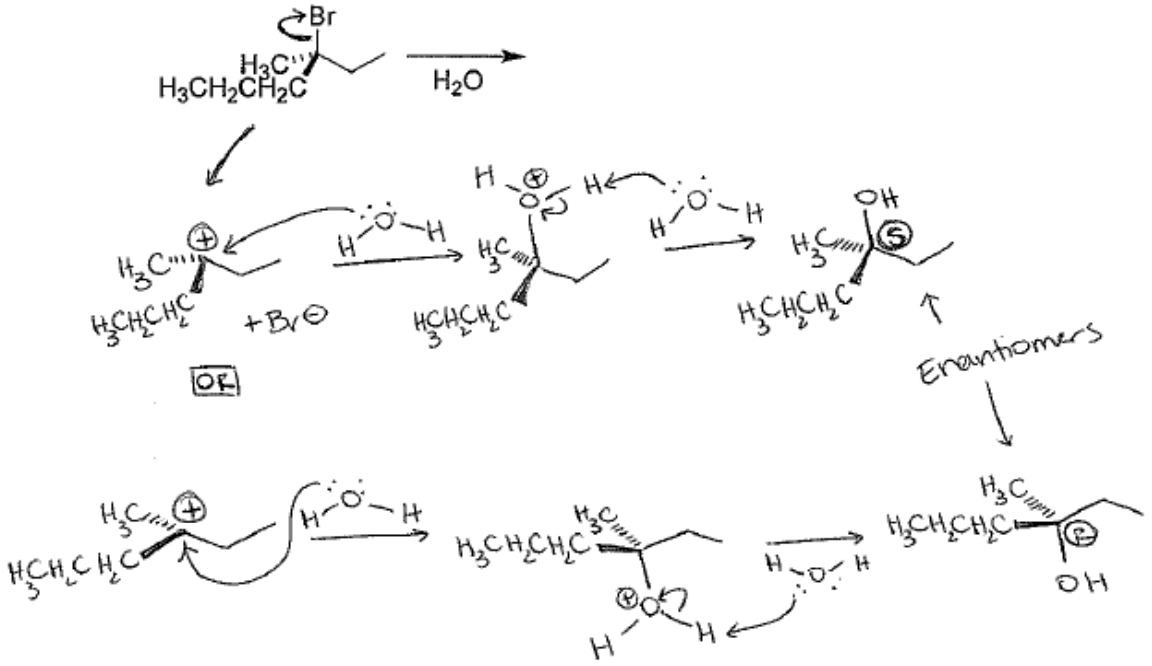


(A) Identical
(B) Enantiomers
(C) Diastereomers
(D) Constitutional isomers

2. (5 pts). A widely used undergraduate experiment is the recrystallization of acetanilide from water. Acetanilide (structure shown below) is moderately soluble in hot water, but much less soluble in cold water. Identify one structural feature of the acetanilide molecule that would be expected to contribute positively to its solubility in water and one that would be expected to contribute negatively.



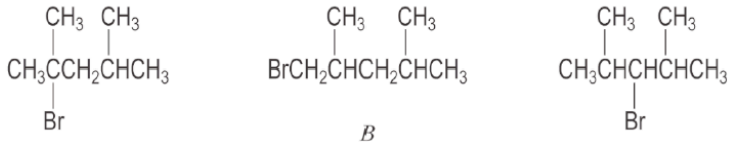
3. (5 pts). Provide the major product(s) and mechanism for the following substitution reaction. Show stereochemistry in any intermediate(s) and product(s). Also classify the reaction as either S_N1 or S_N2.



S_N1 Rxn

4. (9 pts). Three alkyl halides, each with the formula $C_7H_{15}Br$, have different boiling points. One of the compounds is optically active. Following reaction with Mg in ether, then with water, each compound gives 2, 4-dimethylpentane. After the same reaction with D_2O instead of water, a different product is obtained from each compound. Suggest a structure for each of the three alkyl halides.

The different boiling points indicate that the three alkyl halides are either constitutional isomers or diastereomers. The outcome of the Grignard protonolysis shows that all of the alkyl halides have the same carbon skeleton, that of 2,4-dimethylpentane. The protonolysis in D_2O confirms the fact that the bromines are bound at different places on the carbon skeleton. The only three possibilities for the alkyl halides are

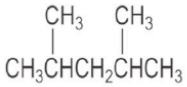


A *B* *C*

Compound *B* is the chiral alkyl halide, and compounds *A* and *C* are the other two. (The absolute configuration of *B* (that is, whether it is *R* or *S*) is not determined by the data.)

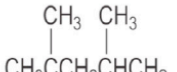
The protonolysis products in H_2O and D_2O are

In H_2O:

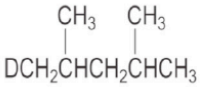


from *A*, *B*, and *C*

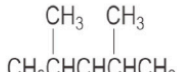
In D_2O:



from *A*

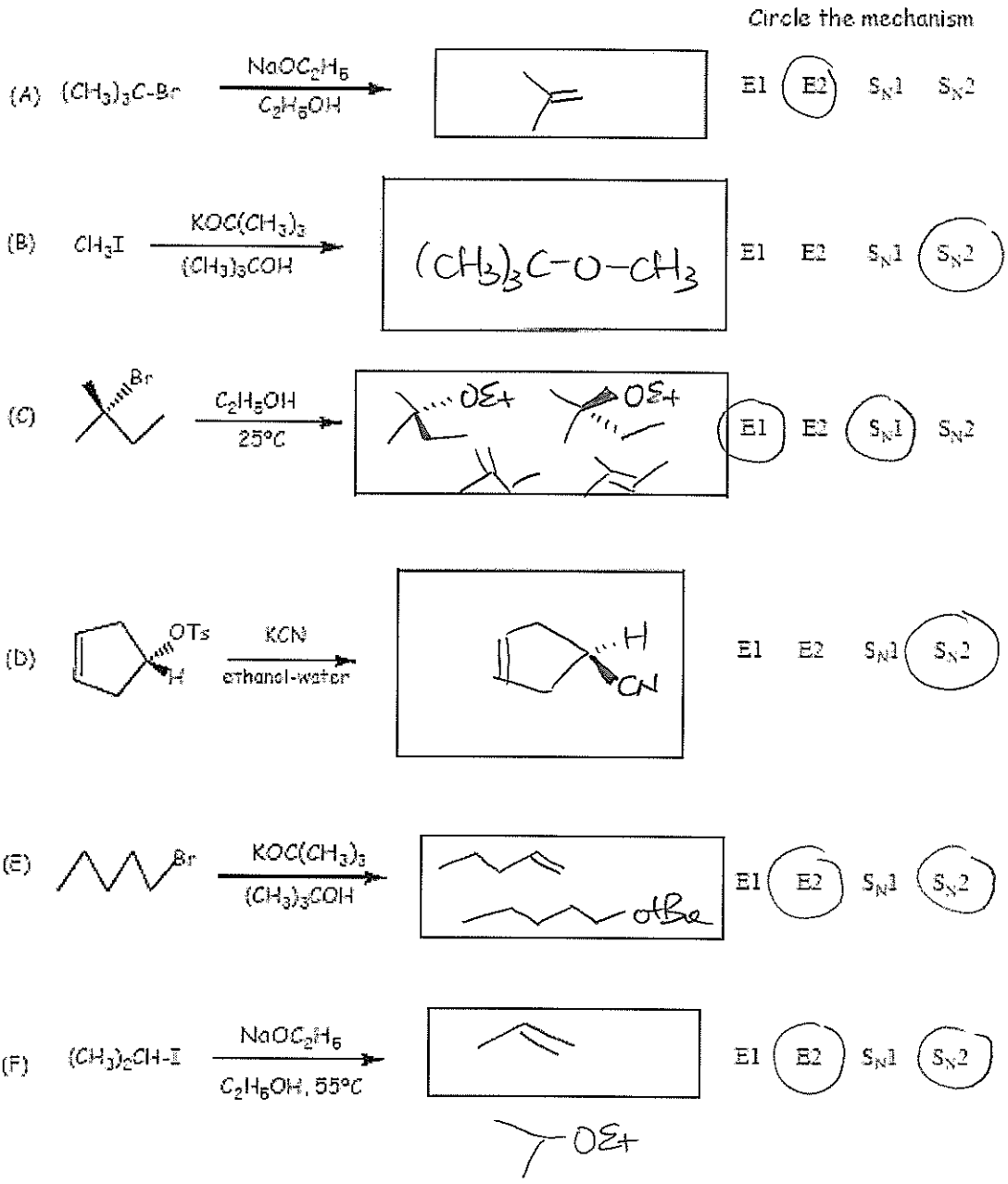


from *B*

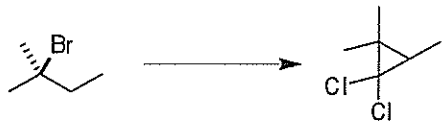


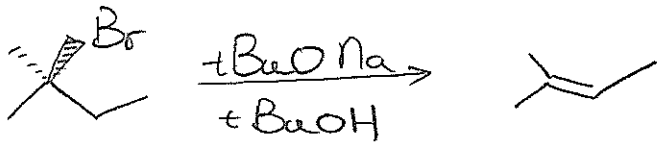
from *C*

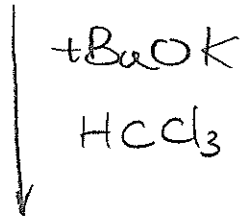
5. (12 pts). Draw the structure(s) of the major product(s) of each reaction. Be sure to include stereochemistry when appropriate. Circle the mechanism that accounts for the formation of this product: (*Note: -OTs is a good leaving group*)

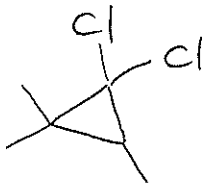


6. (10 pts). Provide the reagents necessary to accomplish the following transformations. Transformations may require more than one step (show intermediate(s) for full credit).





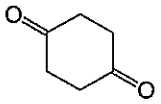




10 pts each

7. (~~10~~ pts). In the laboratory of the firm "Halides 'R' Us", a compound **A** has been found in a vial labeled only "achiral alkyl halide $C_{10}H_{17}Br$". The management feels that the compound might be useful as a pesticide, but they need to know its structure. You have been called in as a consultant at a handsome fee.

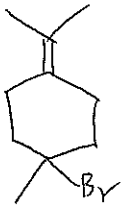
Compound **A**, when treated with KOH in warm ethanol, yields two compounds (**B** and **C**), each with the molecular formula $C_{10}H_{16}$. Compound **A** rapidly reacts in aqueous ethanol to give an acidic solution, which, in turn, gives a precipitate of AgBr when tested with $AgNO_3$ solution. Ozonolysis of **A** followed by treatment with $(CH_3)_2S$ affords $(CH_3)_2C{=}O$ (acetone) as one of the products plus an unidentified halogen-containing material. Catalytic hydrogenation of either **B** or **C** gives a mixture of both *trans*- and *cis*-1-isopropyl-4-methylcyclohexane. Compound **A** reacts with one equivalent of Br_2 to give a mixture of two separable compounds, **D** and **E**, both of which ~~can be shown to be~~ are achiral compounds. Finally, ozonolysis of compound B followed by treatment with aqueous H_2O_2 gives acetone and the diketone **F**.



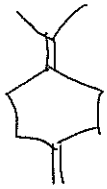
F

Propose structures for compounds A through E that best fit the data (and collect your fee).

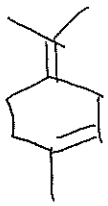
A:



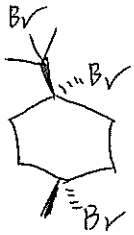
B:



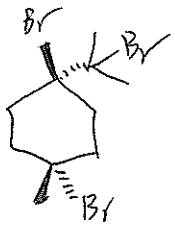
C:



D:

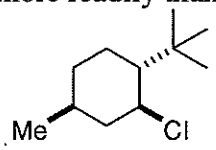


E:

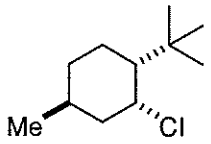


D & E can be switched!

8. (10 pts). Menthyl chloride and neomenthyl chloride have the structures shown below. One of these stereoisomers undergoes elimination on treatment w/ sodium ethoxide in ethanol much more readily than the other.



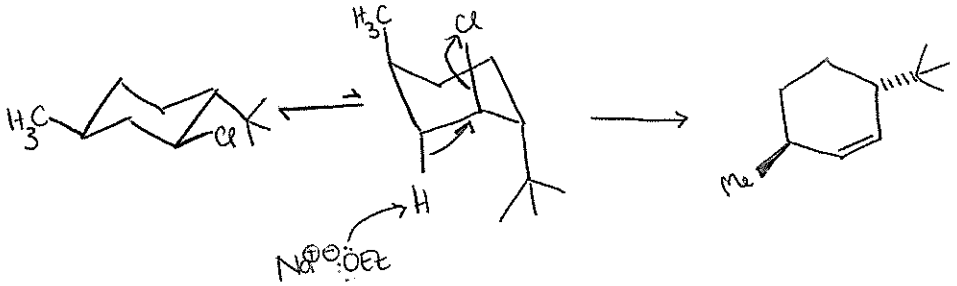
menthyl chloride



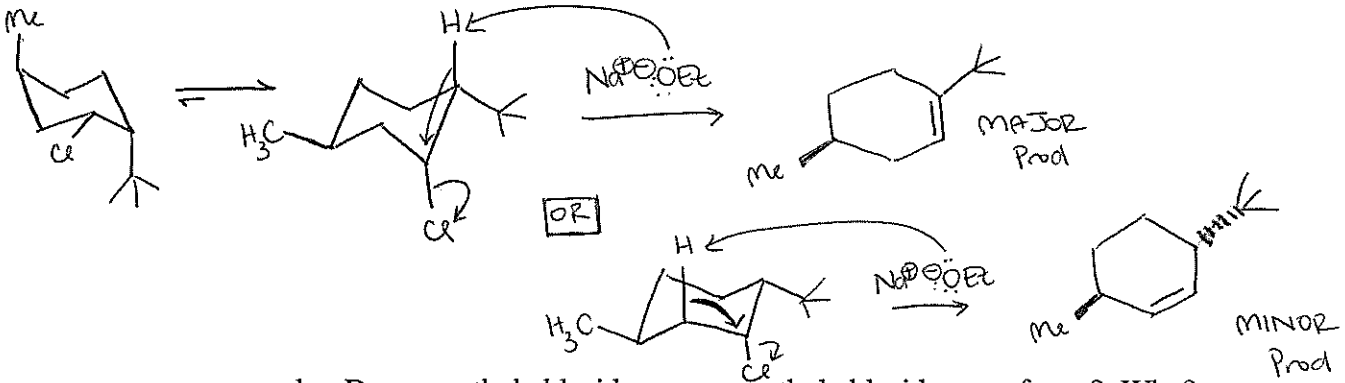
neomenthyl chloride

a. Using arrows to show the flow of electrons, draw a mechanism to account for the dehydrohalogenation for each of the isomers.

Menthyl chloride:



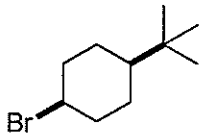
Neomenthyl chloride:



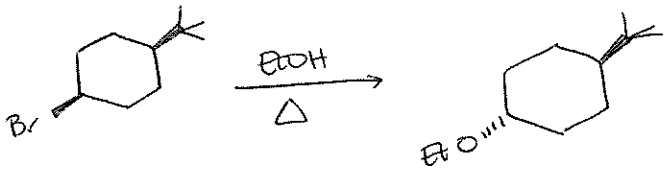
b. Does menthyl chloride or neomenthyl chloride react faster? Why?

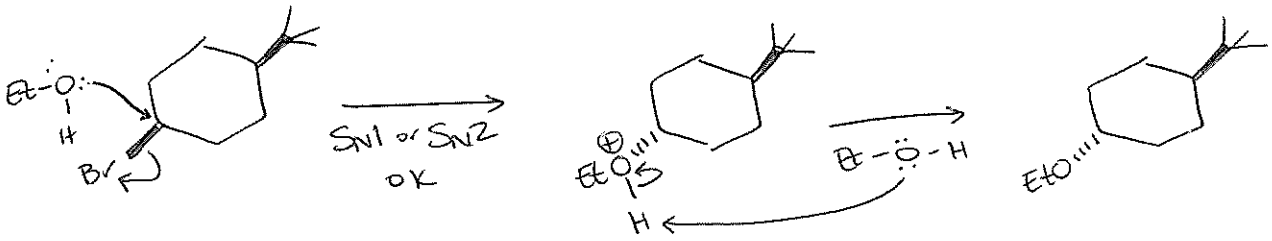
Neomenthyl chloride reacts faster. Menthyl chloride must first chair-flip to a higher E conformation to achieve the anti-periplanar transition state, thus raising the activation energy (+ slowing the rate) of the rxn.

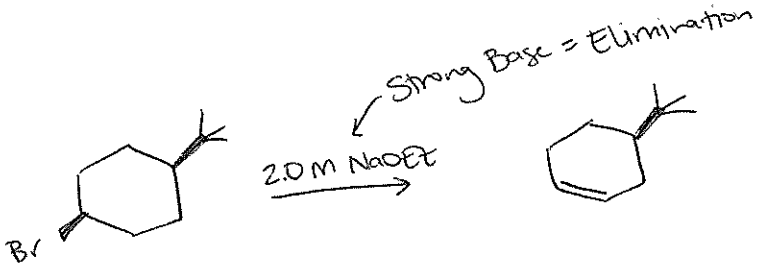
9. (10 pts). When a solution of *cis*-1-*t*-butyl-4-bromocyclohexane in ethanol is refluxed for several hours, the major product is found to be *trans*-1-*t*-butyl-4-ethoxycyclohexane. However if the solution is made 2.0 M in NaOEt, the major product is found to be 4-*t*-butylcyclohexene. Explain the difference (scheme/mechanism required for full credit).

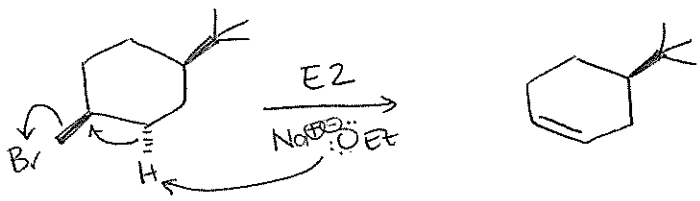


cis-1-*t*-butyl-4-bromocyclohexane

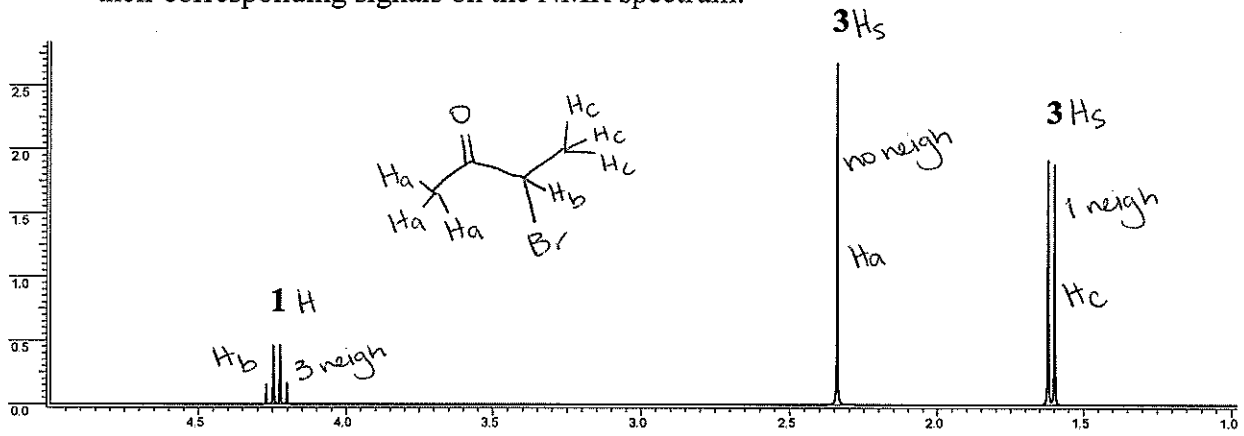


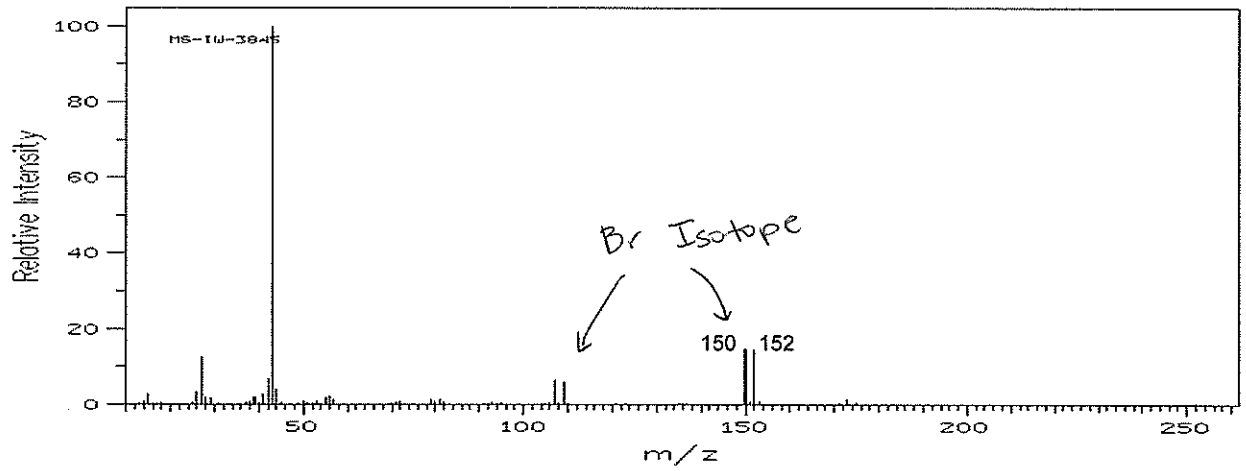


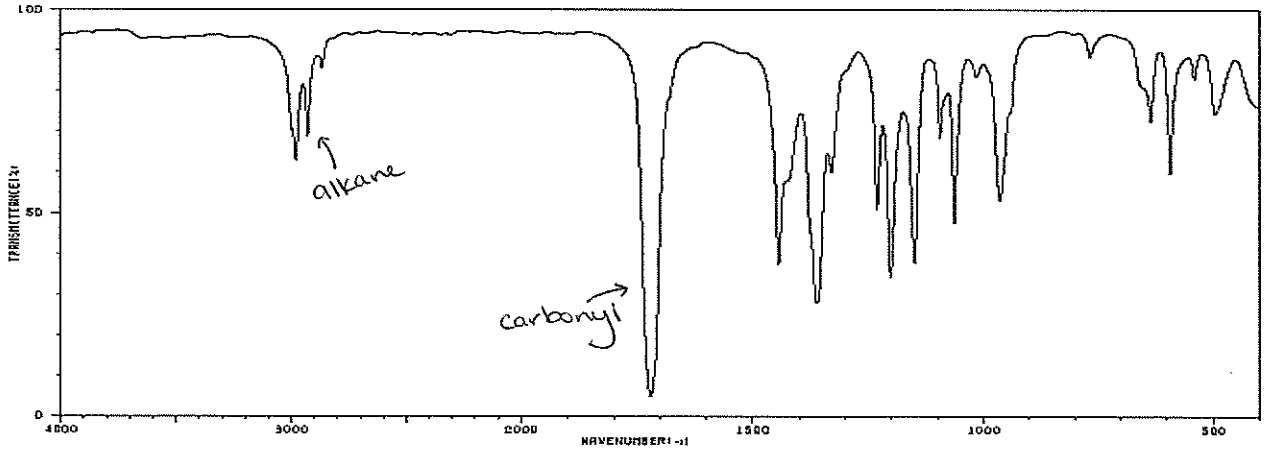


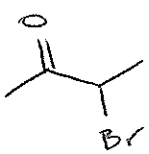


10. (10 pts). Propose a structure for the compound (C_nH_mOX, X= halogen) given the spectra shown below. Be sure to show your reasoning by labeling definitive signals on each spectrum. Also, please label the hydrogens in your proposed structure and match them to their corresponding signals on the NMR spectrum.

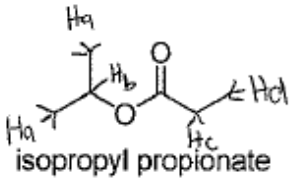








11. (10 pts). Using the grid provided below, predict what the ^{1}H NMR spectrum of isopropyl propionate would look like. For full credit, be sure to label the hydrogens in the structure and match them to their corresponding signals on the ^{1}H NMR spectrum you provide. Also be sure to show integrations in some form.



isopropyl propionate