Note: **There are no questions to be answered on this page,**
Note that some of the data provided may not be needed

Typical ^{1}H NMR chemical shifts δ

$R\text{-}CH_3$	0.7-1.3
$R\text{-}CH_2\text{-}R'$	1.2-1.6
R_3CH	1.4-1.8
$R\text{-}CH_2\text{-}O\text{-}R'$	3.3-4.0
$R\text{-}CH_2Cl$	3.4-3.7
R_2CHCl	3.9-4.4
$RO\text{-}CH_2Cl$	5.2-5.6
$RR'C{=}CH_2$	4.6-5.0
$RCH{=}CHR'$	5.2-5.7
$RC{\equiv}CH$	1.7-3.1
$CH_3\text{—}\overset{\overset{O}{\|}}{C}\text{—}R$	2.0-2.4
$\overset{\|}{C}{=}\overset{\|}{C}\text{—}CH_2\text{—}$	1.7-2.2

Typical ^{13}C NMR chemical shifts δ

$R\text{-}CH_3$	5-25
$R\text{-}CH_2\text{-}R'$	25-35
R_3CH	35-55
R_4C	30-45
$R\text{-}CH_2\text{-}O\text{-}R'$	50-90
$R\text{-}CH_2Cl$	25-50
$R\text{-}COOH$	170-180
$R\text{-}CH{=}CH\text{-}R'$	100-150
$R_2C{=}CR'_2$	100-150
$RC{\equiv}CR$	65-95
$CH_3\text{—}\overset{\overset{O}{\|}}{C}\text{—}R$	170-220

Infrared stretching in cm^{-1}

O-H (alcohol) 3200-3650
C-H (alkane) 2840-3000
C-H (alkene) 3050-3150
C-H (alkyne) 3260-3330
C=O (aldehyde, ketone) 1690-1750
C=C (alkene) 1620-1680
C≡C (alkyne) 2100-2260
$R\text{—}\overset{\overset{O}{\|}}{C}\text{—}OR'$ (ester) 1735-1750

D is the symbol used to denote deuterium the isotope ^{2}H of hydrogen

Partial periodic table of the elements

IA											0
1 H 1.00794	IIA				IIIA	IVA	VA	VIA	VIIA		2 He 4.00260
3 Li 6.941	4 Be 9.01218				5 B 10.811	6 C 12.011	7 N 14.0067	8 O 15.9994	9 F 18.9984		10 Ne 20.1797
11 Na 22.9898	12 Mg 24.3050		IB	IIB	13 Al 26.9815	14 Si 28.0855	15 P 30.9738	16 S 32.066	17 Cl 35.4527		18 Ar 39.948
19 K 39.0983	20 Ca 40.078		29 Cu 63.546	30 Zn 65.39	31 Ga 69.723	32 Ge 72.61	33 As 74.9216	34 Se 78.96	35 Br 79.904		36 Kr 83.80
37 Rb 85.4678	38 Sr 87.62		47 Ag 107.868	48 Cd 112.411	49 In 114.82	50 Sn 118.710	51 Sb 121.75	52 Te 127.60	53 I 126.904		54 Xe 131.29
55 Cs 132.905	56 Ba 137.327		79 Au 196.967	80 Hg 200.59	81 Tl 204.383	82 Pb 207.2	83 Bi 208.980	84 Po (209)	85 At (210)		86 Rn (222)

1. (13 Points) **For multiple choice questions circle the letter of the best answer**

The specific rotation of pure (R)-2-bromo~~pentane~~ BUTANE is -20°, what is the optical rotation of a sample of (S)-2-bromopropane with an optical purity of 50%

(a) zero (b) +15 (d) -15 (e) +10 (f) -10 (g) +7.5 (h) -7.5 (i) none of these

---

Which of the following is produced when 1 equivalent of HBr is added to 1-hexyne in the presence of peroxides?

(a) 2-bromo-1-hexene (b) (E)-1-bromo-1-hexene (c) (Z)-1-bromo-1-hexene

(d) mixture of (b) and (c) (e) (E)-2-bromo-2-hexene (f) (Z)-2-bromo-2-hexene

(g) mixture of (e) and (f) (h) none of these

An increase in which of the following results in a decrease in the rate of a chemical reaction?

(a) Temperature (b) Concentration (c) pH (d) collision frequency

(e) activation energy (f) time of reaction (g) none of these

Which of the following statements is correct for propene $CH_2=CHCH_3$

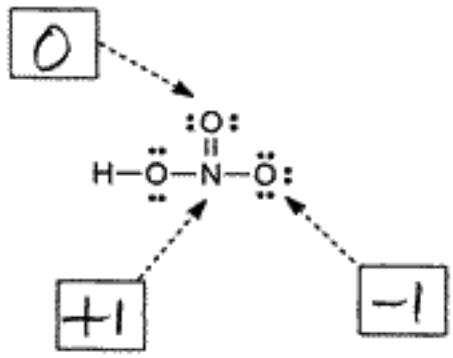
(a) all nine atoms are in the same plane (b) the molecule has eight sigma bonds

(c) Propene has two isomers (E and Z) (d) propene generally acts as a Lewis acid

(e) All C atoms in propene are sp^2 hybridized (f) none of these

---

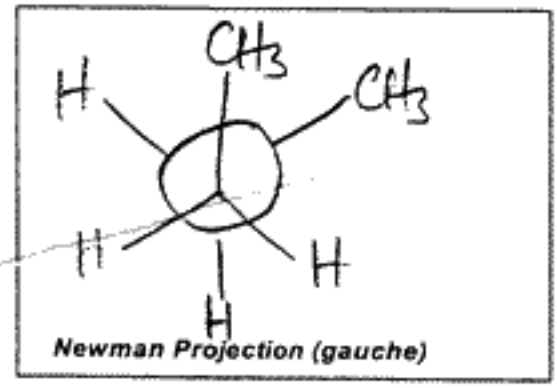
What is the formal charge on each atom indicated by an arrow



How many distinct internal alkynes exist with the molecular formula C_6H_{10}

Answer: 3

2. (19 Points). (a) Assume that the energy difference between gauche and anti conformations of butane corresponds to an equilibrium constant K_{eq} of about 2.0. Show a Newman projection for **gauche** butane and calculate the percentage of **anti** conformer at equilibrium.
Write an equation for K_{eq} and show details of your work.

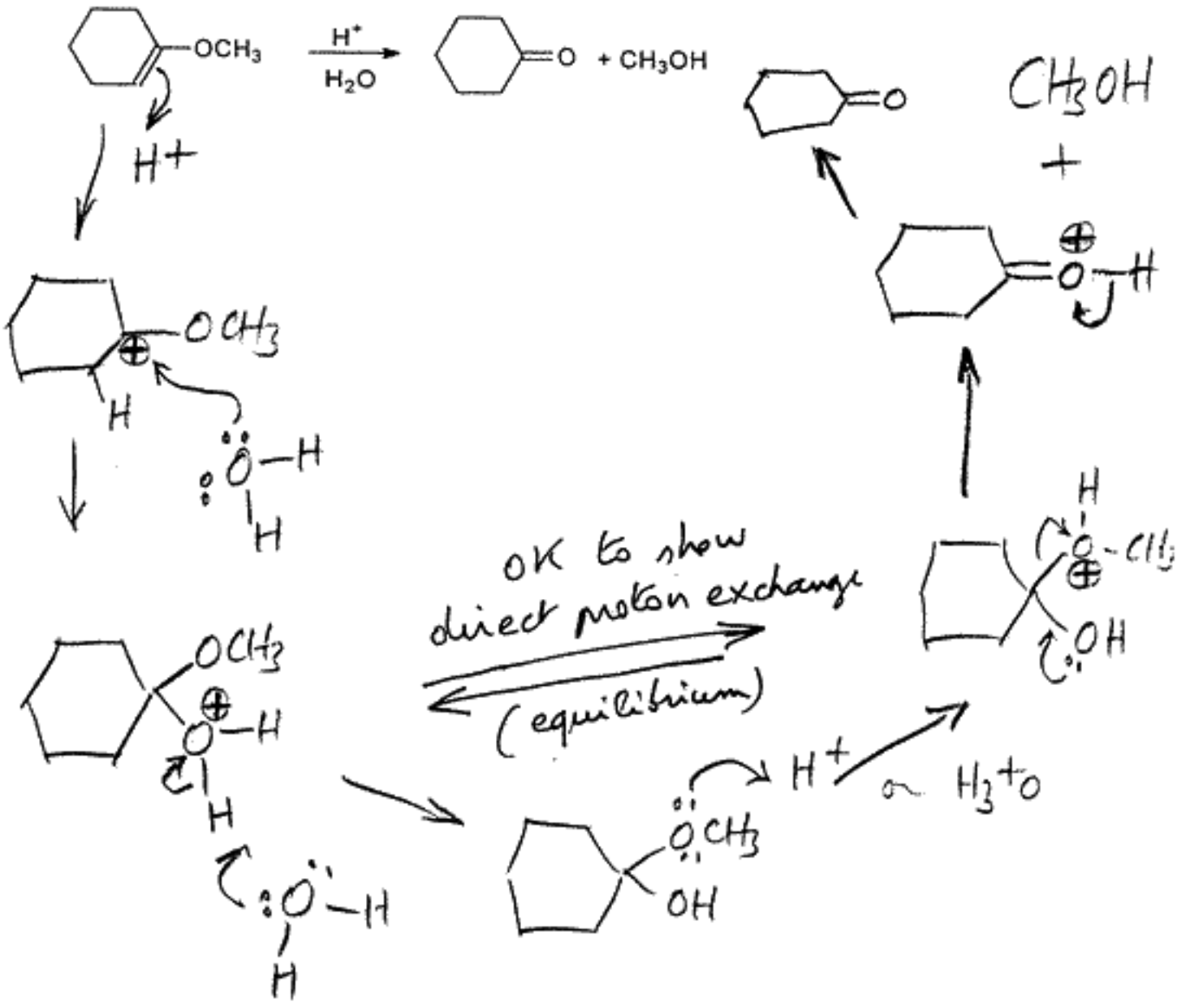


Newman Projection (gauche)

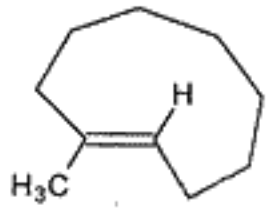
$K_{eq} = \dfrac{[ANTI]}{[GAUCHE]}$

% anti conformer = 66% $= \dfrac{2}{2+1} \times 100$

(b) show a step by step mechanism (with arrows) for the following reaction:

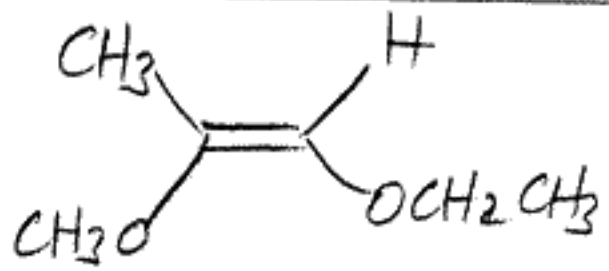


3. (19 Points). (a) Name or draw the following molecules as appropriate (show stereochemistry)



(E)-1-methyl-cyclononene

(Z)-1-ethoxy-2-methoxy-1-propene



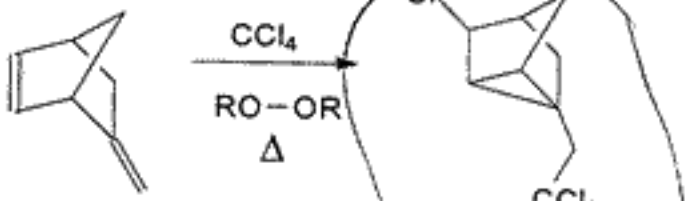
$HC \equiv C-CH_2CH_2OH$

3-butym-1-ol

or 3-butynol

(b) Write a mechanism for the following reaction

(hint: the bond $Cl-CCl_3$ *is easily broken)*



RO-OR

↙ Δ

2RO·

A RADICAL REACTION

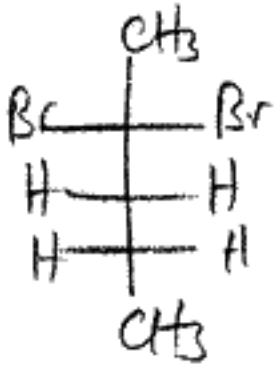
$RO\cdot + CCl_4 \Rightarrow ROCl + \cdot CCl_3$

+

$\cdot CCl_3$

4. (20 Points). (a) Consider the monobromination of (S)-2-bromopentane using Br_2 and light. How many products are obtained by reaction at C-2, C-3 and C-4, write your answer in the box and show a Fisher projection for each specifying whether each is chiral or achiral and, in cases where more than one product is obtained, whether they will be formed in equal or unequal amounts.

Reaction at C-2 →

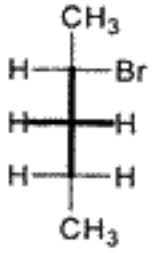


achiral

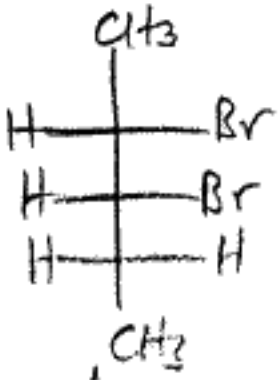
*write "**chiral**" or "**achiral**" next to each product*

Number of products: [1] products formed in **equal** [ ] or **unequal** [ ] amounts

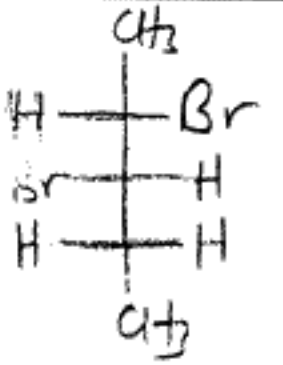
---



Reaction at C-3 →



chiral

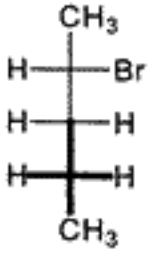


chiral

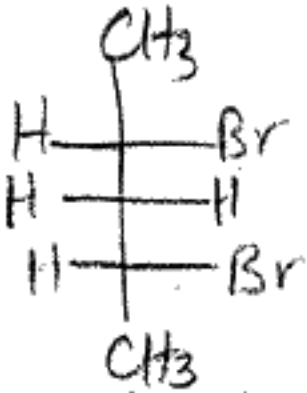
*write "**chiral**" or "**achiral**" next to each product*

Number of products: [2] products formed in **equal** [ ] or **unequal** [✓] amounts

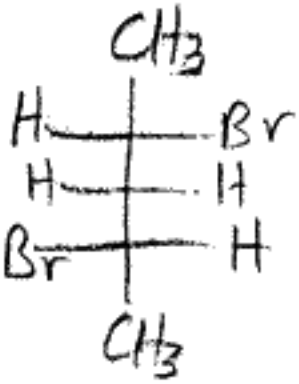
---



Reaction at C-4 →



achiral (meso)

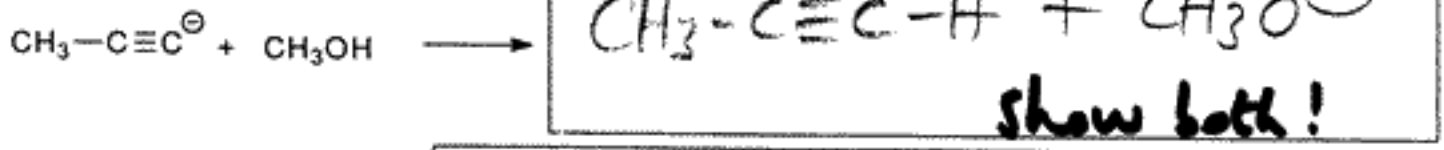


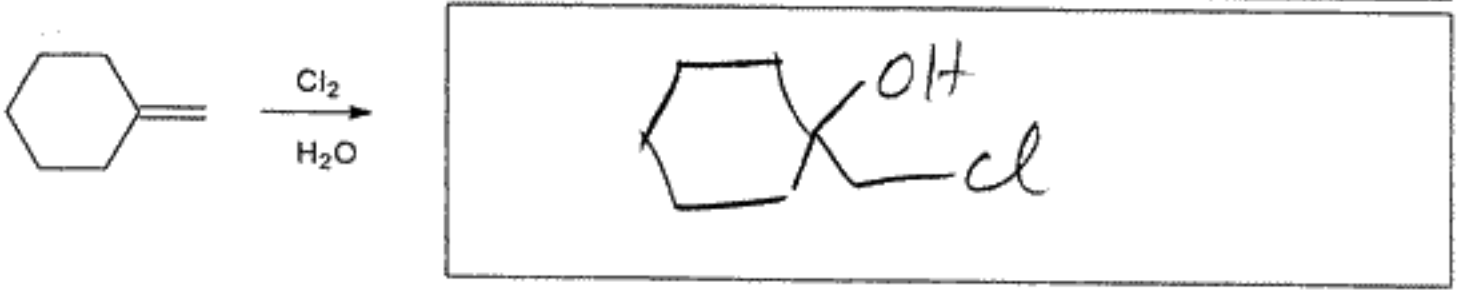
chiral

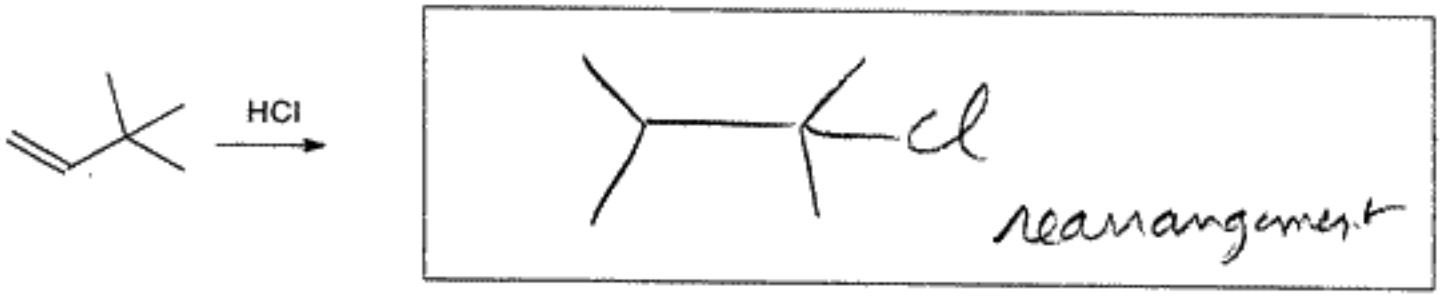
*write "**chiral**" or "**achiral**" next to each product*

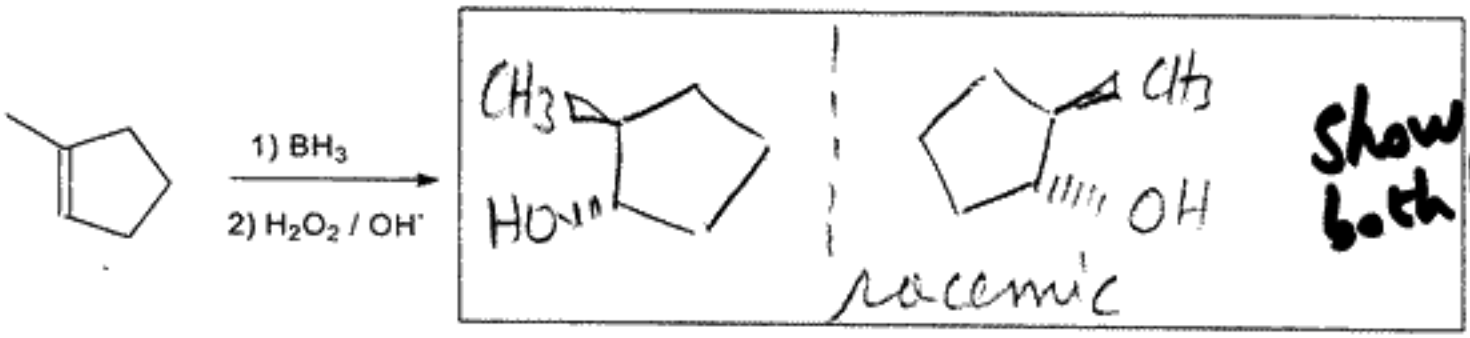
Number of products: [2] products formed in **equal** [ ] or **unequal** [✓] amounts

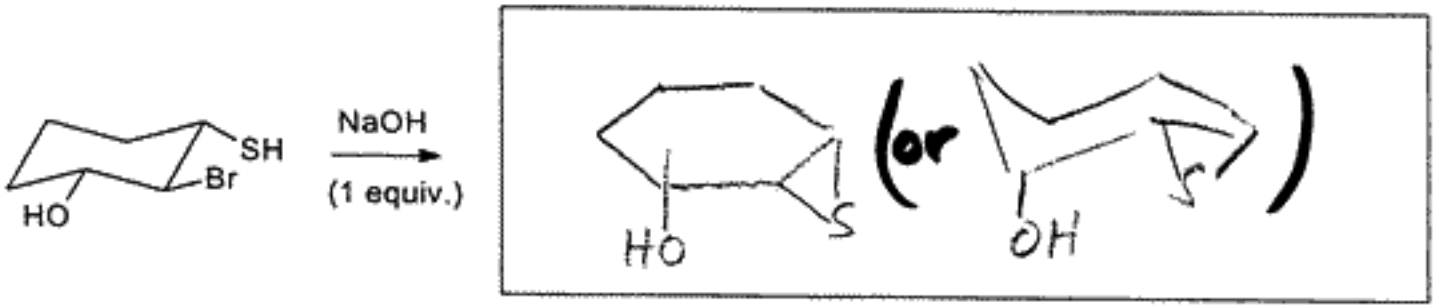
5. (20 Points). Complete the following reactions showing the structure(s) of the major product(s). Write NR if there is no reaction.

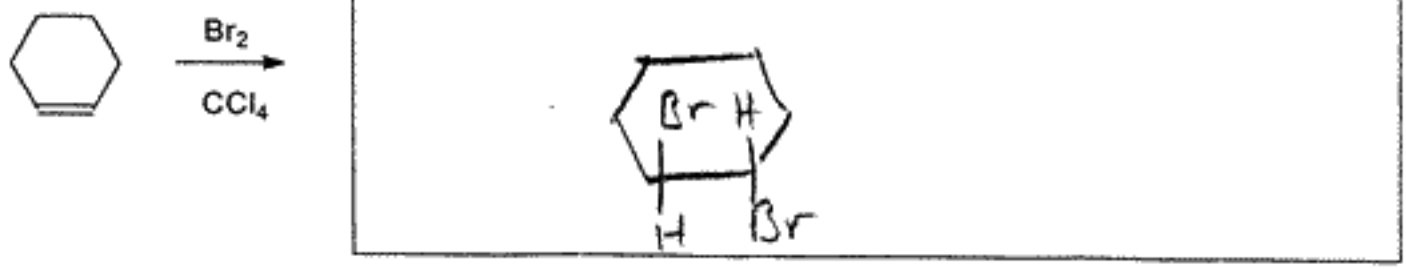








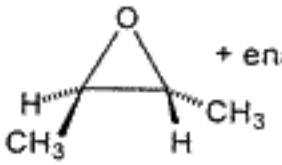




6. (21 Points). Complete the following reactions showing the starting materials or reagents as appropriate. Some reactions may require more than one step, all steps/reagents must be shown.

$CH_3-C\equiv C-CH_3$

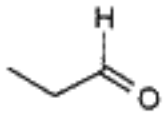
1) Na / NH_3 (or Li / NH_3)
2) MCPBA

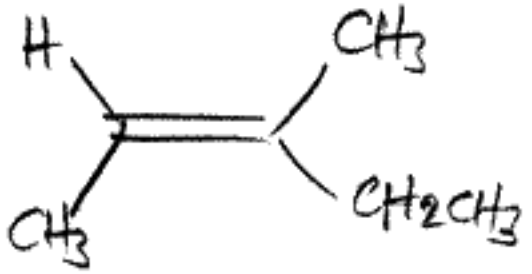


+ enantiomer

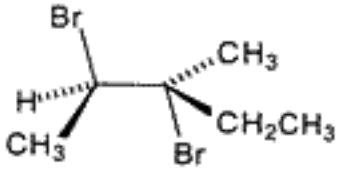
$CH_3CH_2C\equiv CCH_2CH_3$

1) H_2 / Pd / $CaCO_3$ / quinoline
2) O_3
3) CH_3SCH_3

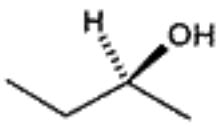




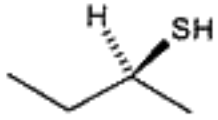
Br_2 / CCl_4

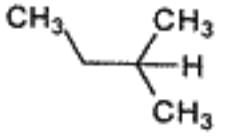


+ enantiomer

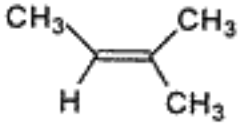


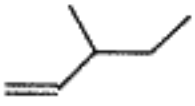
1) PBr_3
2) $\ominus SH$



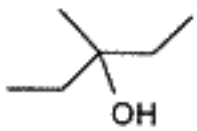


1) Br_2 / hν
2) EtO^- strong base not bulky





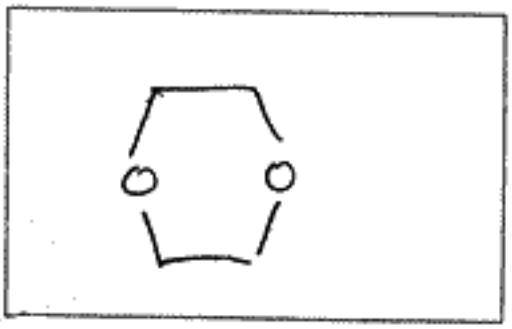
H^+ / H_2O



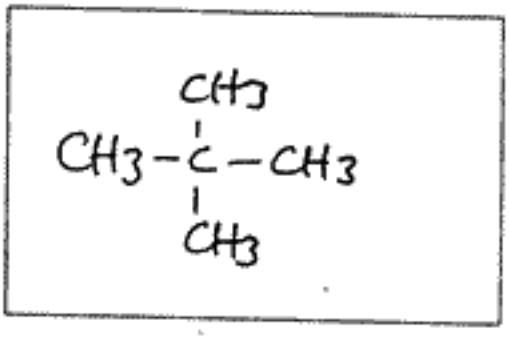
rearrangement

7. (18 Points). (a) Propose a reasonable structure for the organic compunds below that show only one peak in their ^{1}H NMR spectra.

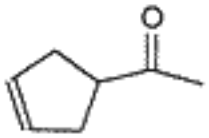
$C_4H_8O_2$



C_5H_{12}

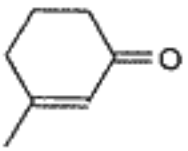


(b) How many peaks are in the ^{13}C NMR "normal" spectrum of:



Answer: 5

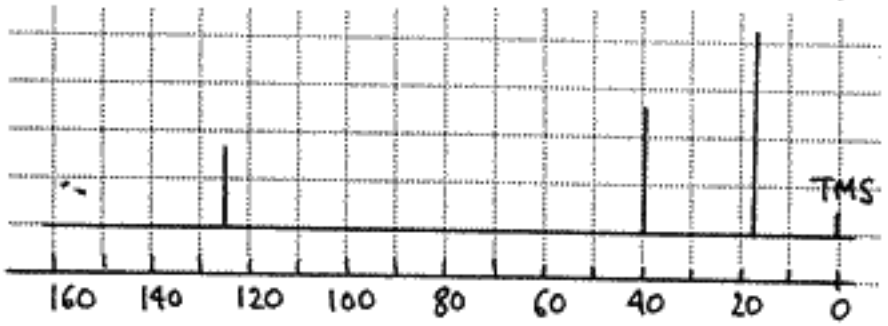
(c) How many peaks are in the DEPT-135 ^{13}C NMR spectrum of:



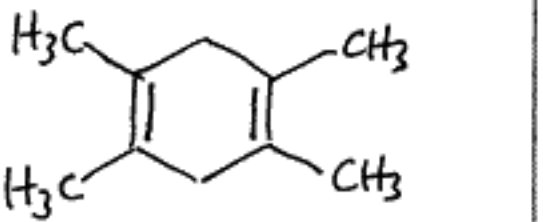
Answer: 5

(d) Propose a structure for the cyclic hydrocarbon $C_{10}H_{16}$ with the following NMR spectra:

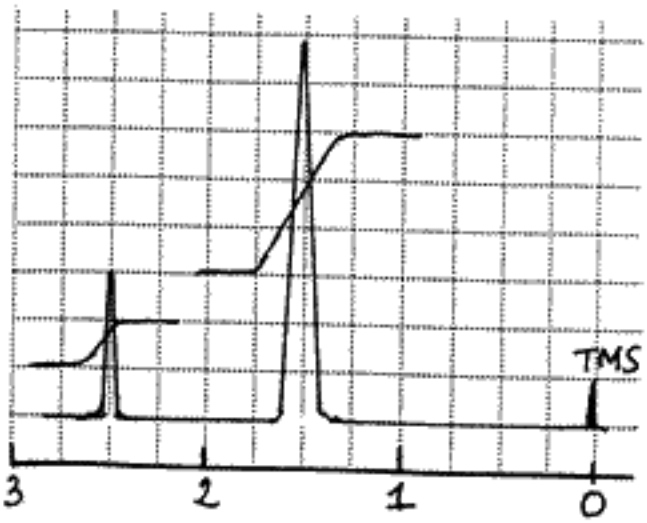
"Normal" ^{13}C NMR ------>



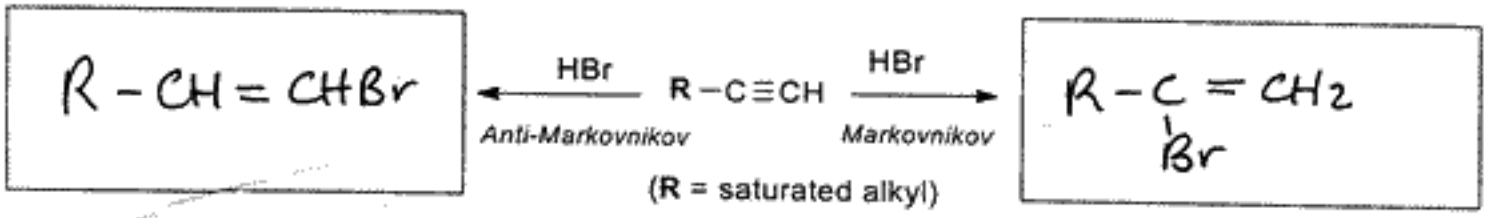
Answer:



^{1}H NMR ------>



8. (15 Points). (a) The addition of one molecule of HBr to a **linear terminal alkyne** can proceed in Markovnikov or anti-Markovnikov fashion depending on reaction conditions. Show the products of each type of addition in the respective boxes below and explain clearly how one could use a single ^{13}C NMR experiment to distinguish *without any ambiguity* one product from the other.



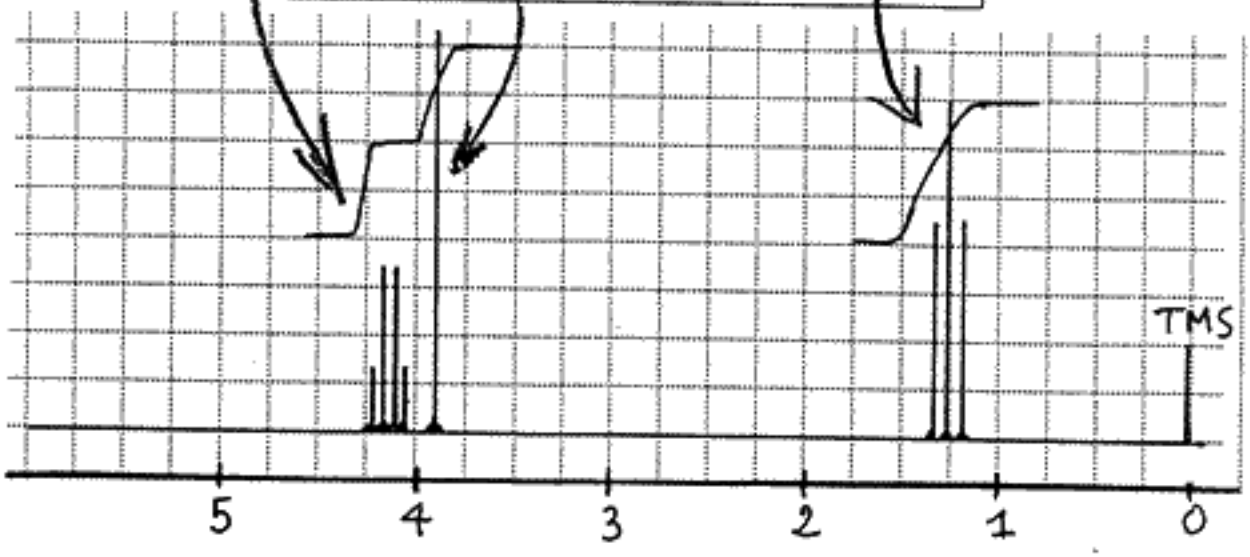
(R = saturated alkyl)

Explanation: DEPT-90 : anti Markov product has 2 peaks
Markov product has no signal

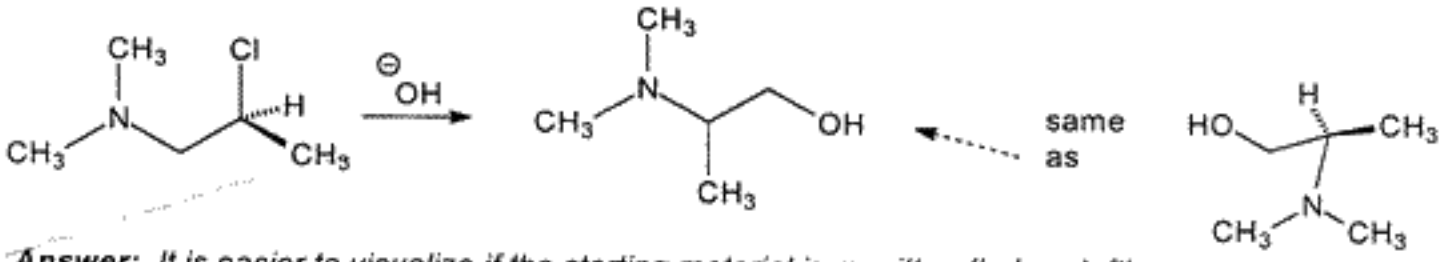
Dept 135 is also OK 3 positive peaks for anti Markov
1 positive peak for Markov
(the CH_3 at chain end)

(b) An unknown compound with the molecular formula $C_4H_7O_2Cl$ has a strong IR band at 1740 cm^{-1} and the ^1H NMR spectrum below. Write a clear structure for the compound and assign all peaks using arrows to indicate which part of the overall structure corresponds to each peak

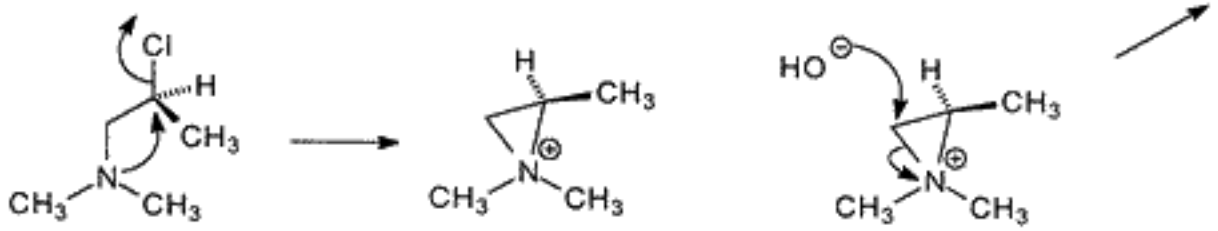
Answer: $Cl\,CH_2-\overset{\overset{O}{\|}}{C}-O-CH_2CH_3$



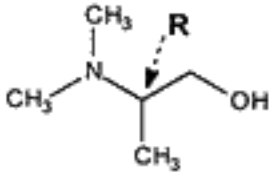
9. (18 Points). (a) Propose a step by step mechanism for the following reaction (show arrows):



Answer: *It is easier to visualize if the starting material is rewritten (below, left)*

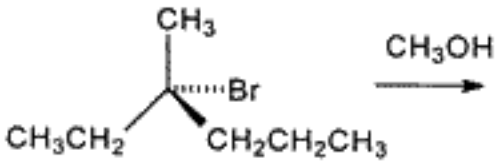


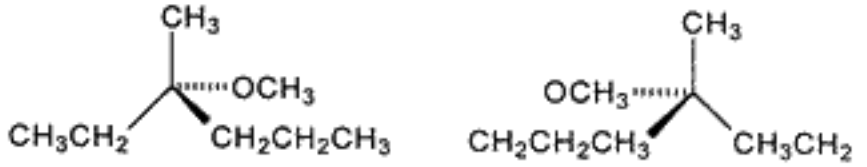
(b) The chiral center of the starting material in the above reaction has the S configuration. Show the chiral center of the product with an arrow, indicate and explain its absolute configuration.



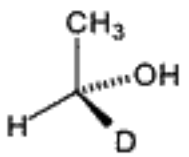
Answer: *The product is R as attack of N onto the chiral center occurs with inversion of configuration in this intramolecular S_N2 reaction*

(c) Complete the following reactions showing the major product(s)



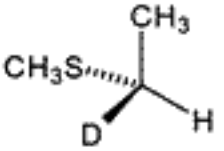


Racemic mixture vis S_N1



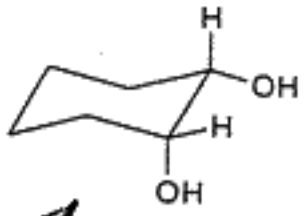
1) TsCl / pyridine

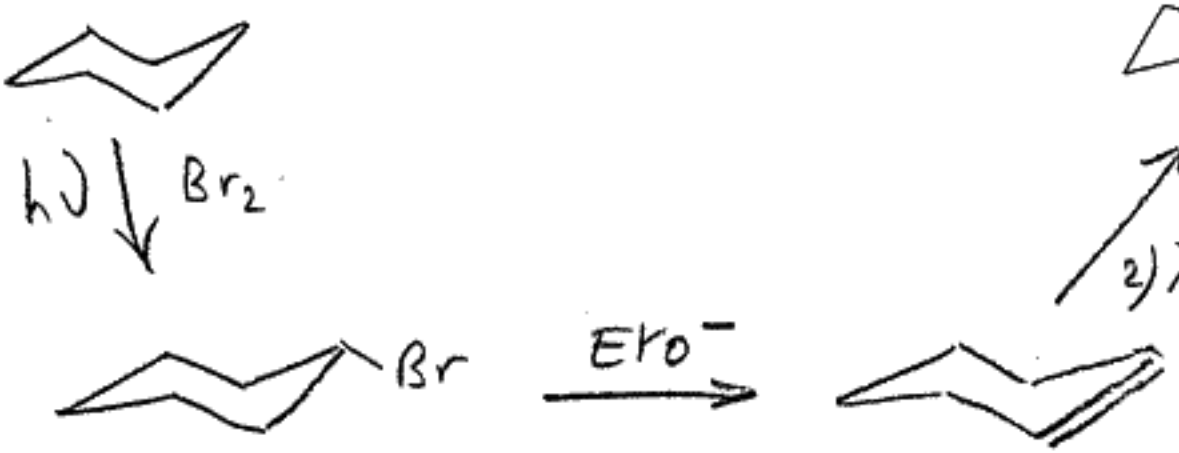
2) $CH_3S^{\ominus}$

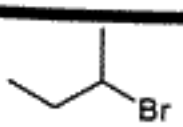


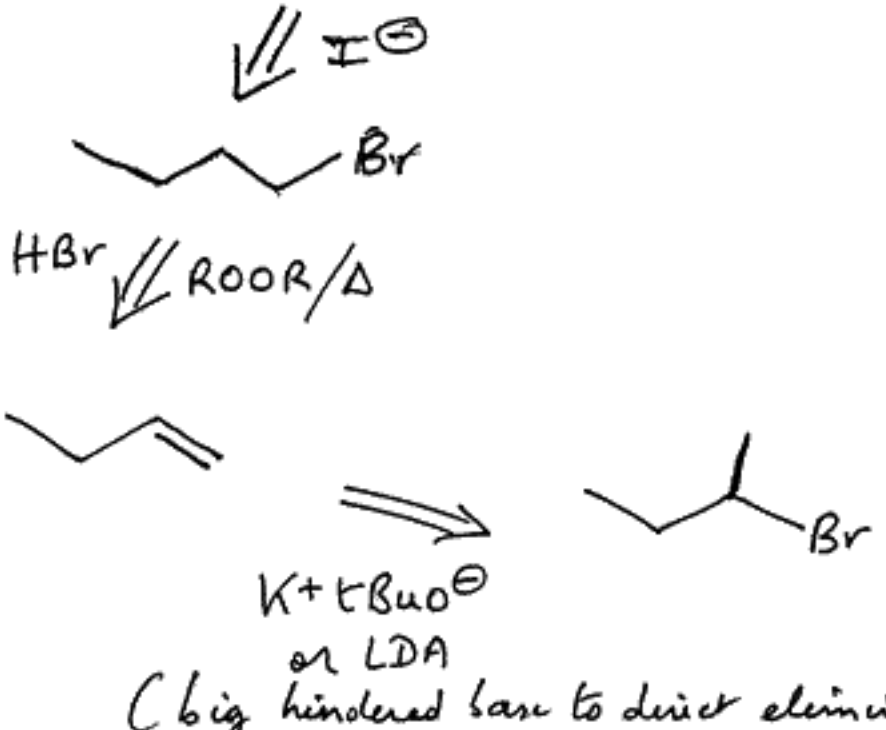
retention followed by inversion via S_N2

10. (18 Points). (a) Starting from cyclohexane, propose a synthesis of:



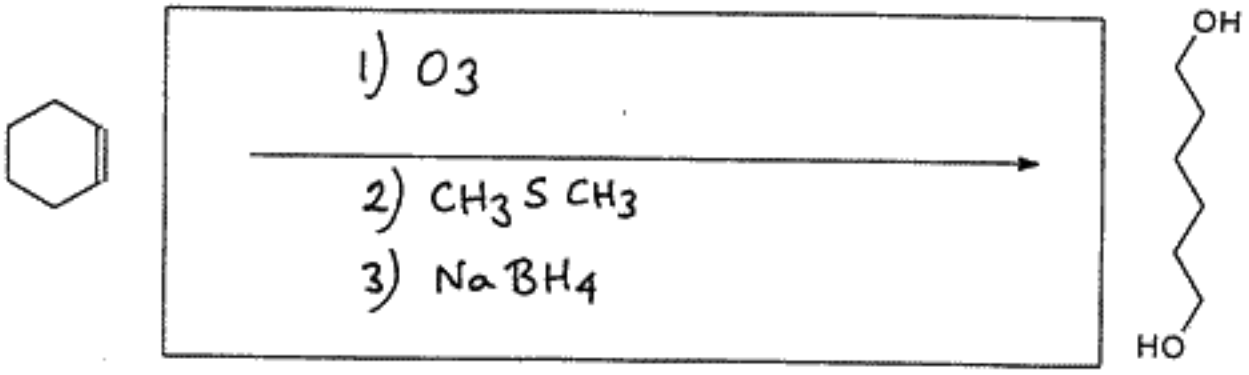


(b) propose a synthesis of  from 

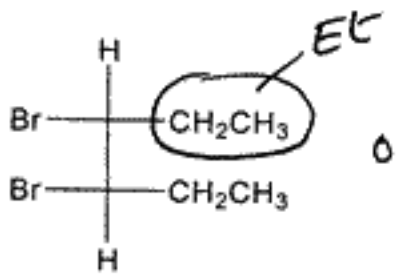


(big hindered base to direct elimination to least substituted H's)

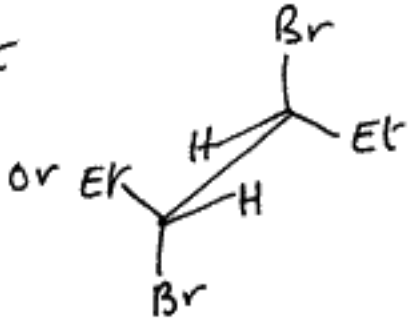
(c) Complete the following reaction showing the missing reagents (several steps may be needed)



11. (14 Points). Starting from **alcohols** with 4 C atoms or less as the sole sources of C atoms, propose a synthesis of ***meso***-3,4-dibromohexane. Show all steps/reagents but no mechanisms.



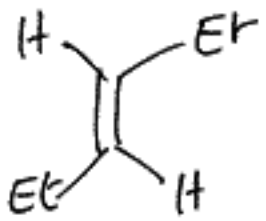
or



$CH_3CH_2CH_2CH_2OH$

Br_2 ⇓ CCl_4

H_2SO_4 ⇑ 180°



$CH_3-CH_2-CH=CH_2$

Li ⇓ NH_3

⇑

Br

$CH_3-CH_2-CH-CH_2Br$

$Et-C\equiv C-Et$

⇓

$Na^{\oplus}$

$CH_3CH_2Br + {}^{\ominus}C\equiv C-CH_2CH_3$ ⇗ $Na^{\oplus}NH_2^{\ominus}$ excess

⇓ PBr_3 or HBr

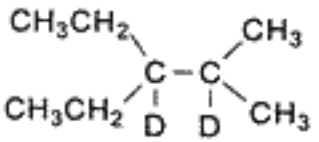
CH_3CH_2OH

⇑ $Na^+NH_2^{\ominus}$

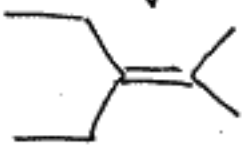
$Na^{\oplus}NH_2^{\ominus}$ ⇘

$HC\equiv C-CH_2-CH_3$

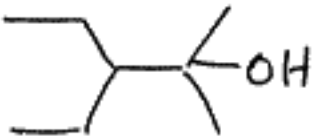
12. (18 Points). Propose a synthesis of the compound below using one molecule of ethene and two molecules of propyne.



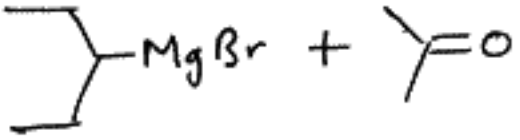
D_2/Lindlar or Li/ND_3



H_2SO_4/Δ



1) ether
2) H_3O^+ acidify (protonate)



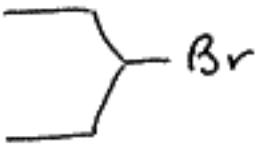
$CH_3-C\equiv CH$

$H^+/Hg^{2+}/H_2O$

Mg/Et_2O

CH_2CH_2

HBr



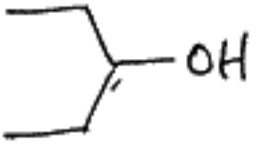
$CH_3-C\equiv CH$

CH_3CH_2Br

PBr_3

1) HB(C6H11)2
2) $H_2O_2/OH^\ominus$

Mg/Et_2O



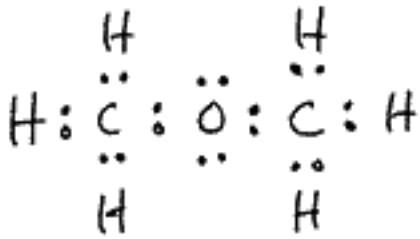
$\Rightarrow CH_3CH_2CHO + CH_3CH_2MgBr$

13. (17 Points) Consider the following ether synthesis:

$$CH_3—O^{\ominus} + CH_3—Br \longrightarrow CH_3—O—CH_3$$

(a) Name the chemist whose name is associated with this reaction: Williamson

(b) Draw the Lewis-dot structure of the product ether



(c) What is the approximate C-O-C bond angle in this product *(circle the letter of the best answer)*

(A) 180° (B) 120° (C) 107° (D) 90° (E) 60° (F) None of these

(d) In the above reaction $CH_3—O^{\ominus}$ is classified as a *(circle the letter of the best answer)*

(A) strong electrophile (B) weak electrophile (C) strong nucleophile (D) weak mucleophile
(E) strong acid (F) weak acid (G) neutral species (H) leaving group

(e) Is water a good solvent for this reaction? ***Answer:*** NO

Explanation: CH_3O^- reacts with H_2O to form OH^- ($K_{eq} \sim 1$) both nucleophiles CH_3O^- and OH^- react to give a mixture of product

(f) Now consider the reaction: $CH_3—O—CH_3 + HBr \longrightarrow CH_3—\overset{\oplus}{O}(H)—CH_3 + Br^{\ominus}$

What is the molecular shape of $CH_3—\overset{\oplus}{O}(H)—CH_3$ *(circle the letter of the best answer)*

(A) linear (B) bent (C) trigonal planar (D) trigonal pyramid (E) tetrahedral

(g) Write the equilibrium constant for the reaction $CH_3OH + H_2O \overset{K}{\rightleftharpoons} CH_3O^- + H_3O^+$

$$K = \frac{[CH_3O^-][H_3^+O]}{[CH_3OH][H_2O]}$$

(h) Given that the pKa of methanol is about 16 which of the following is **closest** to the value of K in this reaction *(circle your answer)*

(A) 55.5 (B) +16 (C) -16 (D) 10^{-16} (E) 10^{+16} (F) 1.8×10^{-18} (G) $1.8 \times 10^{+18}$