Name: _____

CHM 228 Exam 1b Summer 2013

Multiple Choice
Identify the choice that best completes the statement or answers the question.

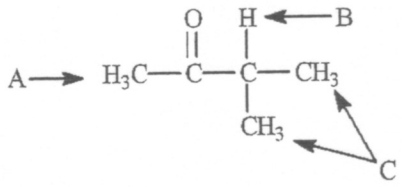
Instructions: Select the most reasonable formula for the compounds with the following mass spectral data.

C

1. Refer to instructions. M^+ at $m/z = 101$
   a. C_5H_6Br
   b. $C_5H_{12}N_2$
   c. $C_6H_{15}N$
   d. $C_9H_{12}O$

C = 12 x 6 = 72
H = 1 x 15 = 15
N = 1 x 14 = 14 = 101

Instructions: Refer to the structure of 3-methylbutan-2-one below to answer the following question(s).



C

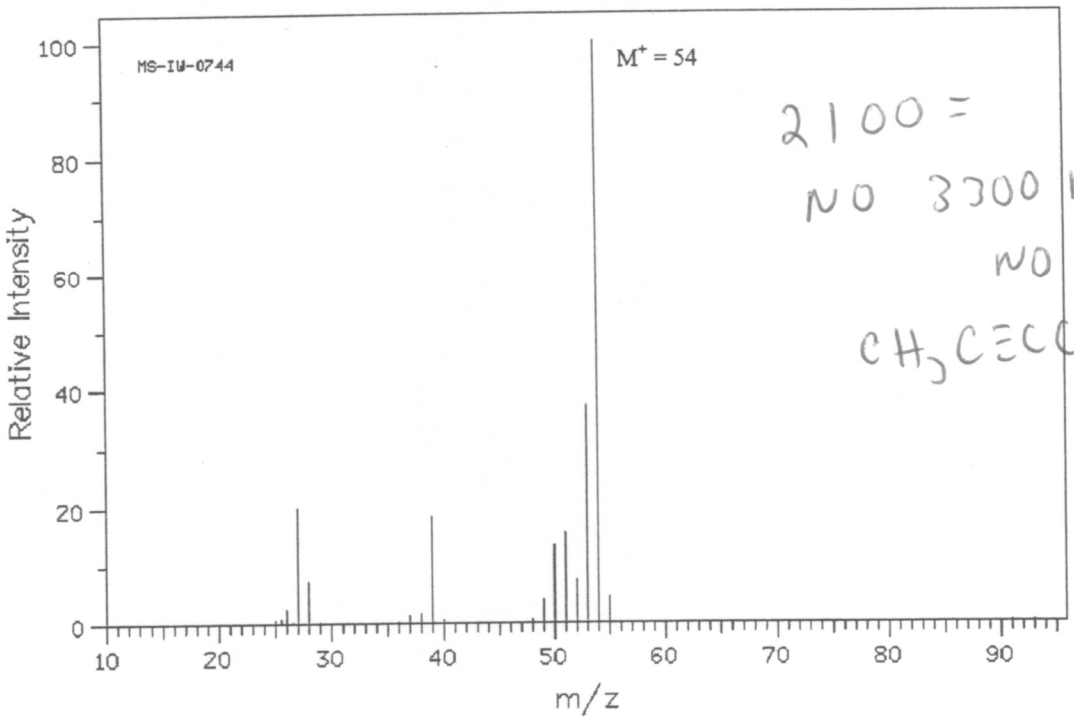
2. Refer to instructions. What is the splitting pattern for the hydrogens in 3-methylbutan-2-one labeled A, B, and C, respectively?
   a. singlet, singlet, singlet
   b. singlet, septet, quartet
   c. singlet, septet, doublet
   d. singlet, septet, doublet, doublet

D

3. Refer to instructions. What is the ratio of peak areas upon integration of the spectrum for A, B, and C respectively?
   a. 3:1:3:3
   b. 1:1:6
   c. 1:1:6
   d. 3:1:6

Problem

4. Below is the mass spectrum of an unknown hydrocarbon. In addition, this hydrocarbon shows characteristic absorption at 2100 cm^{-1} in its IR spectrum. Give the structure of this unknown.



2100 = C≡C

NO 3300 MEANS NO C≡C-H

$CH_3C{\equiv}CCH_3$ FITS

$C_4H_6 = 54$

(Spectrum obtained from: SDBSWeb: http://www.aist.go.jp/RIODB/SDBS/)

5. Cyclohexene and hex-2-yne both have the molecular formula, C_6H_{10}.

   a) How would you use infrared spectroscopy to distinguish between the two compounds?

   b) How could the mass spectrum be used to distinguish between the two compounds?

IR YNE HAS 2100

ENE HAS 3090 + 1640

MASS - SAME M^+

FRAGMENTATION WOULD BE DIFFERENT

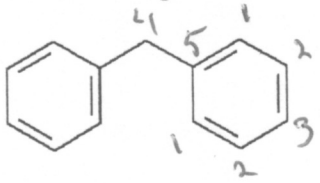
YNE $CH_3C{\equiv}C\text{-}CH_2^+$

$C_4H_5 = 53$

ALLYLIC LIKE

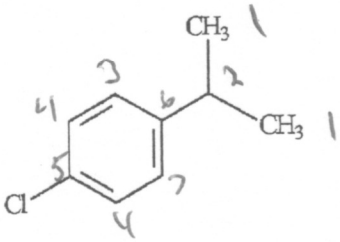
Instructions: For each of the compounds below tell how many signals you would expect the molecule to have in its normal, broadband decoupled ^{13}C NMR spectra.

6. Number of signals:



4 5

7. Number of signals:



4 6

8. Treatment of *tert*-butyl alcohol with hydrogen chloride yields a mixture of *tert*-butyl chloride and 2-methylpropene.

$$(CH_3)_3COH \xrightarrow{HCl} (CH_3)_3CCl + (CH_3)_2C{=}CH_2$$

a) After chromatographic separation, how would you use ^{1}H NMR to help you decide which was which?

b) How would the ^{13}C NMR for the two compounds differ?

^{1}H NMR ENE 2 SIGNALS
ONE AT 5-6 ppm
ONE AT 1.7 ppm

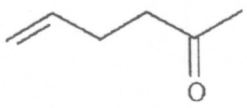
HALIDE 1 SIGNAL $\approx$ 1.5

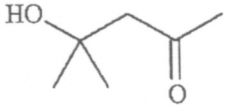
^{13}C ENE 2 PEAKS 100-140 ppm

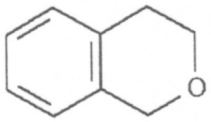
HALIDE 1 PEAK $\approx$ 40 ppm
1 PEAK $\approx$ 20 ppm

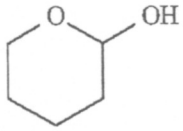
Matching

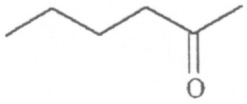
Instructions: Match a structure from the list below to the following IR spectra.

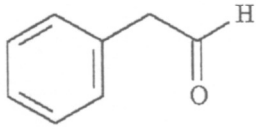
A. 

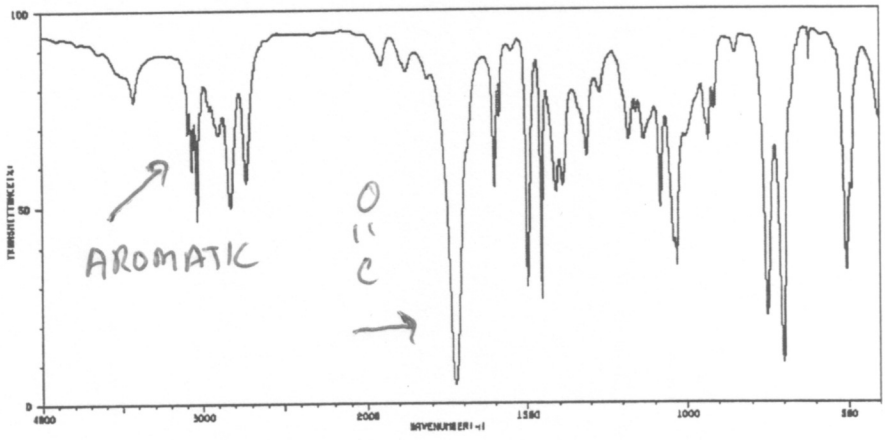
D. 

B. 

E. 

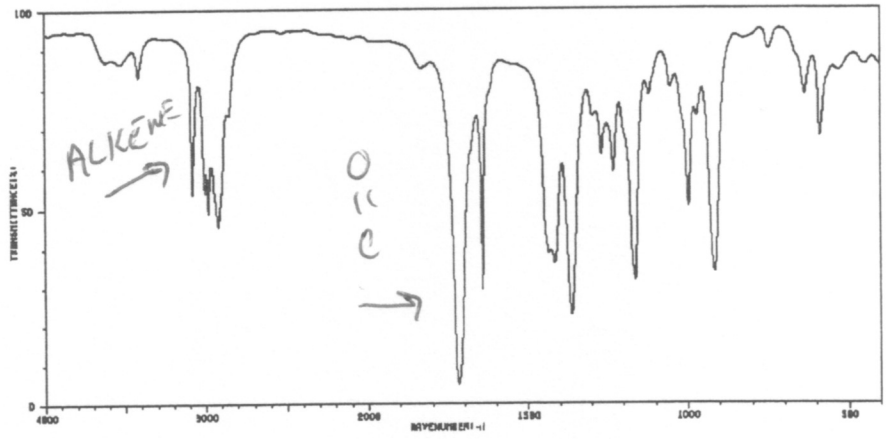
C. 

F. 

F 11. 

F

(Spectrum obtained from: SDBSWeb: http://www.aist.go.jp/RIODB/SDBS/)

A 12. 

A

(Spectrum obtained from: SDBSWeb: http://www.aist.go.jp/RIODB/SDBS/)

Which has a stronger (more intense) characteristic stretching frequency in the IR spectrum, C=C or C=O? Briefly explain why.

C=O LARGER DIPOLE

Describe (using the 4 types of information available in an NMR spectrum), the proton spectrum of the reactant **and** the product when 1, 3-butadiene reacts with Hydrogen gas (H_2) and a catalyst to form butane.

$CH_2=CH-CH=CH_2$

1) 2 SIGNALS
2) 2:1 INTEGRATION
3) 5-6 PPM
4) DOUBLET + TRIPLET

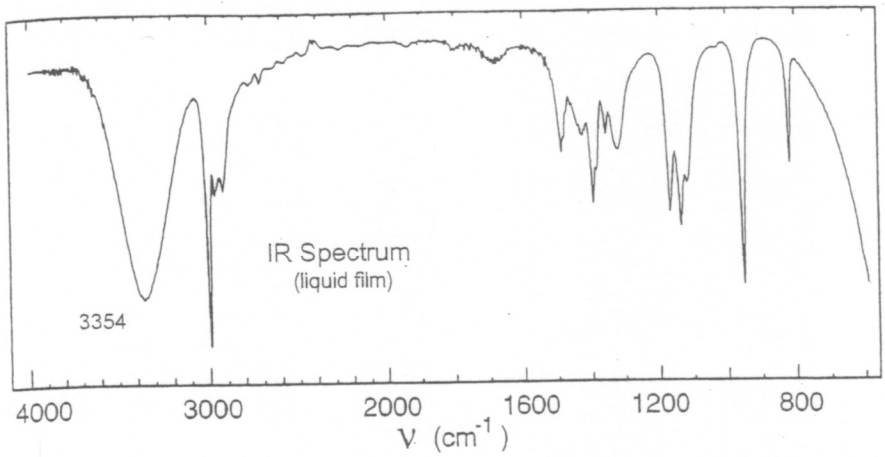
$CH_3CH_2CH_2CH_3$

1) 2 SIGNALS
2) 3:2 INTEGRATION
3) 1.3-0.9 PPM
4) TRIPLET + QUARTET

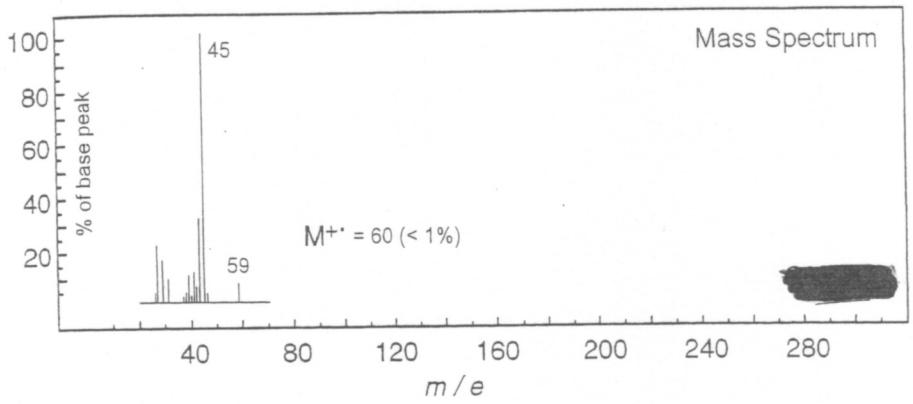
4) ALSO ACCEPTABLE → DOUBLET, QUARTET BUT NOT CORRECT → TRIPLET, SEXTET

6

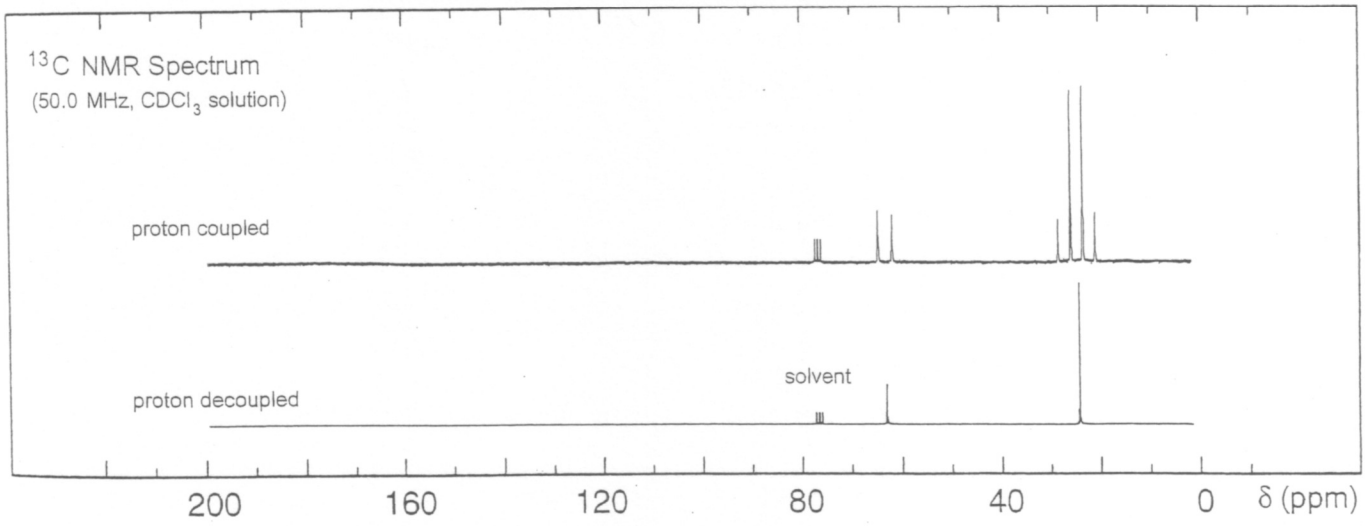
Use the spectra on the following pages to identify the compound. Partial credit for any fact that you can establish, such as D.U., Molecular mass, etc.

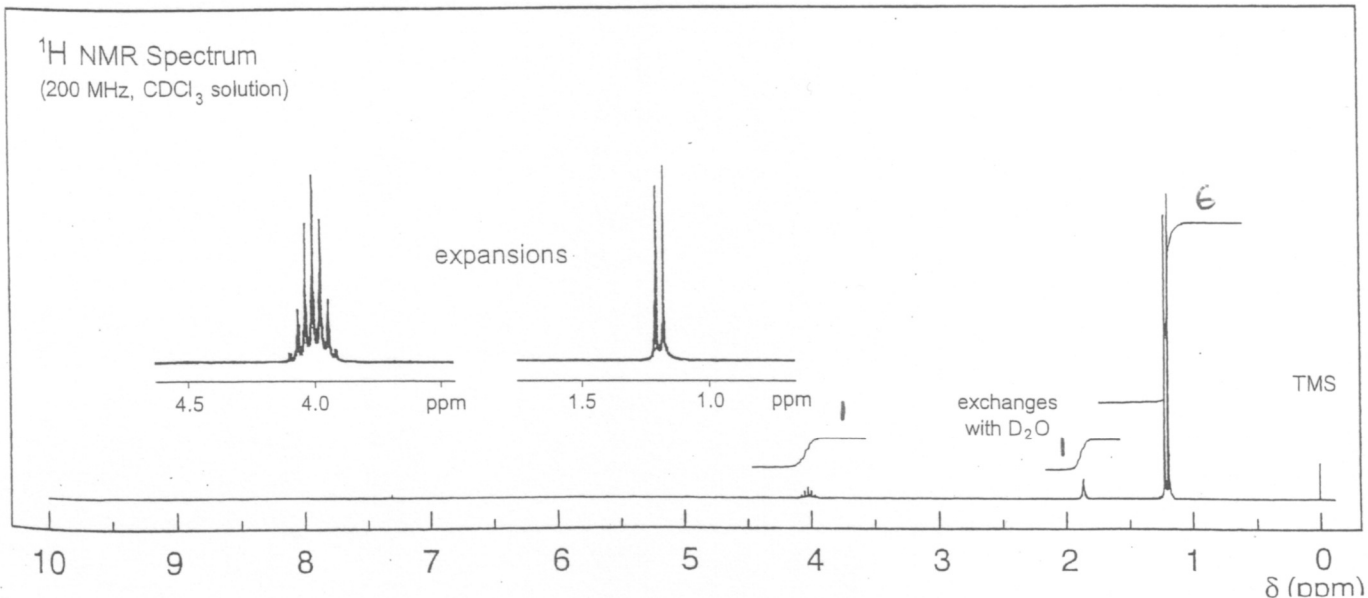


ISOPROPYL ALCOHOL

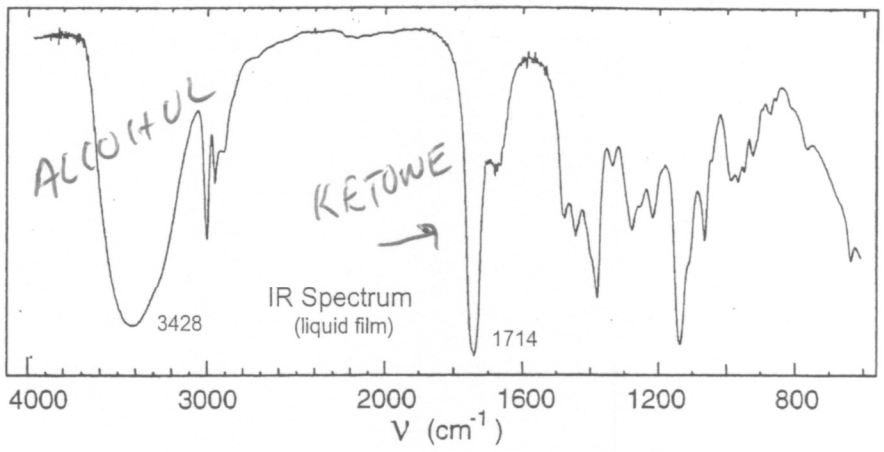


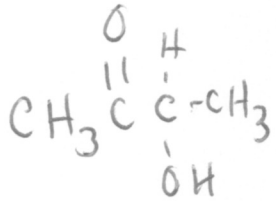
No significant UV absorption above 220 nm



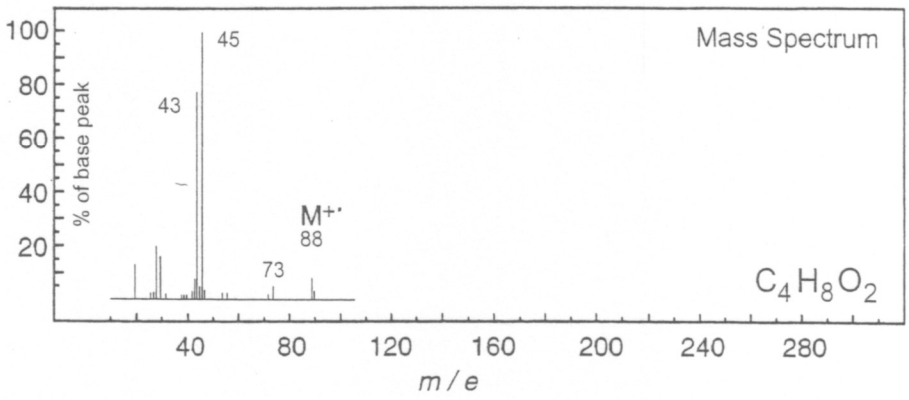


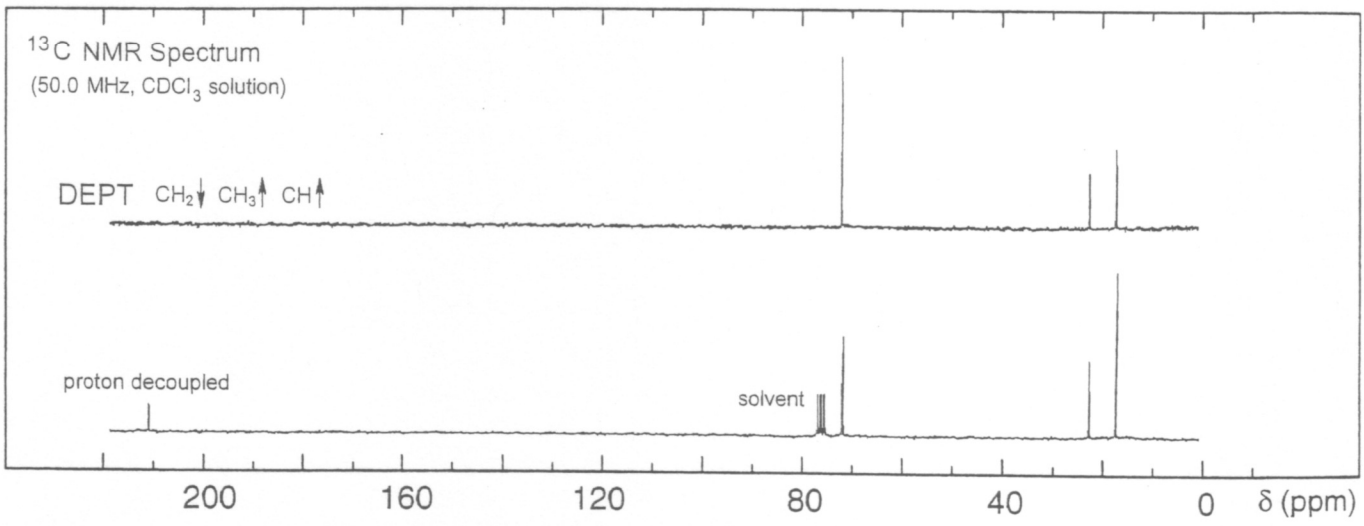
Problem 69

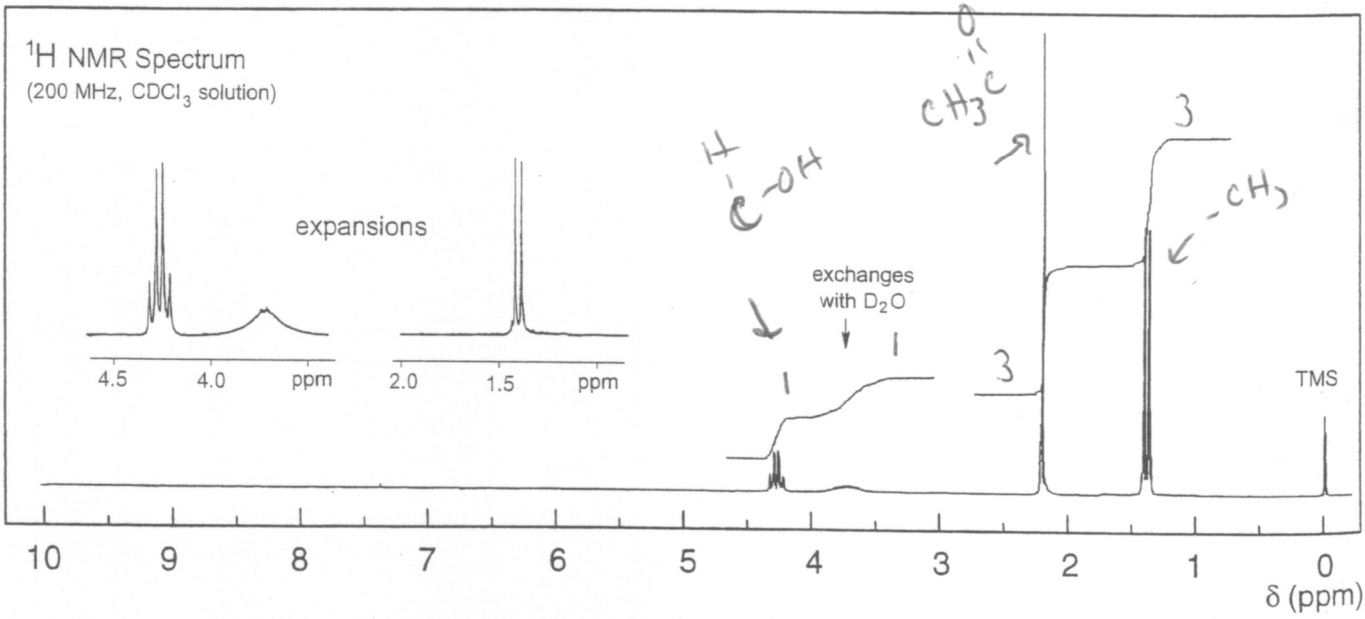


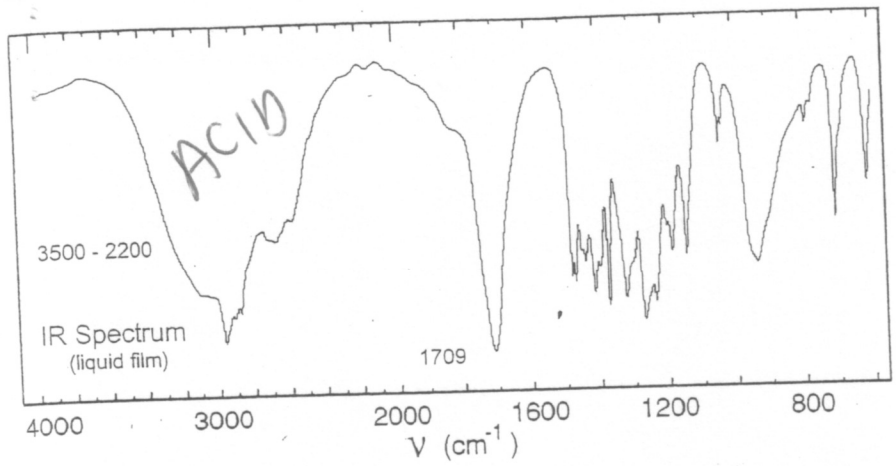


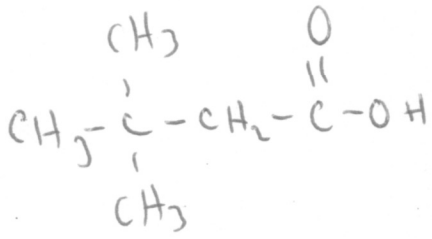
No strong UV absorption above 220 nm

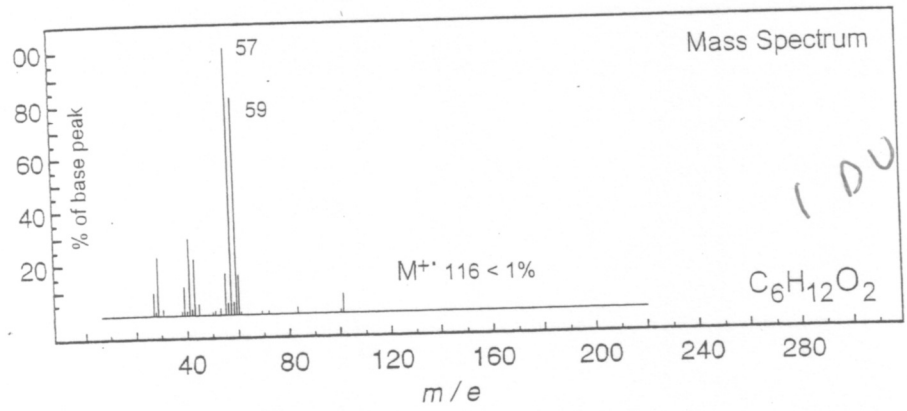




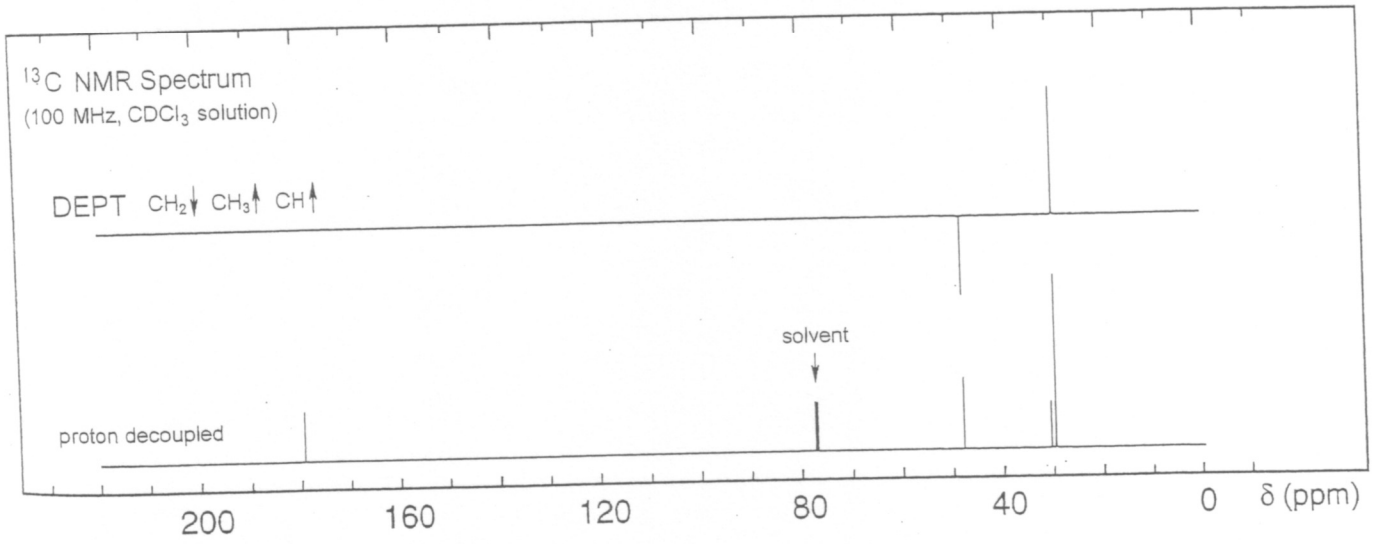


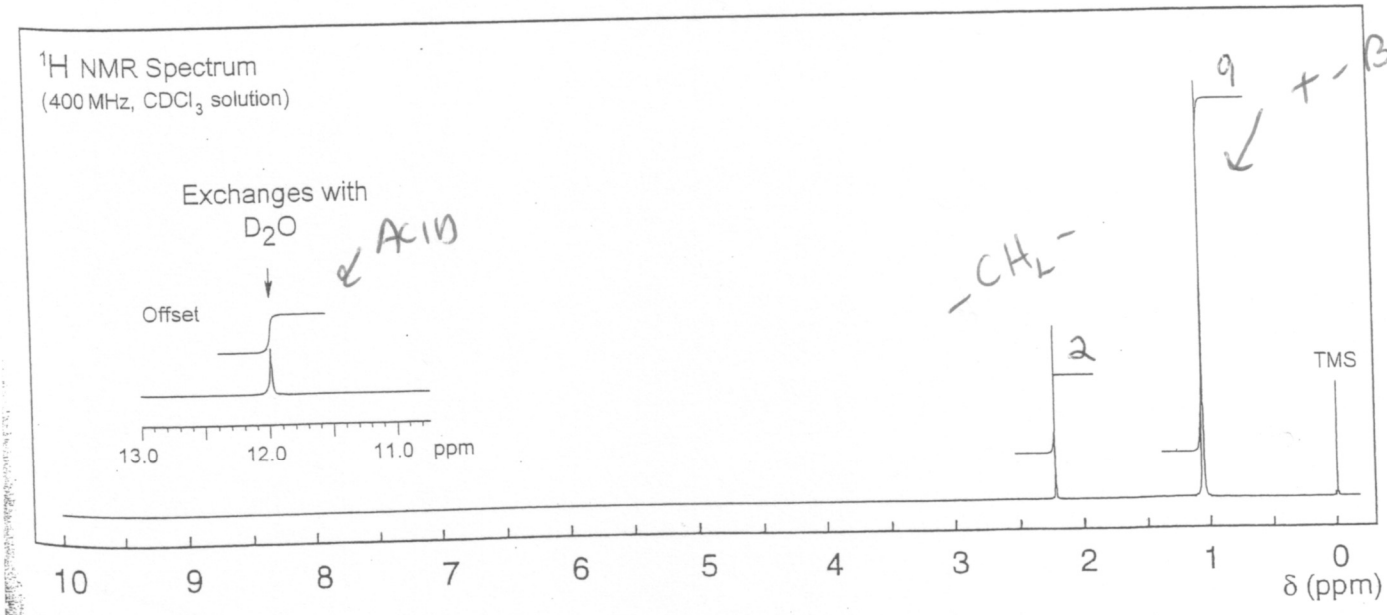


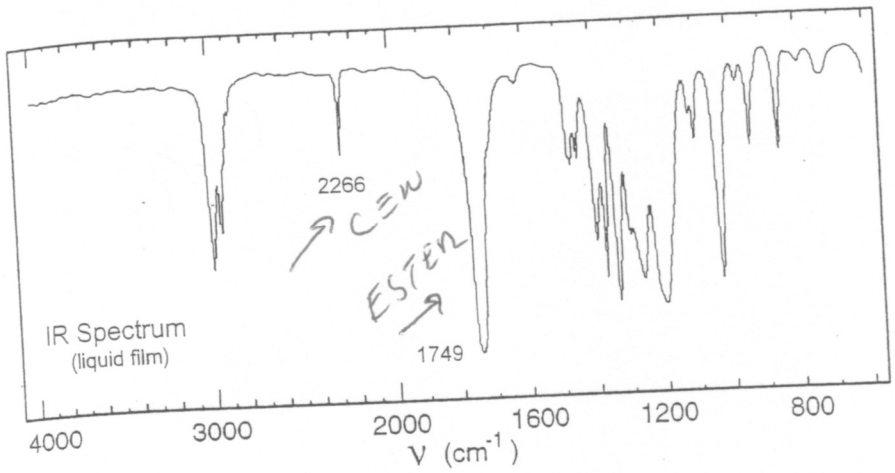


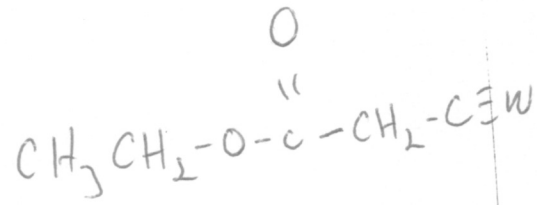


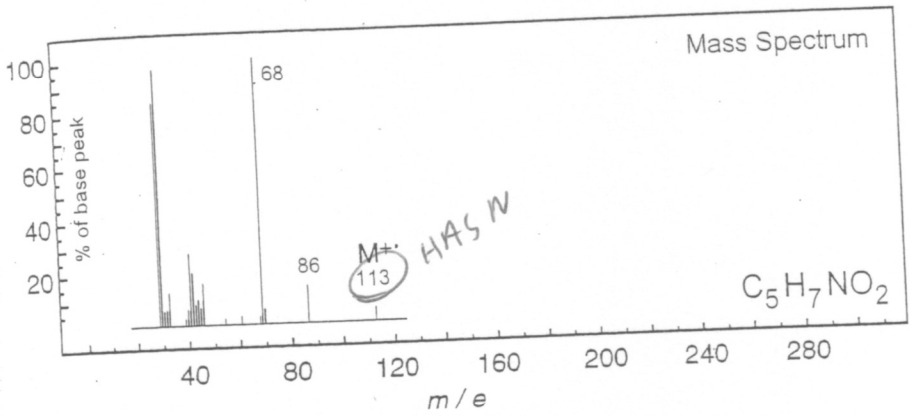
No significant UV absorption above 220 nm



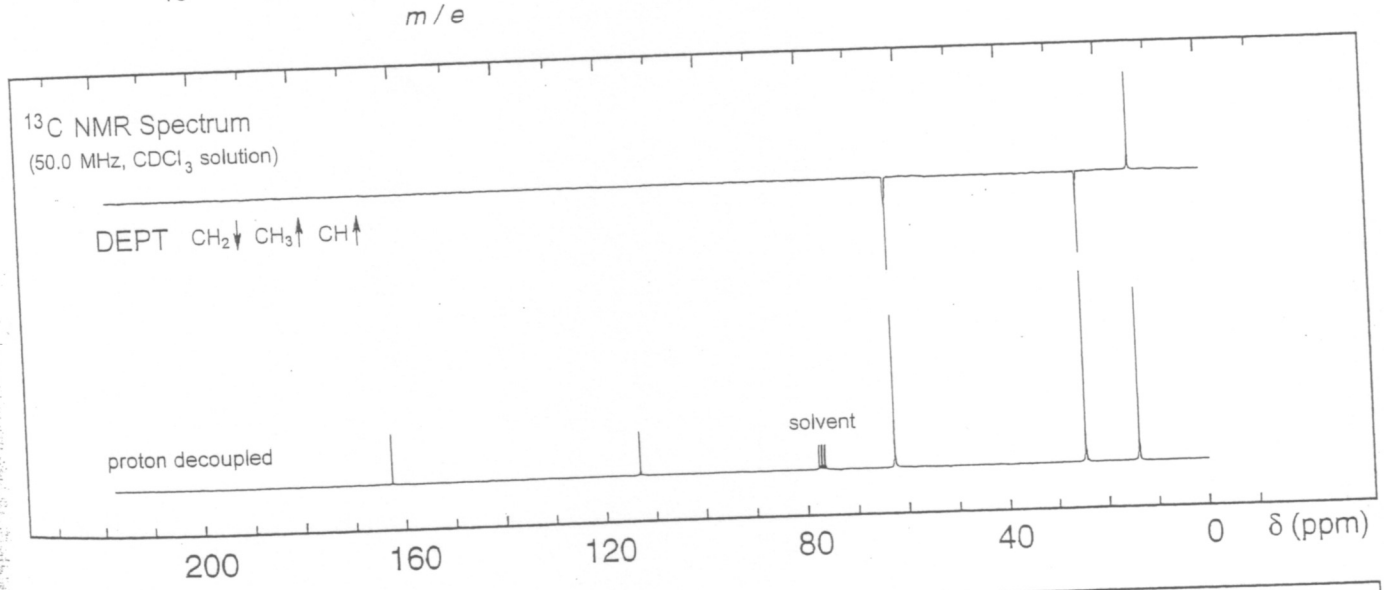


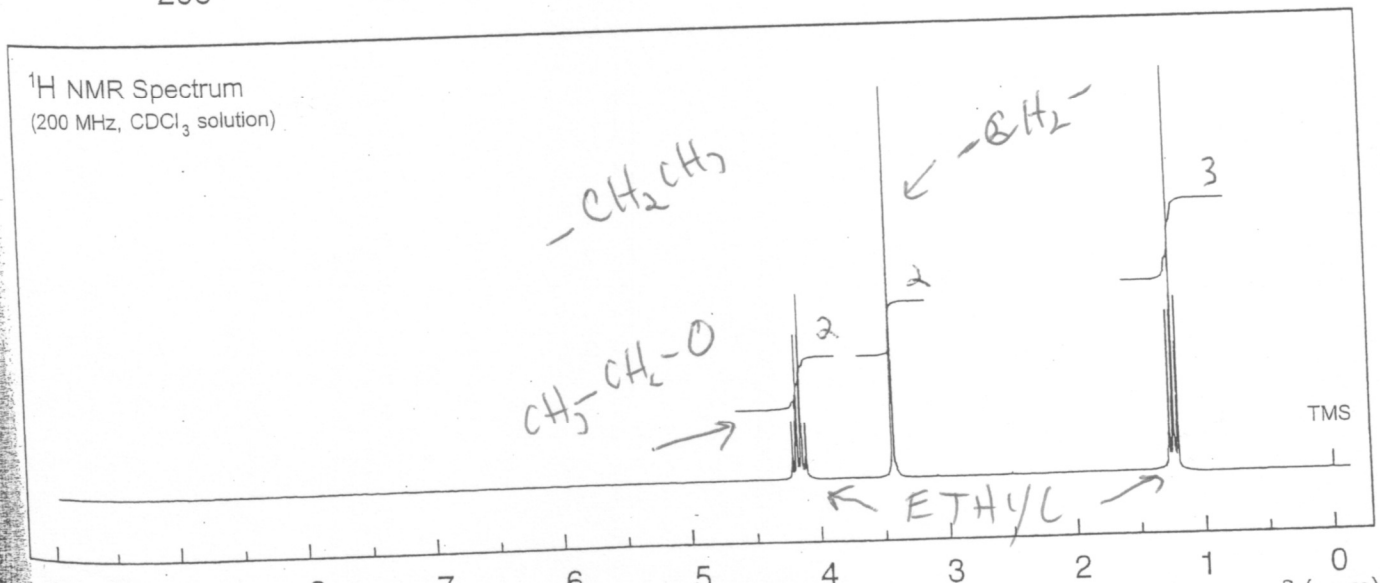






No significant UV absorption above 220 nm





Name: KEY

CHM 228 Summer 2013 Exam 2

Problem

Instructions: Consider the pair of reactions below to answer the following question(s).

a. $CH_3CH_2CH_2Br \xrightarrow{^-OH,\ H_2O} CH_3CH_2CH_2OH + Br^-$

or

b. $CH_3CH_2CH_2Br \xrightarrow{^-SH,\ RSH} CH_3CH_2CH_2SH + Br^-$

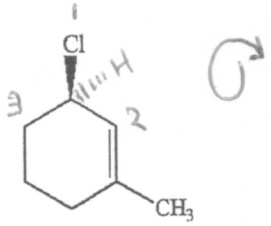
1. Consider the reactions above.

   a) Which reaction would be predicted to be faster? B

   b) Classify the reactions as S_N1 or S_N2.

   c) Explain your answers to the questions above. STRONG NUCLEOPHILE = S_N2
   ^-SH LARGER, MORE POLARIZABLE

2. Consider the following compound:



   a) What is the IUPAC name of the compound?
   a. (*R*)-1-chloro-3-methyl-2-cyclohexene
   b. (*S*)-1-chloro-3-methyl-2-cyclohexene
   c. (*R*)-3-chloro-1-methylcyclohexene
   d. (*S*)-3-chloro-1-methylcyclohexene

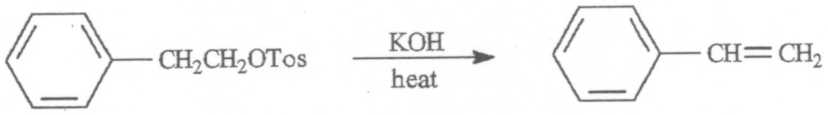
   C

   b) How could this compound be used to produce a conjugated diene?
   a. substitution
   b. elimination
   c. allylic free radical formation
   d. either b or c

   B

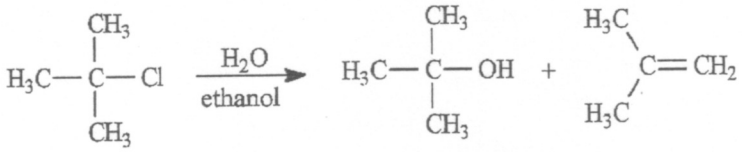
Multiple Choice
Identify the choice that best completes the statement or answers the question.

Instructions: Consider the reaction below to answer the following question.



B 3. Refer to instructions. The mechanism for this reaction is:
   a. S_N2
   b. E2
   c. S_N1
   d. E1

Instructions: Consider the reaction below to answer the following question(s).

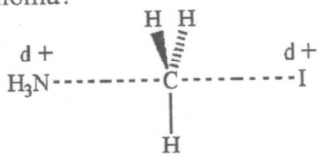


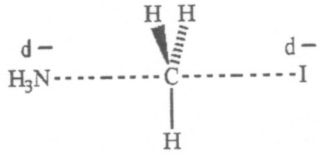
B 4. Refer to instructions. Compound B is the:
   a. S_N2 product
   b. S_N1 product
   c. E2 product
   d. E1 product

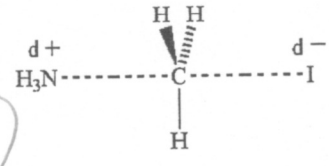
D 5. Refer to instructions. Compound C is the:
   a. S_N2 product
   b. S_N1 product
   c. E2 product
   d. E1 product

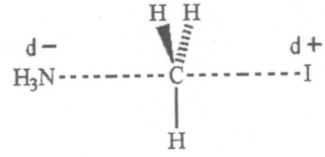
E 6. Which conditions favor an efficient (fast, high yield) S_N2 reaction between an appropriate alkyl halide and a nucleophile with a charge?
   a. high concentration of a strong nucleophile, polar protic solvent
   b. high concentration of a weak nucleophile, nonpolar solvent
   c. low concentration of a strong nucleophile, polar aprotic solvent
   d. low concentration of a weak nucleophile, nonpolar solvent
   e. high concentration of a strong nucleophile, polar aprotic solvent

___ 7. Which of the following represents the transition state of the S_N2 reaction between methyl iodide and ammonia?

a. 

b. 

c. 

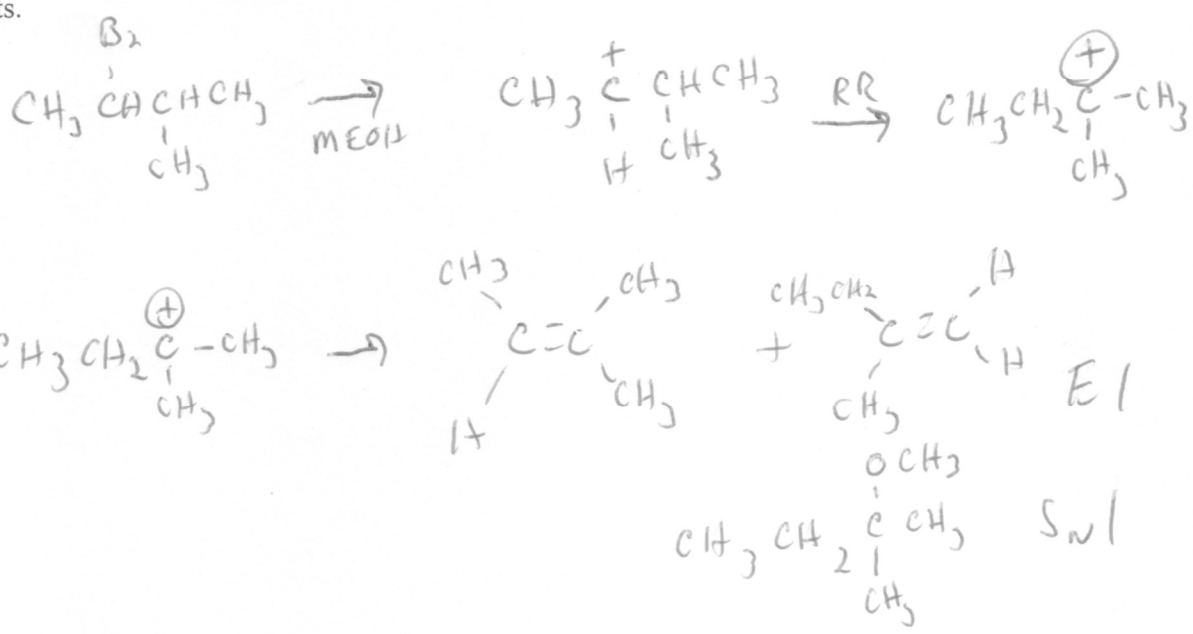
d. 

Short Answer

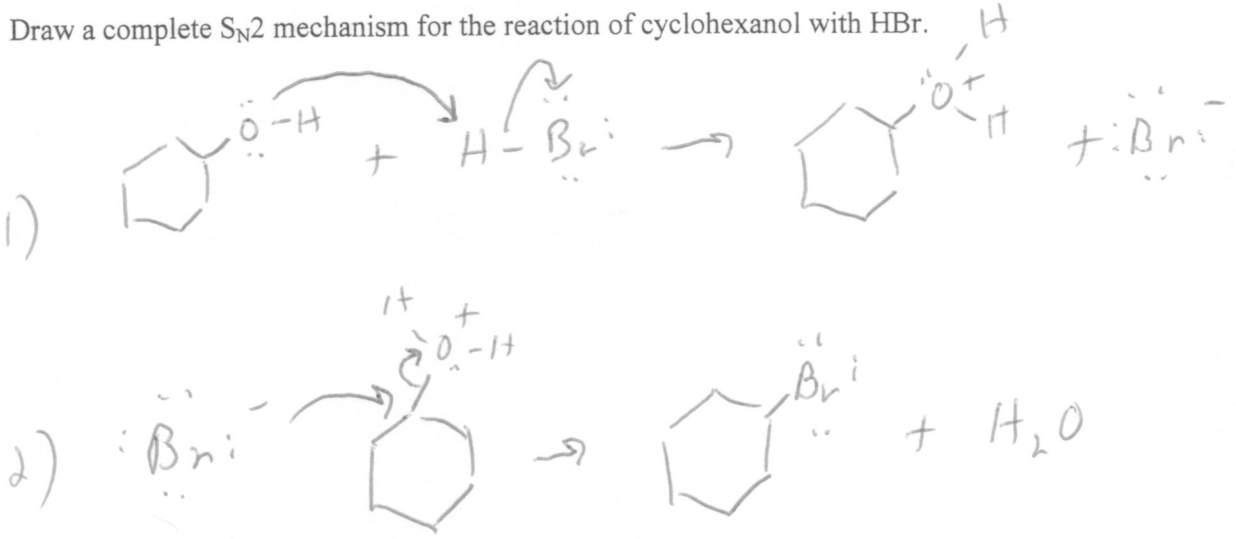
8. Order these compounds with respect to S_N2 reactivity. (1 = most reactive, 3 = least).

2-chloro-2-methylpropane	1-chloropropane	2-chlorobutane
3	1	2

9. Solvolysis (in methanol) of 2-bromo-3-methylbutane gives several products. Draw structures of all E1 and S_N1 products.



10. Draw a complete S_N2 mechanism for the reaction of cyclohexanol with HBr.



11. Which compound reacts faster in a S_N1 reaction. Briefly explain your choice.

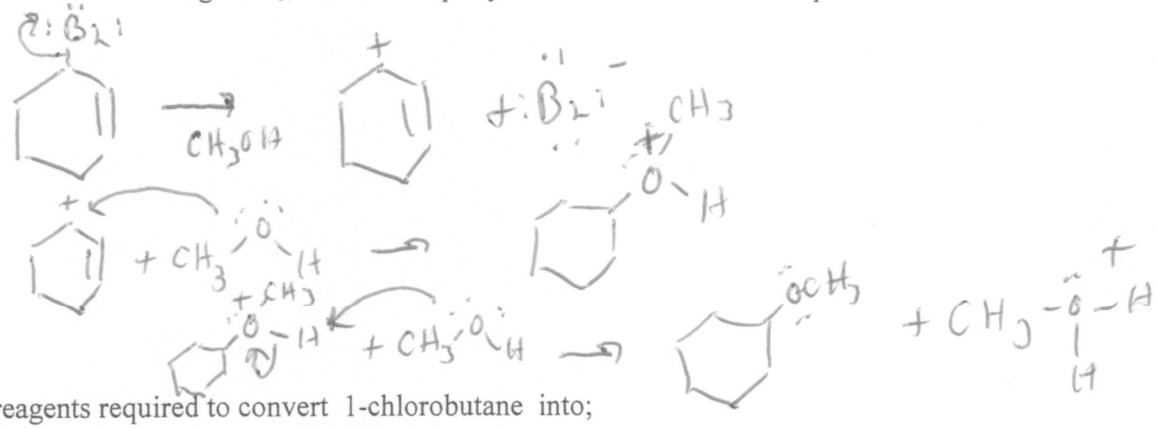
2-bromo-2-methylbutane or 2-bromo-3-methylbutane.

3°

2°

3° MAKES BETTER CATION

12. 3-bromocyclohexene undergoes S_N1 reaction rapidly in methanol. Draw a complete mechanism.



13. Show the reagents required to convert 1-chlorobutane into;

1-hexyne 1) $NaNH_2$ 2) $HC{\equiv}CH$

1-butanol ^-OH

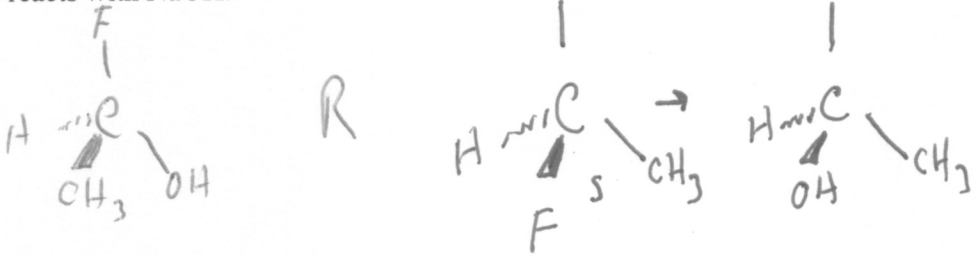
14. Which is the strongest nucleophile? Choose one from each pair. Briefly explain your choice.

Iodide or chloride I^- MORE POLARIZABLE

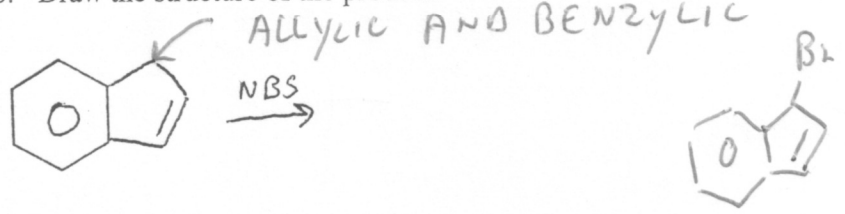
$CH_3CH_2CH_2O^-$ or $CH_3\overset{\overset{O^-}{|}}{C}HCH_3$ $CH_3CH_2CH_2-O^-$ LESS HINDERED

15. Make a **stereochemical** drawing of the product.

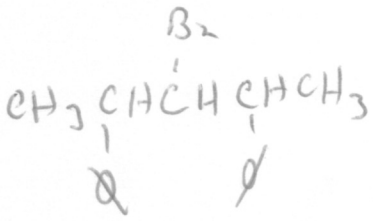
(S)-1-bromo-1-fluoroethane reacts with NaOH.



16. Draw the structure of the product.



17. Draw the structure of an alkylhalide that will produce only 2,4-diphenylpent-2-ene in an E2 reaction.



For extra credit, make a stereochemical drawing of the halide that will produce the E isomer.