Name:_____Key_____ (please print)
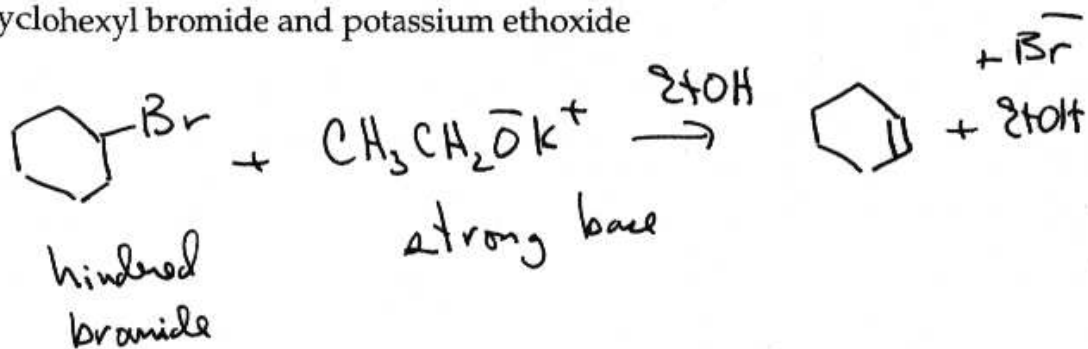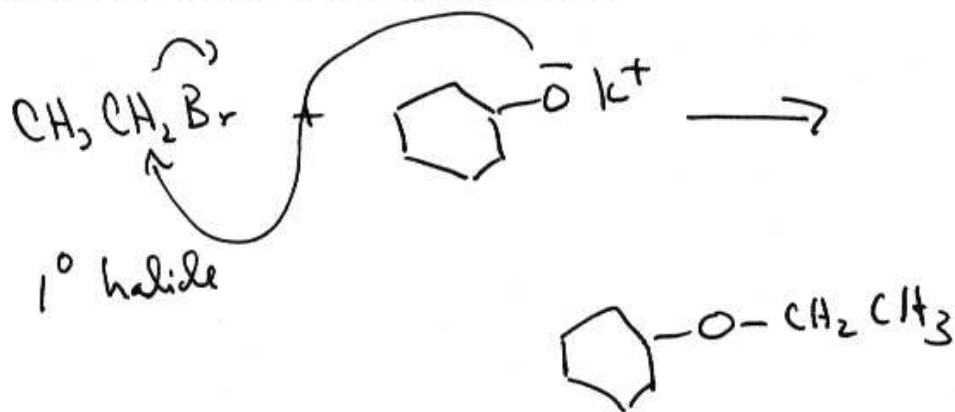
1. (20 pts) Predict the major organic product of each of the following reactions.

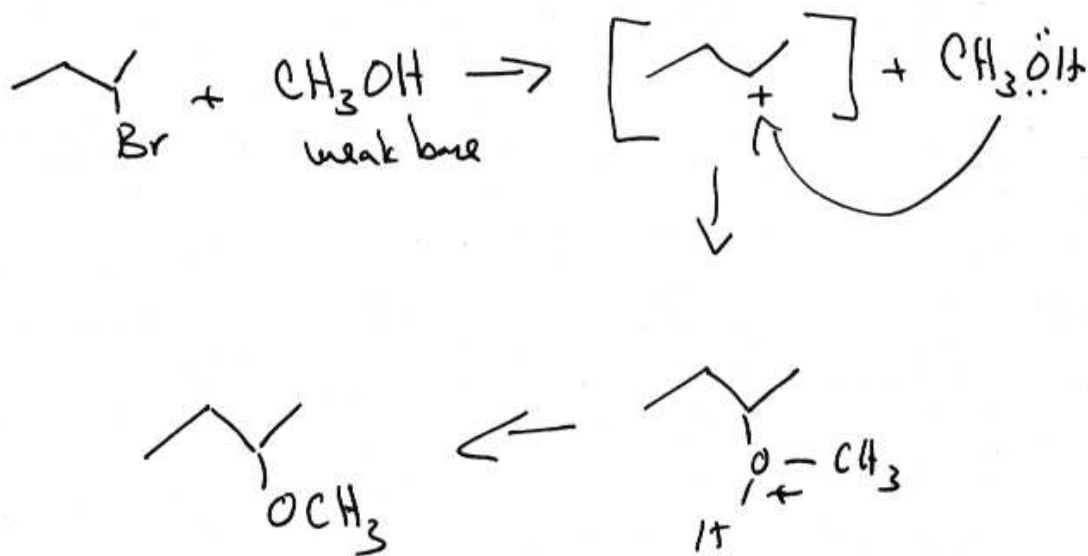a) cyclohexyl bromide and potassium ethoxide

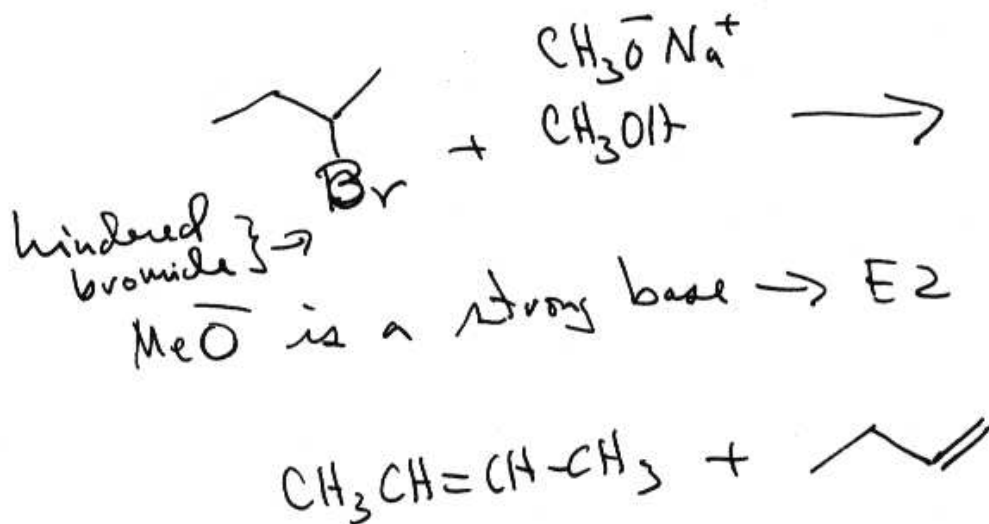hindered bromide   strong base
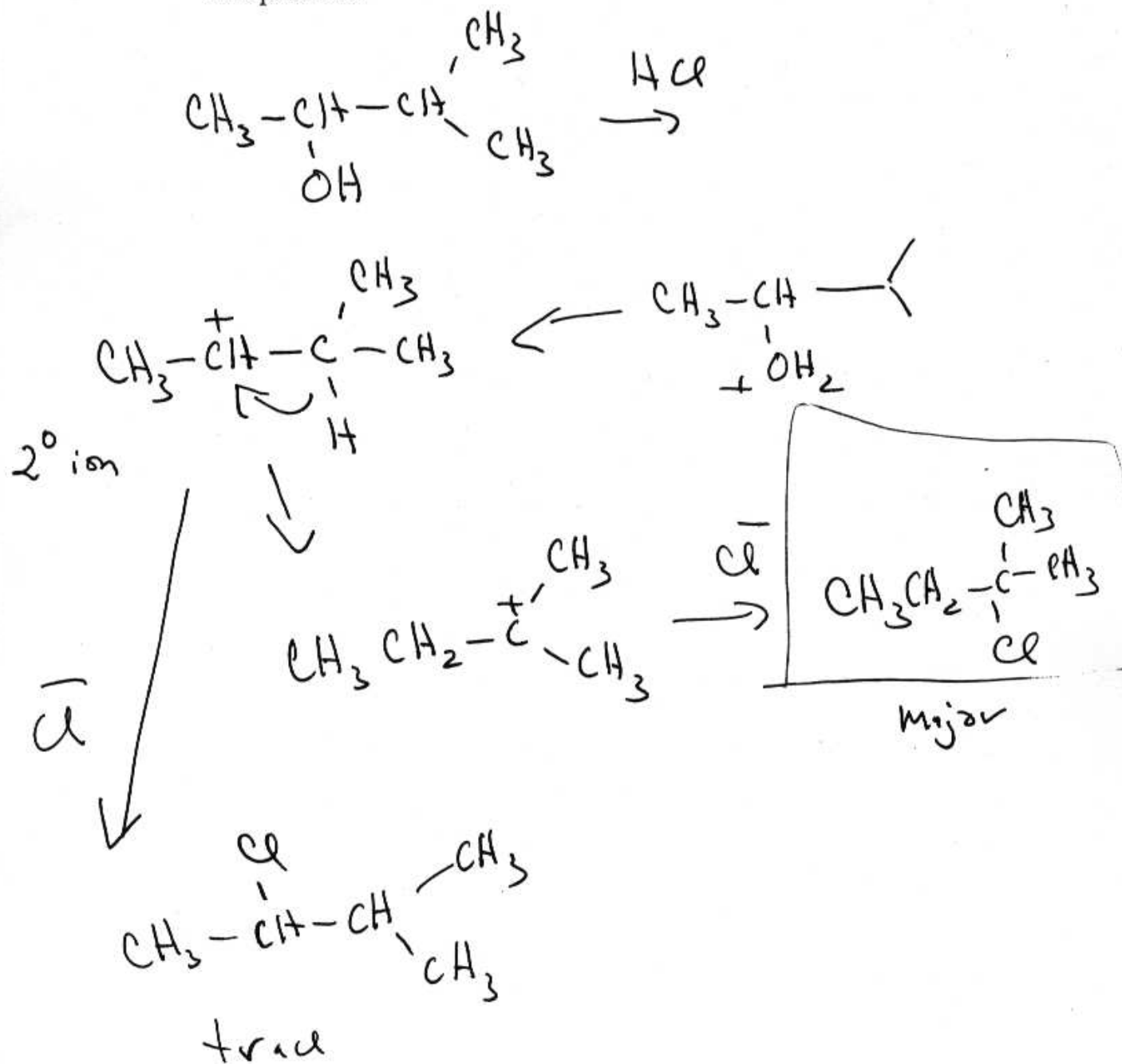
b) ethyl bromide and potassium cyclohexanolate

$1°$ halide

c)   *sec*-butyl bromide solvolysis in methanol


d)   *sec*-butyl bromide solvolysis in methanol containing 2 M sodium methoxide.

hindered bromide } →

MeŌ is a strong base → E2

$CH_3CH=CH-CH_3$ +

2.   (10 pts) Treatment of 3-methyl-2-butanol with HCl yielded
      only a trace of 2-chloro-3-methylbutane. An isomeric chloride
      was isolated in 97% yield. Suggest a reasonable structure for
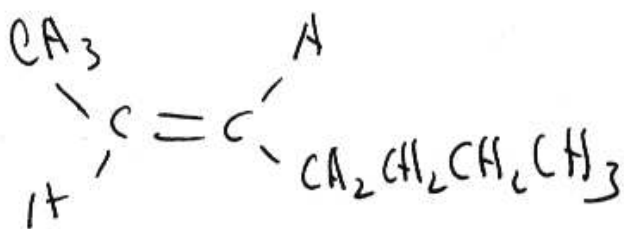   this product.

$$CH_3-CH-CH\overset{CH_3}{\underset{CH_3}{\diagup}} \quad \overset{HCl}{\longrightarrow}$$
$$\underset{OH}{\vert}$$

$$CH_3-\overset{+}{CH}-\overset{CH_3}{\underset{\underset{H}{\vert}}{C}}-CH_3 \quad \longleftarrow \quad CH_3-CH\overset{\diagup}{\underset{\underset{+OH_2}{\vert}}{\diagdown}}$$

$2°$ ion

$$CH_3CH_2-\overset{+}{C}\overset{\diagup CH_3}{\diagdown CH_3} \quad \overset{\overline{Cl}}{\longrightarrow} \quad \boxed{CH_3CH_2-\overset{CH_3}{\underset{\underset{Cl}{\vert}}{\overset{\vert}{C}}}-CH_3}$$
major

$\overline{Cl}$

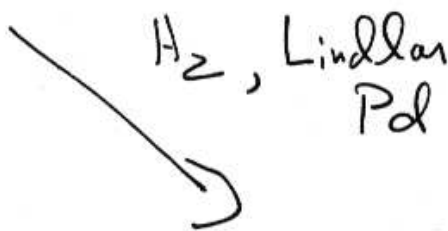$$CH_3-\overset{Cl}{\underset{\vert}{CH}}-CH\overset{\diagup CH_3}{\diagdown CH_3}$$
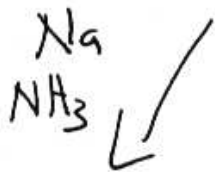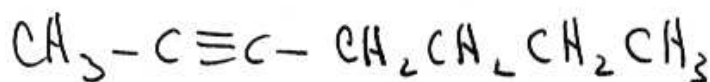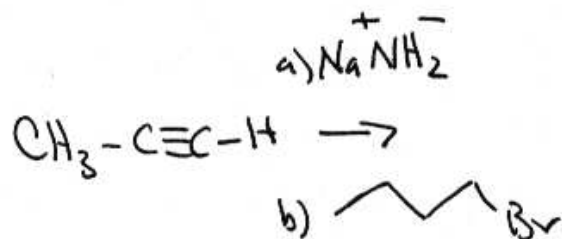trace

3. (10 pts) What two stereoisomeric substitution products would you expect to isolate from the hydrolysis of *cis*-1,4-dimethylcycylohexyl bromide? From the hydrolysis of *trans*-1,4-dimethylcycylohexyl bromide?
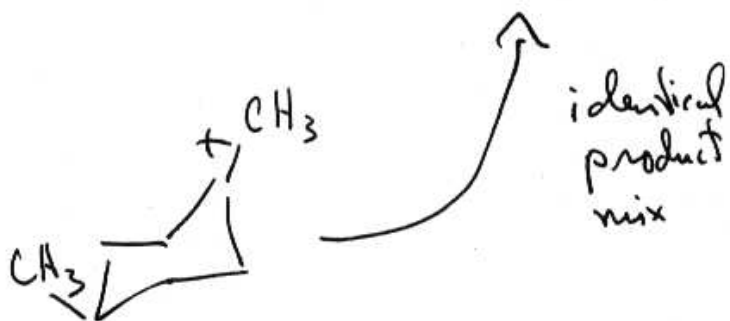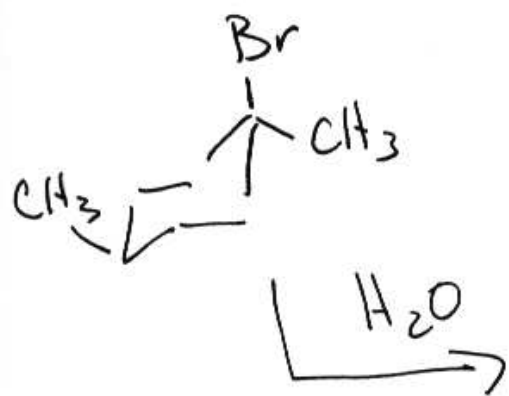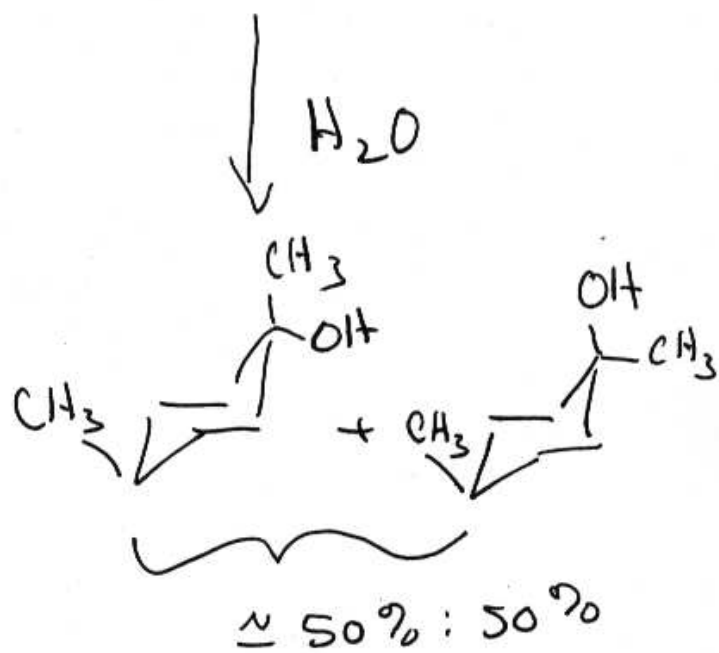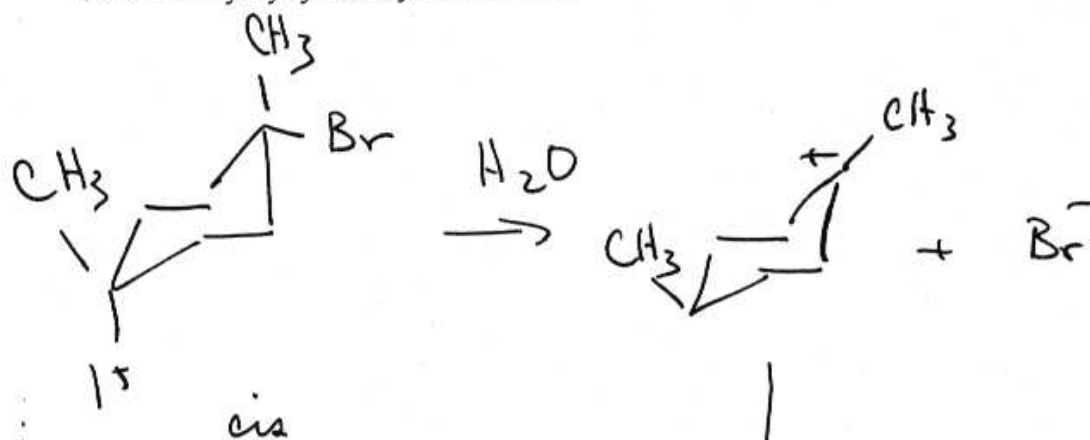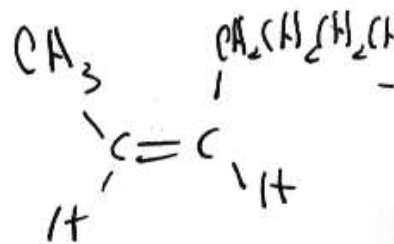
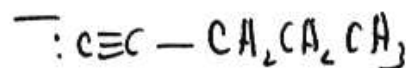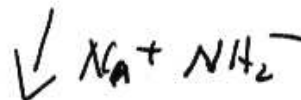4. (10 pts) Suggest efficient of (E)- and (Z)-2-heptene from propyne and any necessary organic or inorganic reagents.

$$CH_3-C\equiv C-H \xrightarrow{\substack{a) Na^+NH_2^- \\ b)}}$$

$$CH_3-C\equiv C-CH_2CH_2CH_2CH_3$$

Na / NH$_3$ H$_2$, Lindlar Pd

$$\underset{(E)-2-heptene}{\underset{H}{\overset{CH_3}{\diagdown}}C=C\underset{CH_2CH_2CH_2CH_3}{\overset{H}{\diagup}}}$$

$$\underset{(Z)-2-heptene}{\underset{H}{\overset{CH_3}{\diagdown}}C=C\underset{H}{\overset{CH_2CH_2CH_2CH}{\diagup}}}$$

5.   (10 pts) How would prepare 2-octanone from HCCH and any
      necessary reagents? How could you prepare 4-octanone?

$HCCH + Na \xrightarrow{NH_3} HCC:^- Na^+$

$H_2C=\overset{OH}{\underset{\cdot}{C}}-(CH_2)_5 CH_3 \xleftarrow[H_2SO_4]{H_2O} H-C\equiv C-CH_2 CH_2 CH_2 CH_2 CH_2 CH_3$

(trace H_2SO_4)

$CH_3-\overset{O}{\overset{\|}{C}}-(CH_2)_5-CH_3$

$HCCH \xrightarrow{Na NH_3} HCC:^- Na^+ \quad CH_3 CH_2 CH_2 Br$

$HCC-CH_2CH_2CH_3$

$\downarrow Na^+ NH_2^-$

$\uparrow H_2O, H_2SO_4$
H_2SO_4
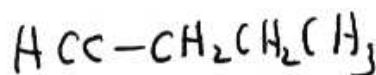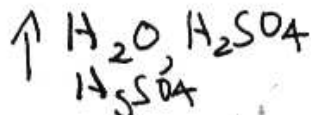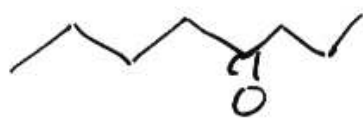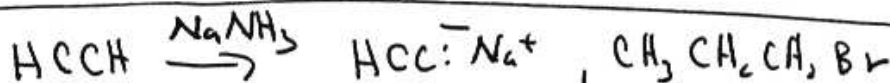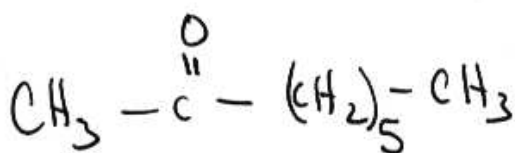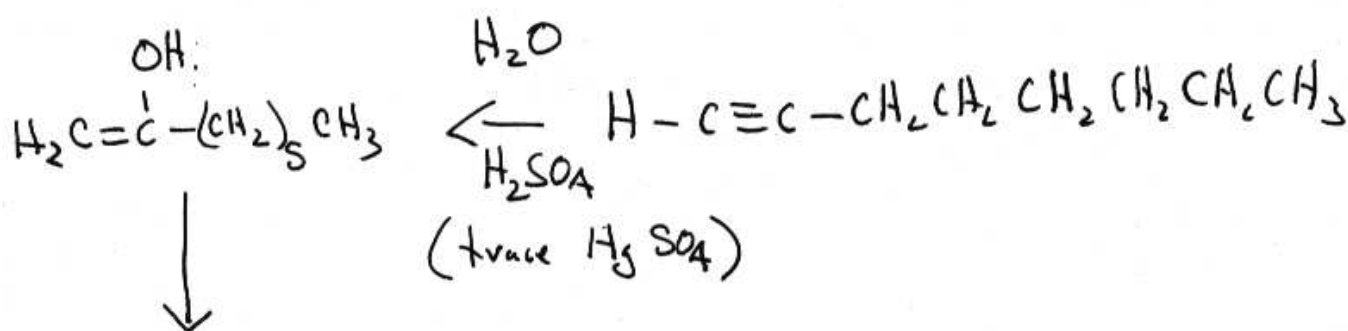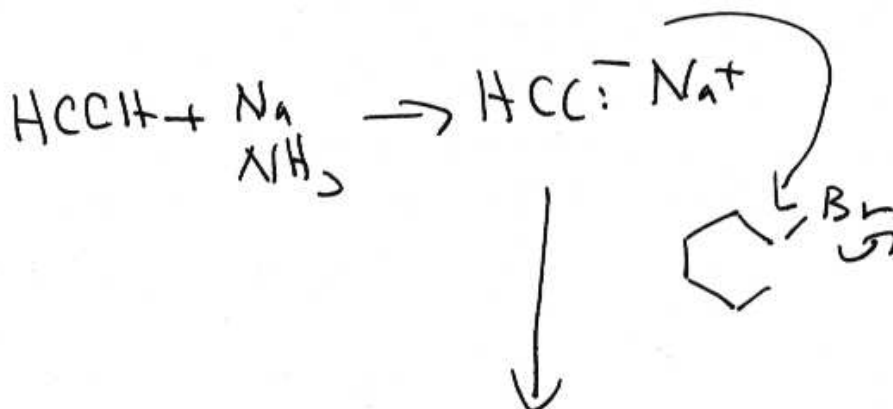
$:C\equiv C-CH_2CH_2CH_3$

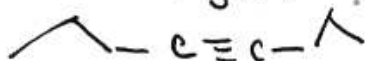6. (20 pts) How would prepare each of the following compounds from propene and any necessary organic or inorganic reagents?

a) allyl bromide

$$CH_3 - CH_2 = CH_2 \xrightarrow[\Delta]{NBS} CH_2 - CH = CH_2$$
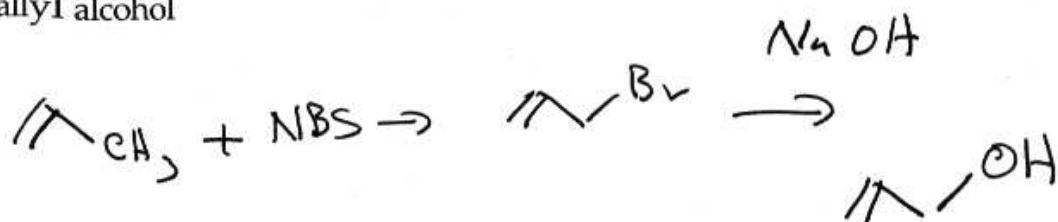$$\qquad\qquad\qquad\qquad\qquad\quad |$$
$$\qquad\qquad\qquad\qquad\qquad Br$$

b) allyl alcohol

$$\diagup\!\!\!\!\diagdown_{CH_3} + NBS \rightarrow \diagup\!\!\!\!\diagdown\!\!\!\diagup^{Br} \xrightarrow{NaOH} \diagup\!\!\!\!\diagdown\!\!\!\diagup^{OH}$$

c) $CH_2=CH-CH_2-C\equiv CH$

$H C\equiv C H$ $\xrightarrow{\begin{array}{c}Na^+ \\ \overline{N}\overset{..}{H}_2\end{array}}$

$\overset{//\wedge}{}CH_3 + NIBS \longrightarrow$ $\overset{//\wedge}{}CH_2\overset{+\ominus\ +2.5}{\underset{Br}{\overset{|}{C}}} + \ H C\equiv C:^- Na^+$

+2.5
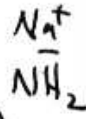
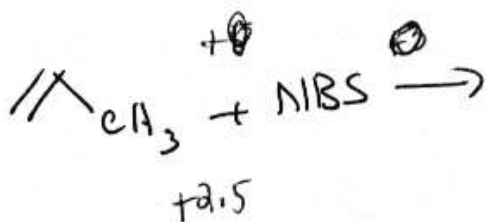$//\wedge\diagup C\equiv CH$
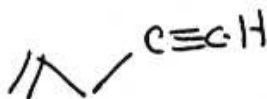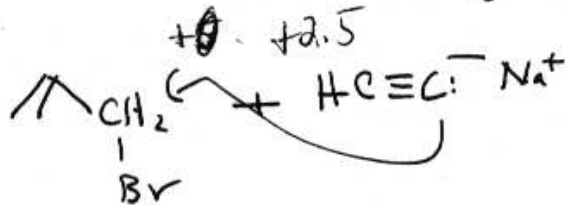
d)   1-bromo-2-chloropropane

$\overset{//\wedge}{}CH_3 + \overset{+2.5}{NIBS} \longrightarrow //\wedge CA_2-Br$

$\downarrow HCl$ +2.5

$CH_3-\overset{\overset{Cl}{|}}{CH}\diagdown CH_2Br$
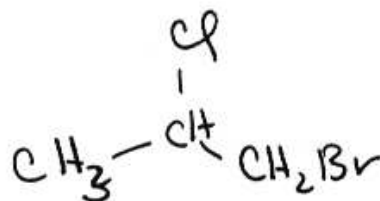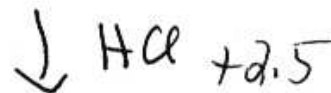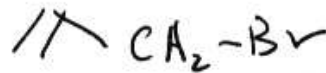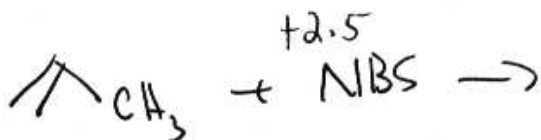
7. (20 pts) Suggest reasonable explanations for each of the following.

a) The first order rate constant for the solvolysis of $(CH_3)_2C=CHCH_2Cl$ in ethanol is 6000 times greater than that of allyl chloride.

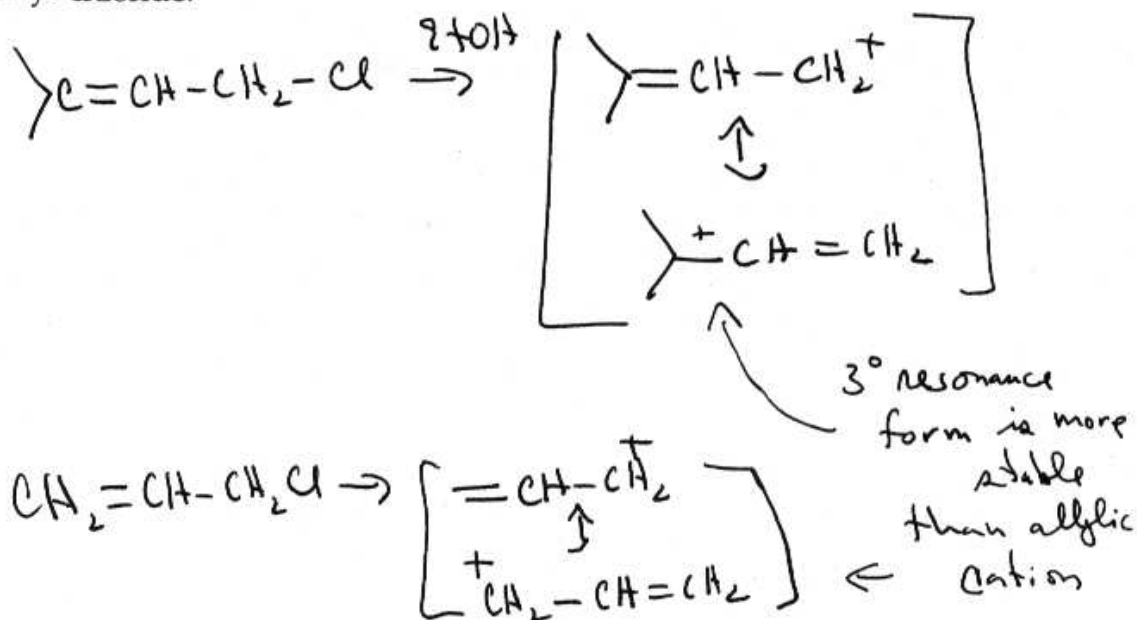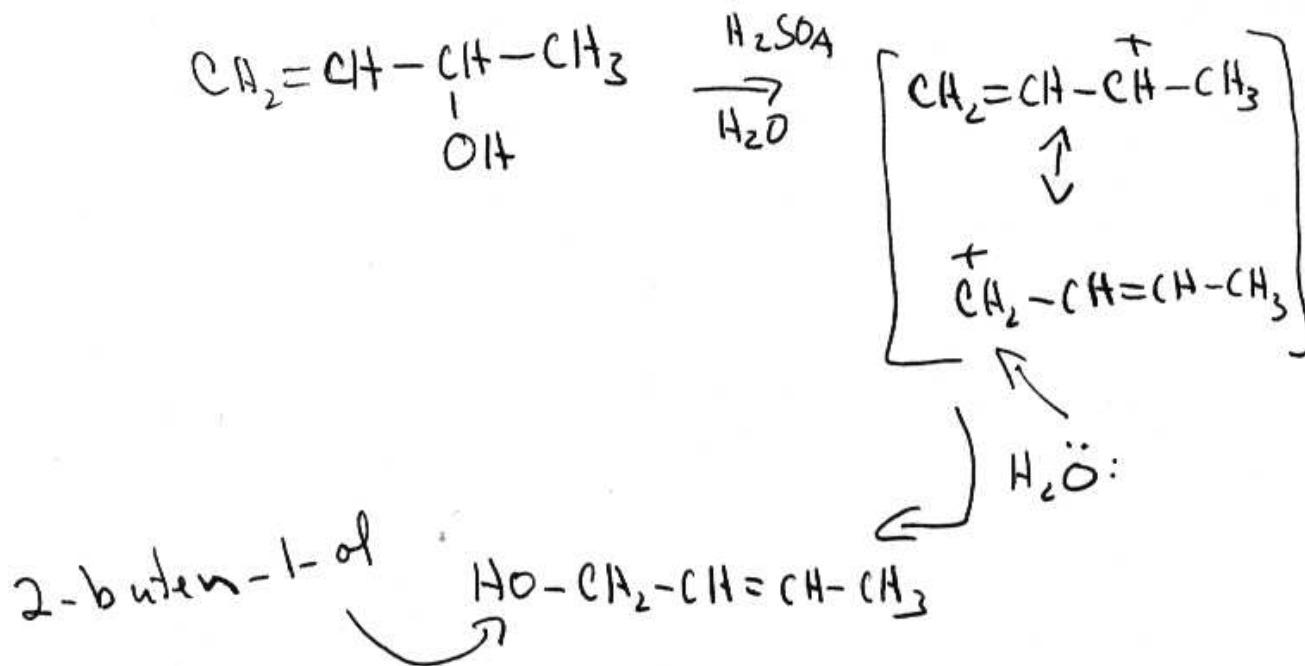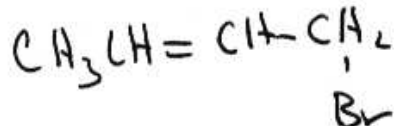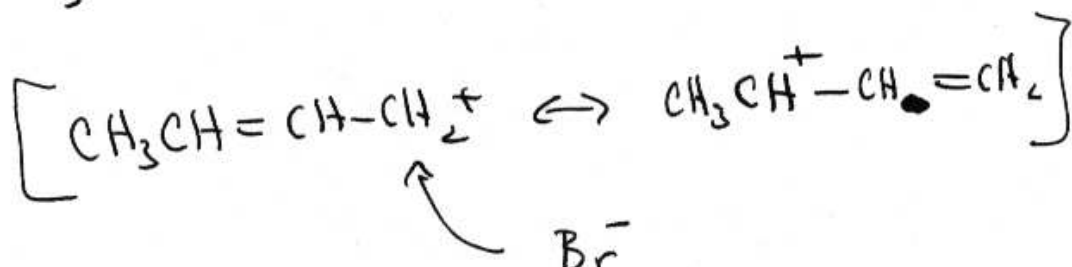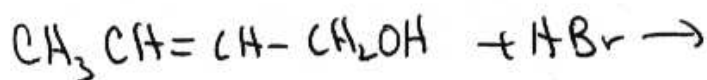$$>C=CH-CH_2-Cl \xrightarrow{EtOH} \left[\begin{array}{c} >=CH-CH_2^+ \\ \updownarrow \\ >\overset{+}{}CH=CH_2 \end{array} \right]$$

$$CH_2=CH-CH_2Cl \rightarrow \left[\begin{array}{c} =CH-C\overset{+}{H}_2 \\ \updownarrow \\ \overset{+}{C}H_2-CH=CH_2 \end{array} \right] \leftarrow$$

3° resonance form is more stable than allylic cation

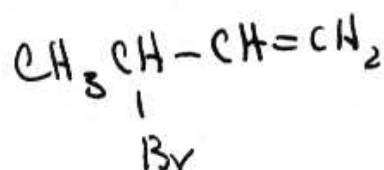b) After a solution of 3-buten-2-ol in aqueous sulfuric acid had been allowed to stand for a week, it was found to contain both 3-buten-2-ol and 2-buten-1-ol.

$$CH_2=CH-\underset{\underset{OH}{|}}{CH}-CH_3 \xrightarrow[H_2O]{H_2SO_4} \left[\begin{array}{c} CH_2=CH-\overset{+}{CH}-CH_3 \\ \updownarrow \\ \overset{+}{C}H_2-CH=CH-CH_3 \end{array} \right]$$

$H_2\overset{..}{O}:$

2-buten-1-ol

$HO-CH_2-CH=CH-CH_3$

c) Treatment of $CH_3CH=CHCH_2OH$ with HBr gave a mixture of 1-bromo-2-butene and 3-bromo-1-butene.

$$CH_3 CH= CH- CH_2OH + HBr \longrightarrow$$

$$\left[CH_3CH=CH-CH_2^+ \longleftrightarrow CH_3CH^+-CH=CH_2 \right]$$

Br⁻

$$CH_3CH= CH-CH_2$$
             |
             Br

1-bromo-2-butene

$$CH_3CH-CH=CH_2$$
        |
        Br

3-bromo-1-butene

d) Treatment of 3-buten-2-ol with HBr gave the same mixture of bromides as in part (c).

$$CH_3 - CH - CH= CH_2 \xrightarrow{HBr}$$
        |
        OH

3-buten-2-ol

$$\left\{ \begin{array}{l} CH_3CH=CH-CH_2Br \\ CH_3-CH-CH=CH_2 \\ | \\ Br \end{array} \right\}$$

Br⁻ $\left[CH_3-CH\cdots CH\cdots CH_2 \right]^+$
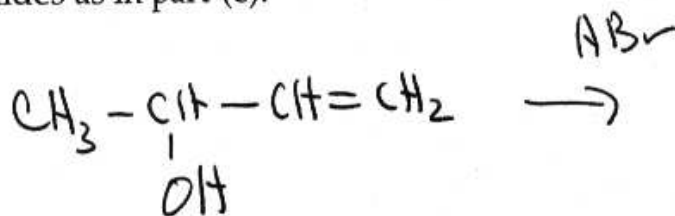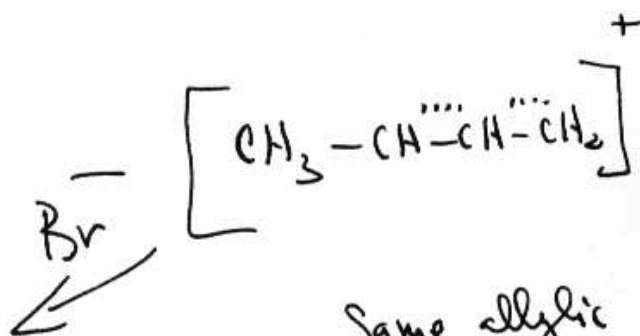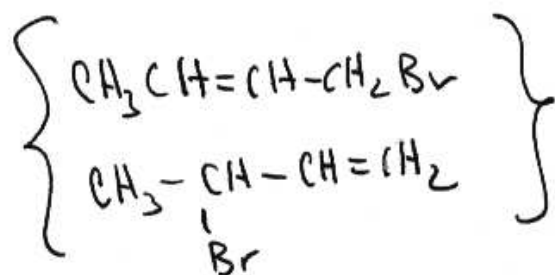
Same allylic cation as in (c)