Midterm I answer

2021.04.09

1. Which proton will show the signal < 0 ppm in ^{1}H NMR? (5 point)

(A) R-C-**H** (B) R-S-**H** (C) R-Al-**H** (D) R-COO**H** (E) R-O-O**H**

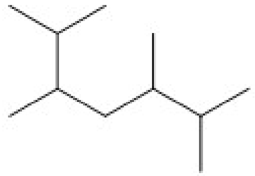
protons in electron-poor environments	protons in electron-dense environments
deshielded protons	shielded protons
downfield	upfield
high frequency	low frequency
large δ values	small δ values

$\longleftarrow$ δ ppm

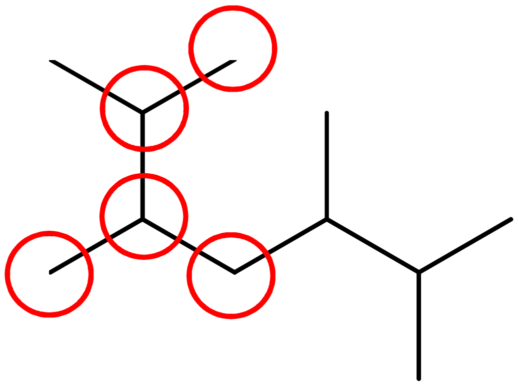
$\longleftarrow$ frequency

2. For compound **A**, after underwent a radical reaction, how many kinds of monochlorination product would form? (5 point)

(A) 3 (B) 4 (C) 5 (D) 8 (E) 10



A



A

3. Which statement is true for “a proton is upfield”? (5 point)

(A) it has more splitting

(B) it has less splitting

(C) it connects to high electronegative atom

(D) it’s peak shown at high frequency

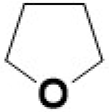
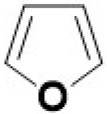
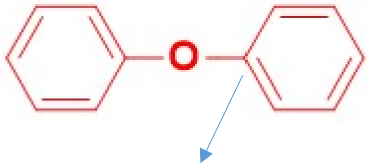
(E) it’s peak shown at low frequency

protons in electron-poor environments	protons in electron-dense environments
deshielded protons	shielded protons
downfield	upfield
high frequency	low frequency
large δ values	small δ values

$\longleftarrow$ δ ppm

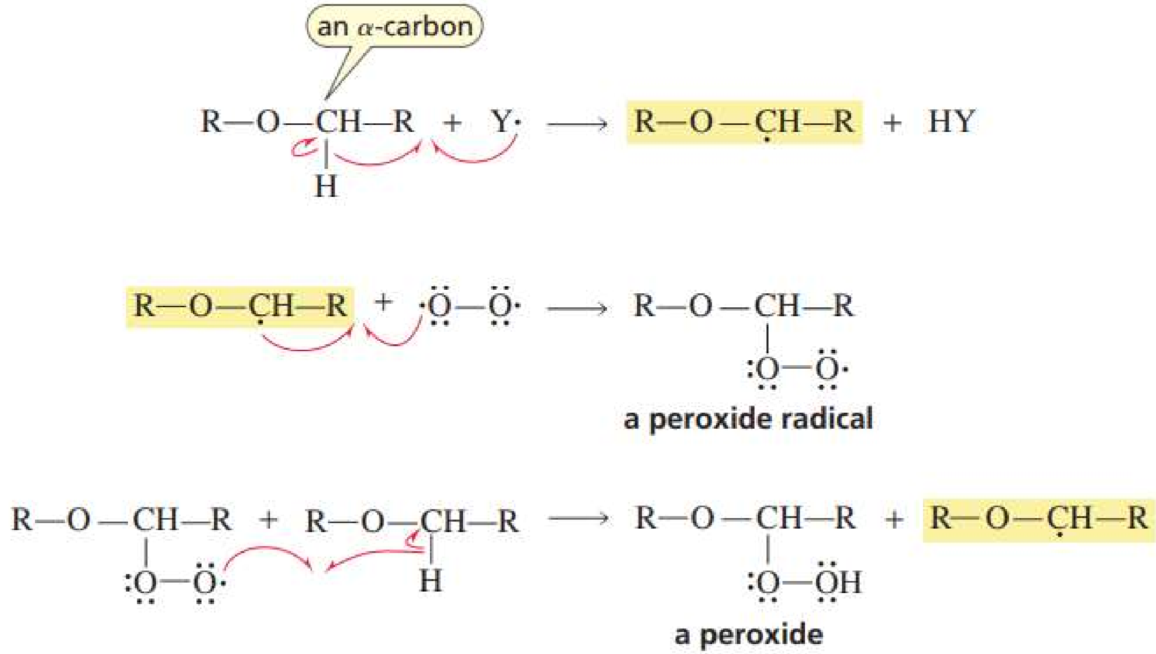
$\longleftarrow$ frequency

4. Which of following compound is least apt to form a peroxide? (5 point)

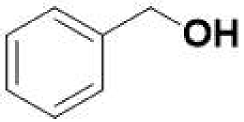
(A)  (B)  (C)  (D)  (E) tert-butyl methyl ether

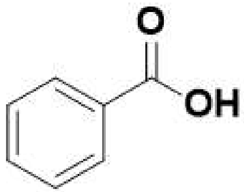
No proton

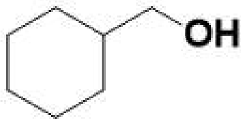
MECHANISM FOR PEROXIDE FORMATION

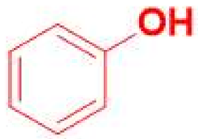


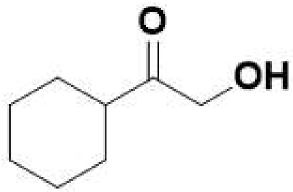
5. Which compound produced the IR spectrum shown below? (5 point)

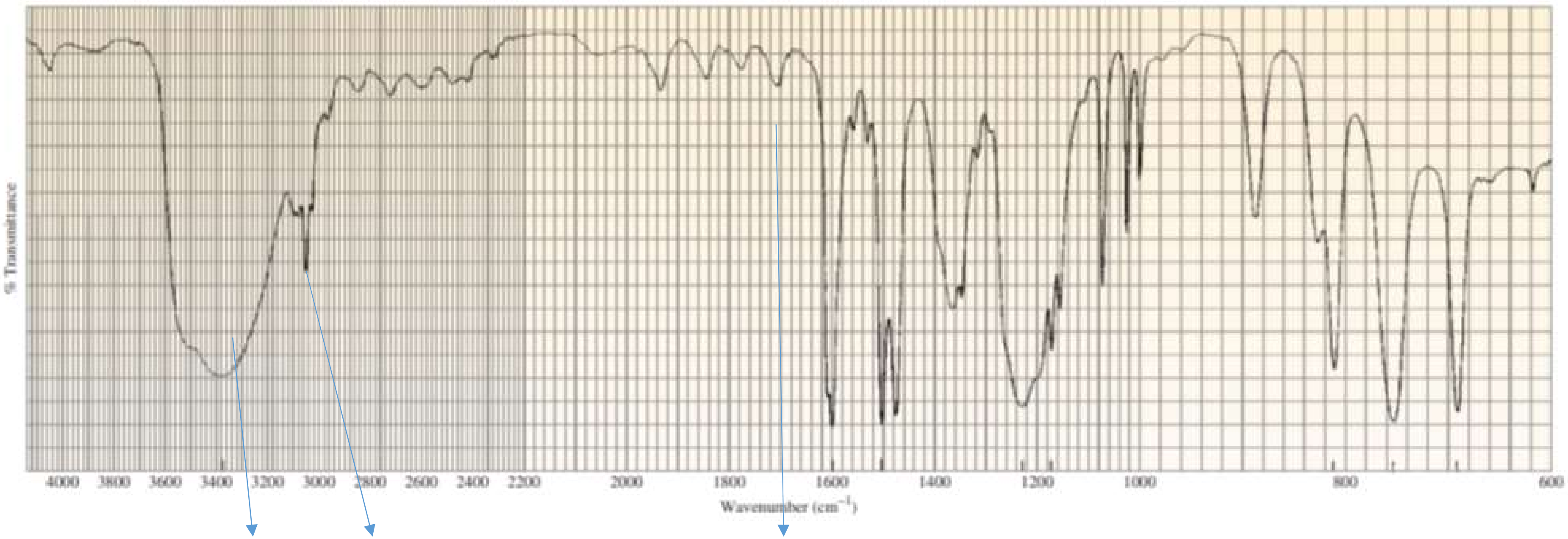
(A) 

(B) 

(C) 

(D) 

(E) 



O-H

>3000 cm^{-1}
No C^{sp3}-H

No large 1700 cm^{-1}
No carbonyl

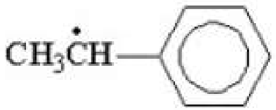
6. Which of the following is the most stable radical? (5 point)

I. $CH_2{=}\dot{C}H$

II. $CH_2{=}CHCH_2\dot{C}H_2$

III. $CH_3\dot{C}HCH_3$

IV. $CH_3\dot{C}H_2$

V. 

(A) I (B) II (C) III (D) IV (E) V

The Stability of Allylic and Benzylic Radicals

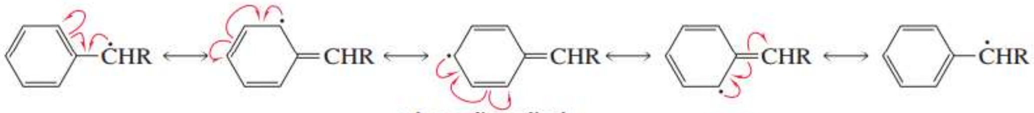
An **allylic radical** has an unpaired electron on an allylic carbon and, like an allylic cation, has two resonance contributors (Section 8.7).

$$R\dot{C}H-CH{=}CH_2 \longleftrightarrow RCH{=}CH-\dot{C}H_2$$

an allylic radical

Electron delocalization increases the stability of a molecule.

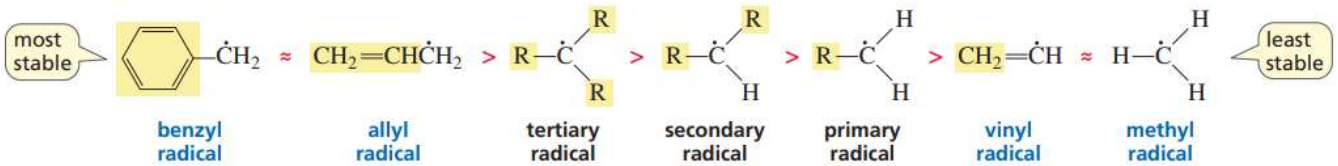
A **benzylic radical** has an unpaired electron on a benzylic carbon and, like a benzylic cation, has five resonance contributors (Section 8.7).



a benzylic radical

Because electron delocalization stabilizes a molecule (Section 8.6), allyl and benzyl radicals are more stable than other primary radicals. They are even more stable than tertiary radicals.

relative stabilities of radicals



7. Regarding the use of Hammond Postulate to explain why free radical brominations are more selective than free radical chlorinations, which of the following statement is not correct? (5 point)

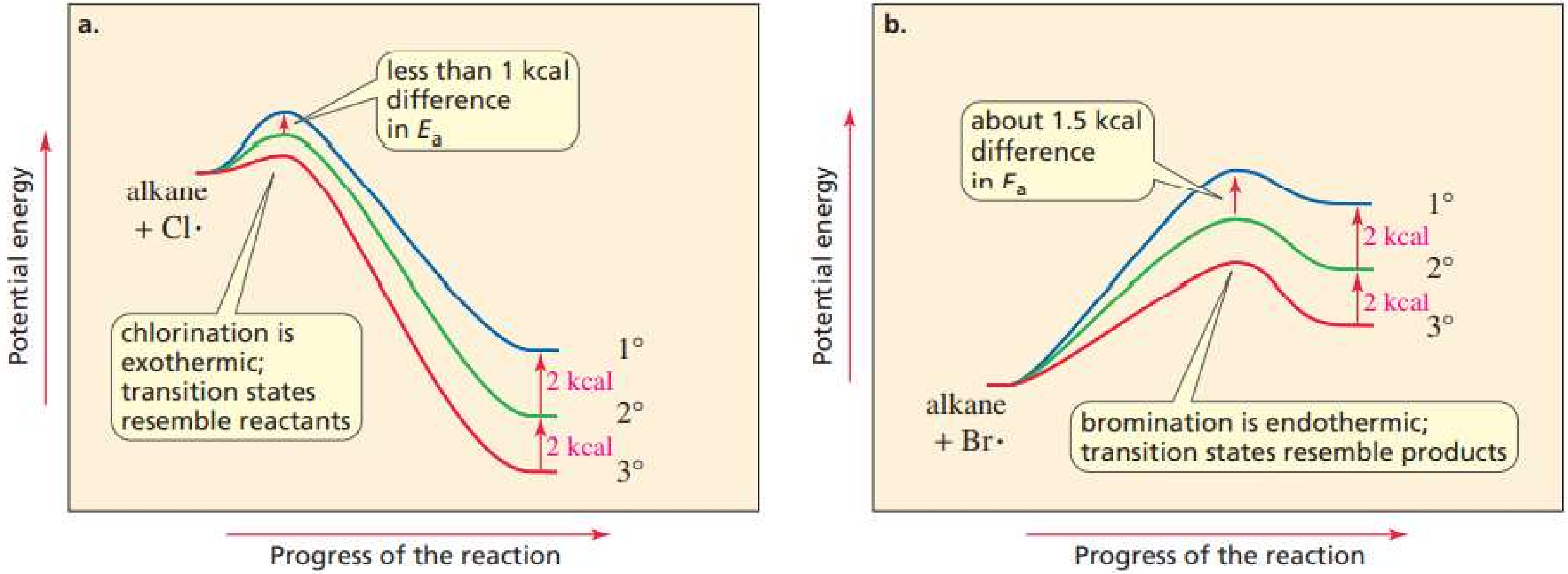
(A) The first propagation step in free radical bromination is endothermic.

(B) The first propagation step in free radical chlorination is exothermic.

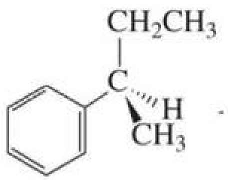
(C) The transition state for the bromination is product-like (ie, radical-like).

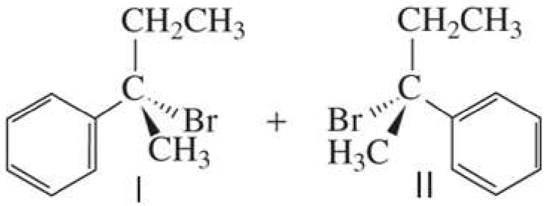
(D) The transition state for the chlorination is product-like (ie, radical-like).

(E) The stability of the intermediate radical in the bromination determines the bromination selectivity.



8. A sample of (*R*)-2-phenylbutane, reacts with Br_2 in the presence of light, and all the products having the formula $C_9H_{13}Br$ were isolated. Two possible isomers are shown below:





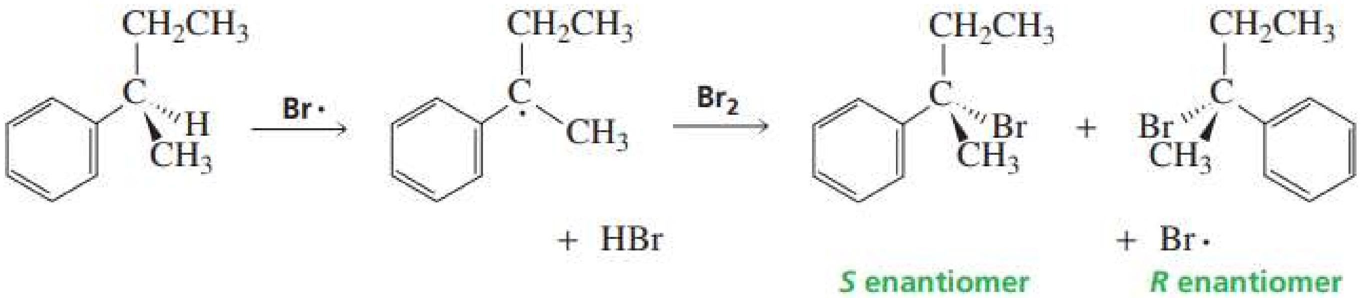
Of these: (5 point)

(A) only I was formed. (B) both I and II were formed in equal amounts.

(C) neither I nor II was formed. (D) only II was formed.

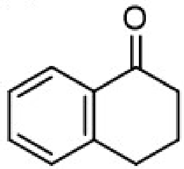
(E) both I and II were formed in unequal amounts.

Identical amounts of the *R* and *S* enantiomers are also obtained if a hydrogen bonded to an asymmetric center is substituted by a halogen. Breaking the bond to the asymmetric center destroys the configuration at the asymmetric center and forms a planar radical intermediate. The incoming halogen has equal access to both sides of the plane, so a racemic mixture is formed.

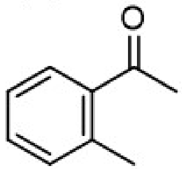


9. Which of the following compounds does not possess the same chromophore? (5 point)

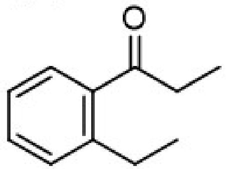
(A)



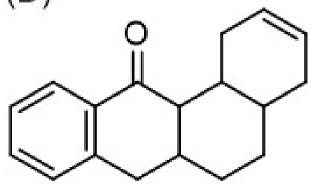
(B)



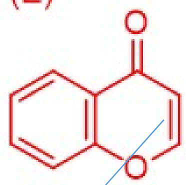
(C)



(D)



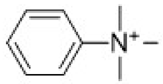
(E)



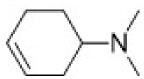
Also can resonance

10. Rank a set of compounds in order of decreasing λ_{max}: (5 point)

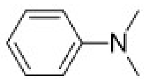
(a)



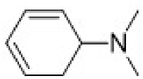
(b)



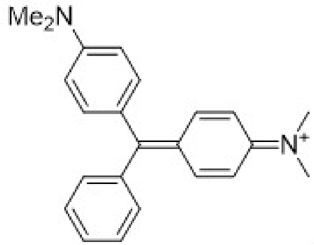
(c)



(d)

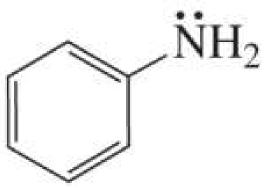


(e)

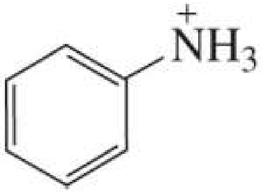


(A) e > c > a > d > b (B) c > e > a > d > b (C) e > d > a > c > b (A) a > e > c > d > b

(E) d > e > a > c > b



aniline
280 nm



anilinium ion
254 nm

30-40 nm red shift w/ one extra C=C

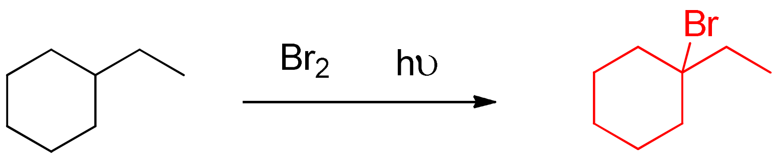
Table 14.6 Values of λ_{max} and ε for Ethylene and Conjugated Polyenes

Compound	λ_{max} (nm)	ε (M^{-1} cm^{-1})
$H_2C{=}CH_2$	165	15,000
	217	21,000
	256	50,000
	290	85,000
	334	125,000
	364	138,000

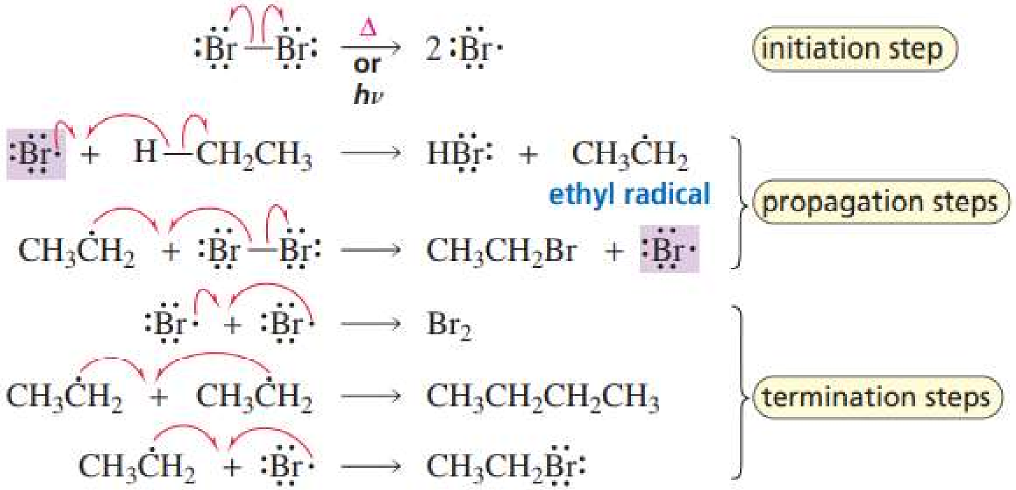
Conjugation ↗; λ_{max} and ε ↗

11. Complete each of following reactions by providing **major product**.

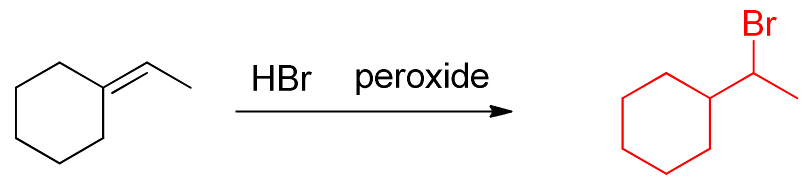
(a) (5 point)

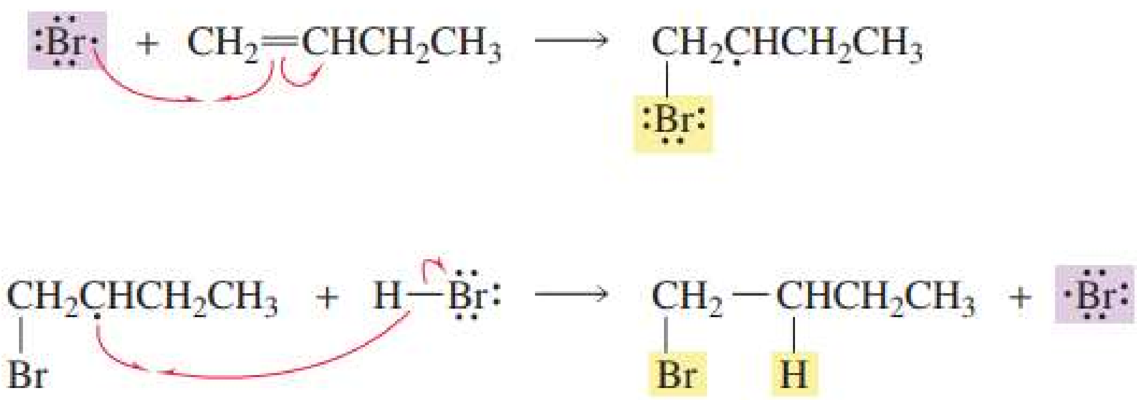


MECHANISM FOR THE MONOBROMINATION OF ETHANE

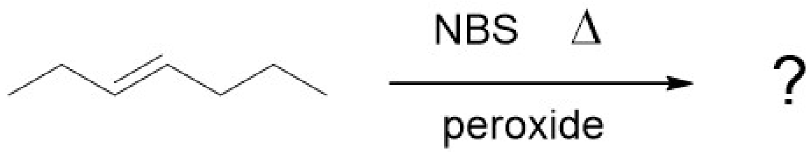


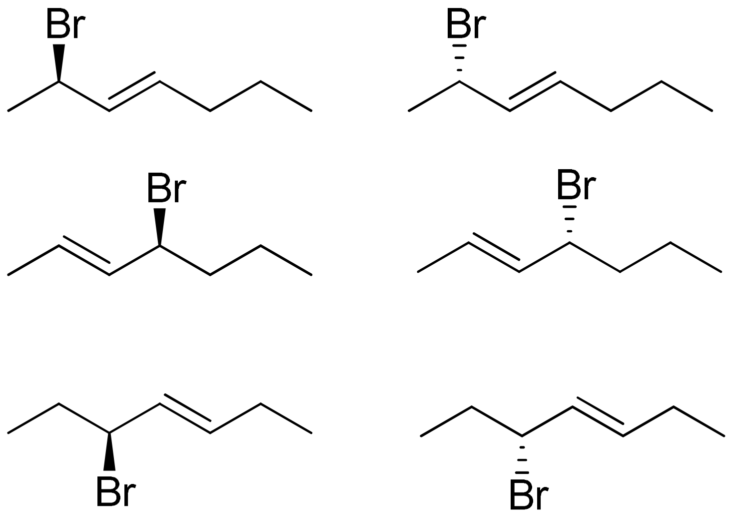
(b) (5 point)


HBr peroxide
Br


:Br· + CH2=CHCH2CH3 ⟶ CH2CHCH2CH3
:Br:
CH2CHCH2CH3 + H—Br: ⟶ CH2—CHCH2CH3 + ·Br:
Br
Br H

(c) provide **all product** include **stereoisomer** (12 point)



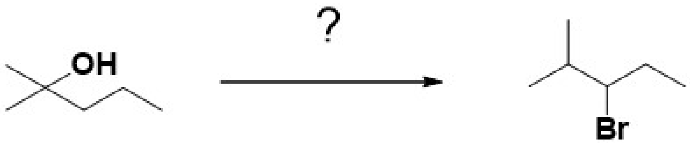


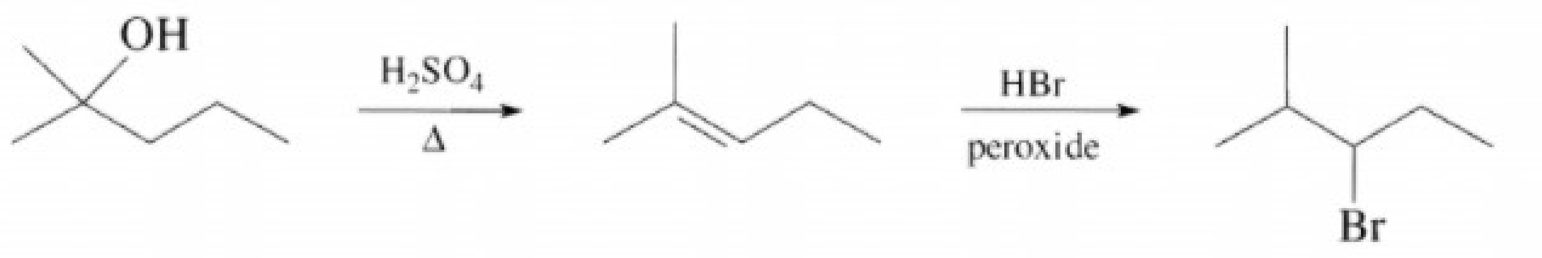
*bromination on C3 and C5 is same product

Total 6 kinds of product

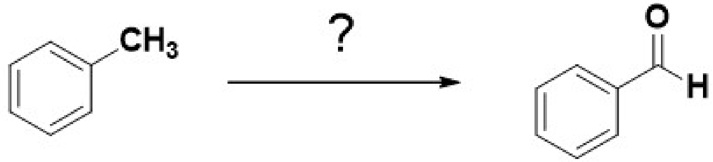
12. Design a multi-step synthesis to show how each compounds could be prepared from the given starting material. Show all necessary reagent(s) and also **intermediate.**

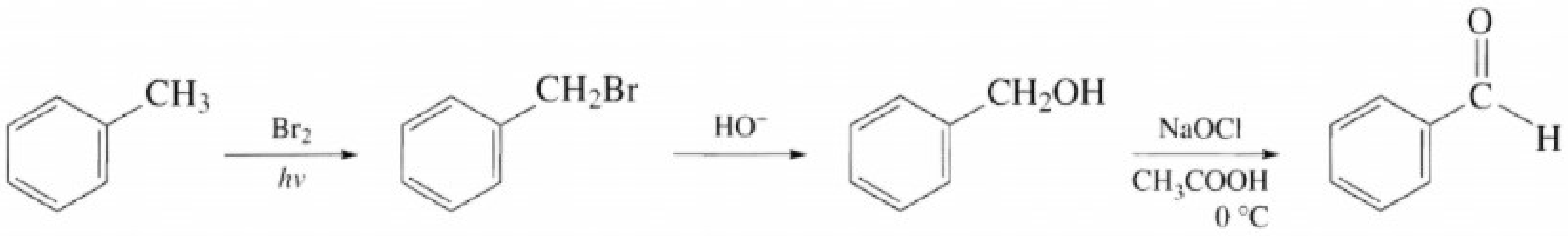
(a) (10 point)



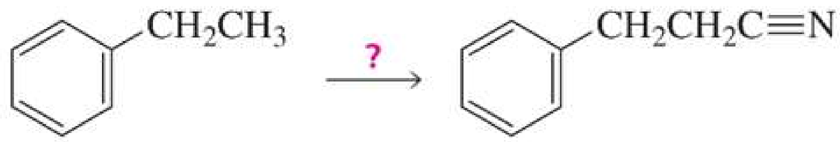


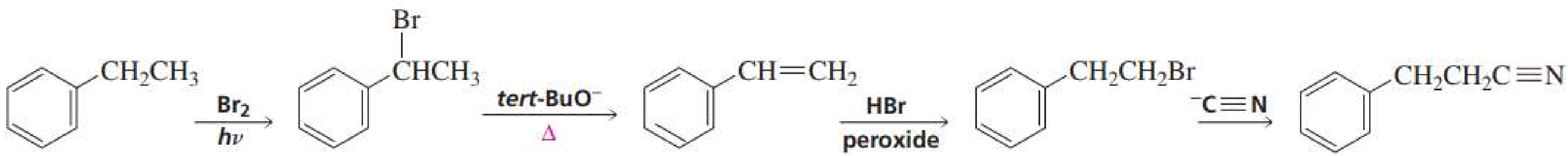
(b) (10 point)



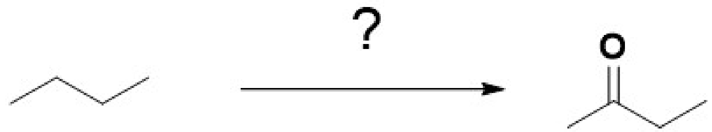


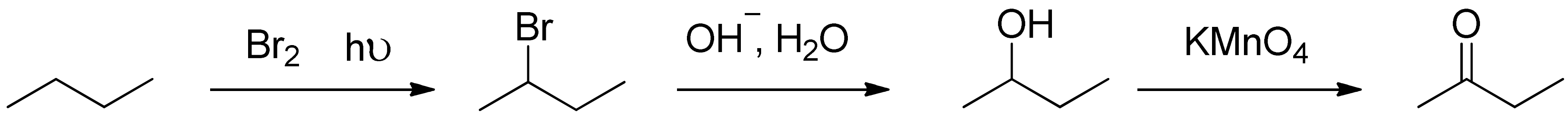
(c) (10 point)


CH2CH3
?
CH2CH2C≡N

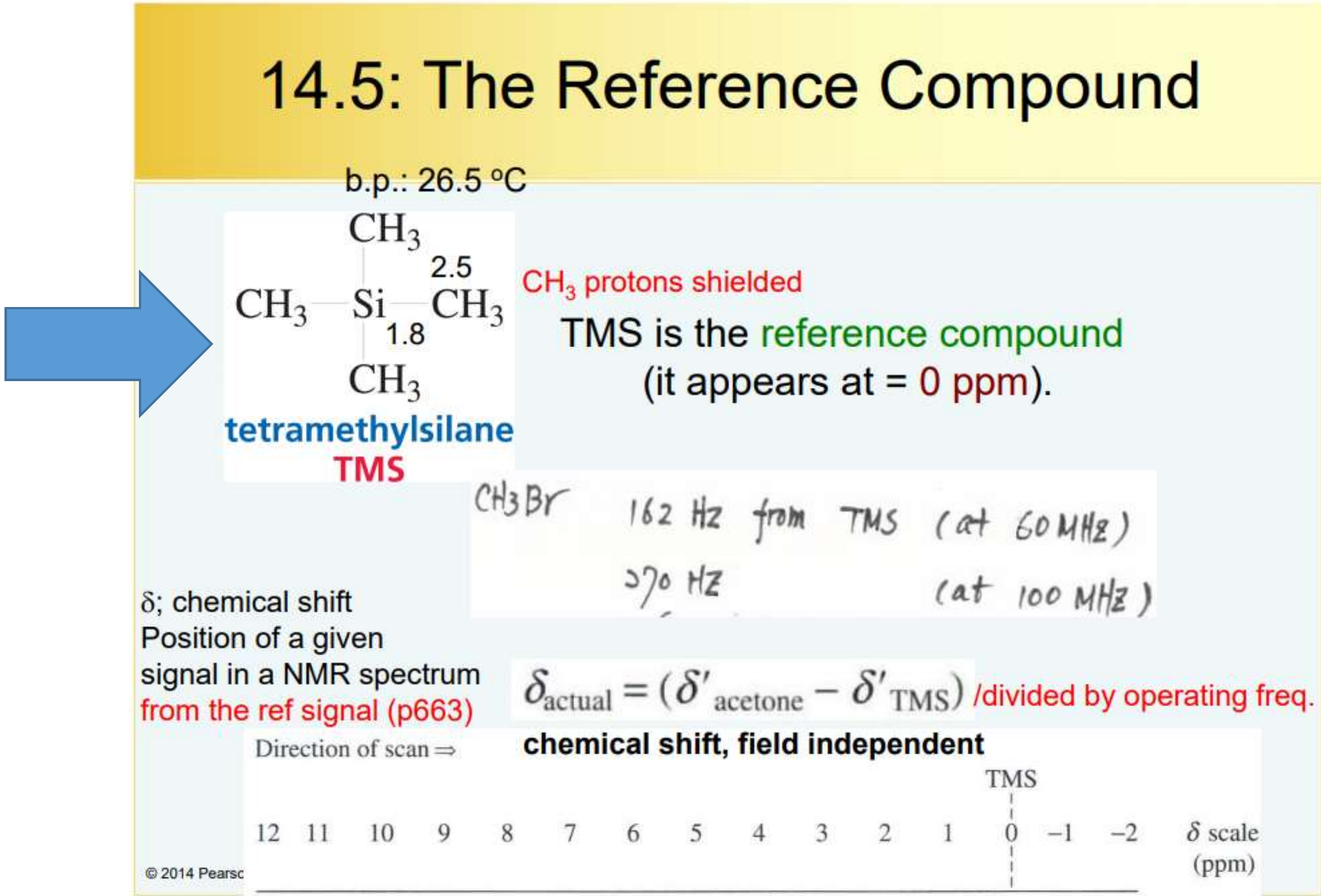

CH2CH3
Br2
hν
Br
CHCH3
tert-BuO⁻
Δ
CH=CH2
HBr
peroxide
CH2CH2Br
⁻C≡N
CH2CH2C≡N

(d) (10 point)

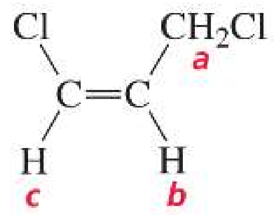


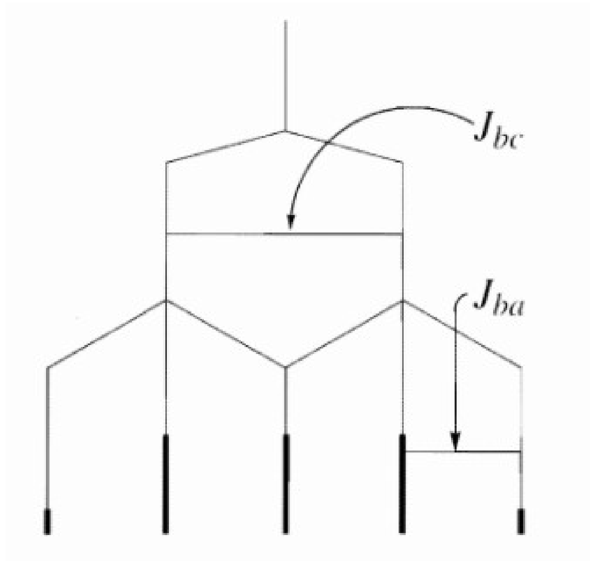


13. Which compound would be the reference in ^{1}H NMR (that is, show a peak at 0 ppm)? Please provide its name and structure. (5 point)



14. Draw a splitting diagram for the H_b proton if $J_{bc} = 10$ and $J_{ba} = 5$, then show the integral ratio of each peak. (10 point)

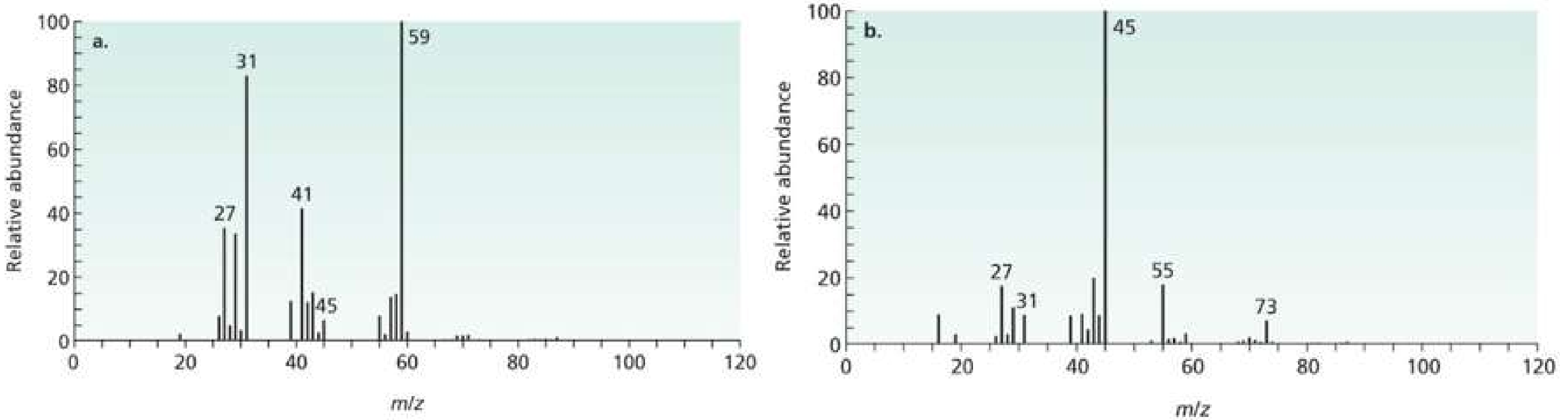


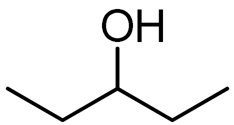


1 : 2 : 2 : 2 : 1

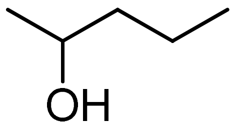
(1+1)

15. The reaction of (Z)-2-pentene with water and a trace of H_2SO_4 forms two products. Identify the products from their mass spectra. (9 point)



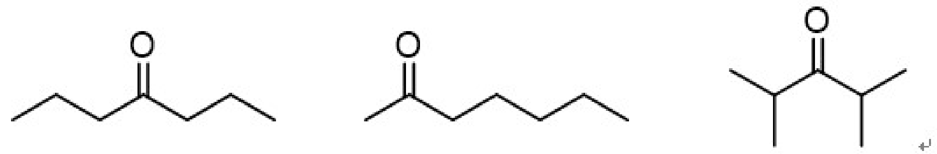


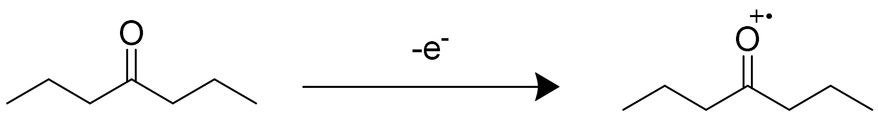
A

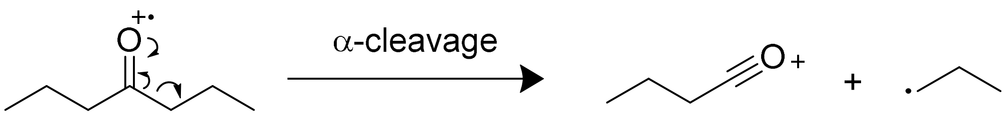


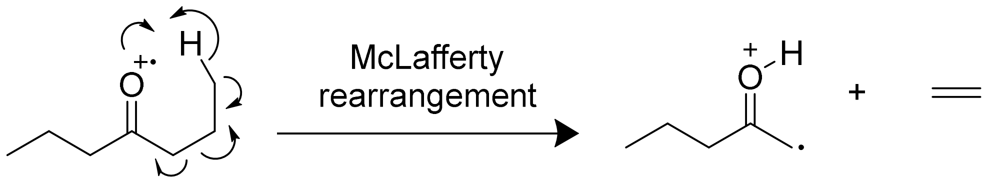
B

16. Draw the mechanism for formation of the fragments you would expect to see in the mass spectrum of each of the following compounds: (18 point)

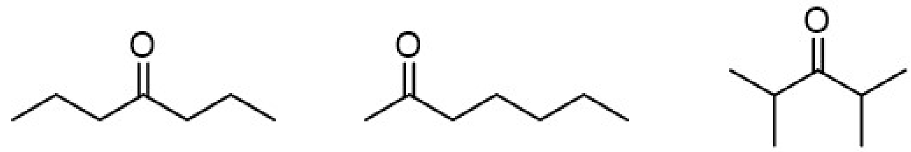


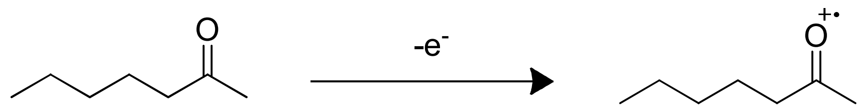


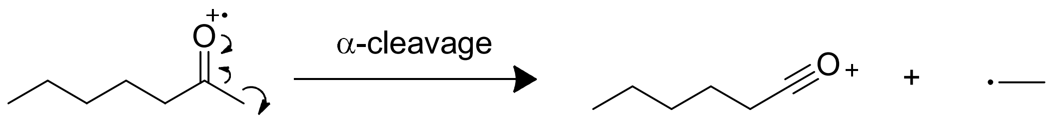


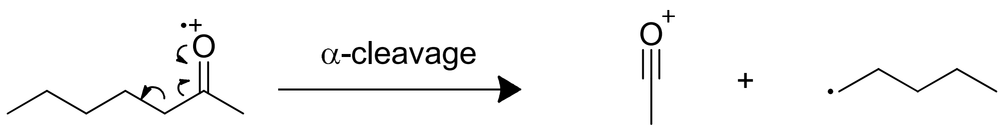


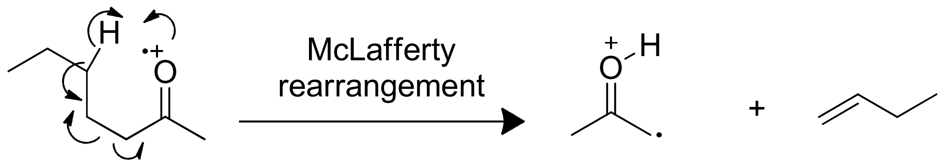
16. Draw the mechanism for formation of the fragments you would expect to see in the mass spectrum of each of the following compounds: (18 point)



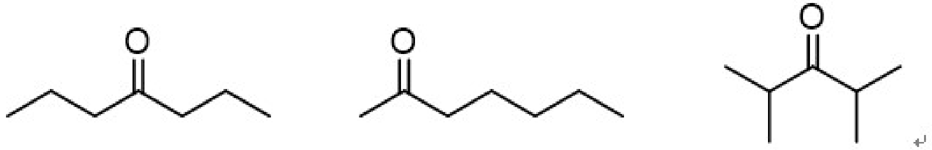


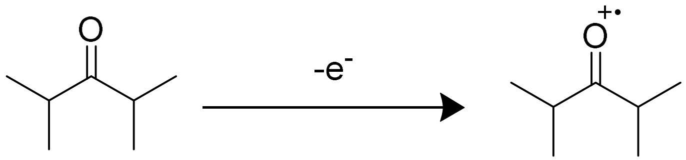


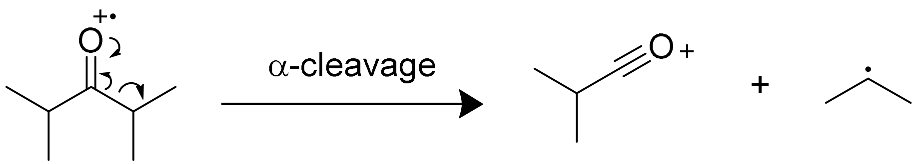




16. Draw the mechanism for formation of the fragments you would expect to see in the mass spectrum of each of the following compounds: (18 point)







17. If a compound shows a signal at 4.0 ppm in 300 MHz ^{1}H NMR spectrum, where does this signal appear in 500 MHz ^{1}H NMR spectrum? In 500 MHz ^{1}H NMR spectrum, what is frequency difference compare to the signal at 0.0 ppm? (5 point each)

PROBLEM 9 ♦

a. If two signals differ by 1.5 ppm in a 300 MHz spectrometer, by how much do they differ in a 500 MHz spectrometer?

b. If two signals differ by 90 Hz in a 300 MHz spectrometer, by how much do they differ in a 500 MHz spectrometer?

b.
$$\frac{\text{Hz}}{\text{MHz}} = \text{ppm}$$
$$\frac{90\ \text{Hz}}{300\ \text{MHz}} = 0.3\ \text{ppm}$$
$$\frac{x\ \text{Hz}}{500\ \text{MHz}} = 0.3\ \text{ppm}$$
$$x = 150\ \text{Hz}$$
They differ by 150 Hz.

>> 4.0 ppm, difference = 4.0 x 500 = 2000 (Hz)

18. Predict the relative intensities of the molecular ion peak (M^+), M+2 peak, M+4 peak, and M+6 peak in mass spectrum for a compound which contain 3 chlorine atoms. (8 point)

For one chlorine, M/M+2 = 3/1

For three chlorine,

$$M^+\ peak: (\frac{3}{4})^3 = \frac{27}{64}$$

$$M + 2\ peak:\ C_1^3(\frac{3}{4})^2(\frac{1}{4})^1 = 3 \times \frac{9}{64} = \frac{27}{64}$$

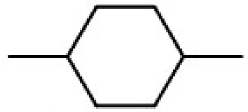
$$M + 4\ peak:\ C_2^3(\frac{3}{4})^1(\frac{1}{4})^2 = 3 \times \frac{3}{64} = \frac{9}{64}$$

$$M + 6\ peak:\ (\frac{1}{4})^3 = \frac{1}{64}$$

$$\Longrightarrow 27 : 27 : 9 : 1$$

*驗算: 分子相加 = 64

19. The following compound will undergo a chlorine radical reaction. Please predict all the monochlorination product(s) and the ratio of each product. (9 point each)

(a)  (b) 

Primary	Secondary	Tertiary
1.0	3.8	5.0

▲relative rates of alkyl radical formation by a chlorine radical

Now we see that both *probability* (the number of hydrogens that can be removed that lead to the formation of a particular product) and *reactivity* (the relative rate at which a particular radical is formed) must be taken into account when determining the relative amounts of the products obtained from the radical chlorination of an alkane.

relative amount of 1-chlorobutane

number of hydrogens × relative reactivity

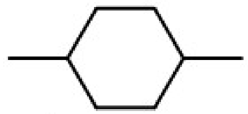
$6 \times 1.0 = 6.0$

relative amount of 2-chlorobutane

number of hydrogens × relative reactivity

$4 \times 3.8 = 15$

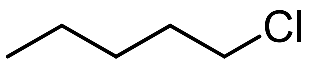
19. The following compound will undergo a chlorine radical reaction. Please predict all the monochlorination product(s) and the ratio of each product. (9 point each)

(a)  (b) 

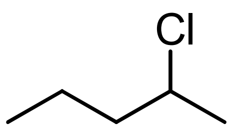
Primary	Secondary	Tertiary
1.0	3.8	5.0

▲relative rates of alkyl radical formation by a chlorine radical

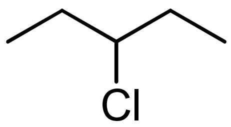
(a)



$6 \times 1.0 = 6.0, \quad \frac{6.0}{28.8} = 20.8\%$



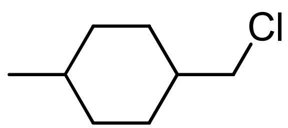
$4 \times 3.8 = 15.2, \quad \frac{15.2}{28.8} = 52.8\%$



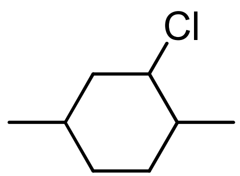
$2 \times 3.8 = 7.6, \quad \frac{7.6}{28.8} = 26.4\%$

Total = 28.8

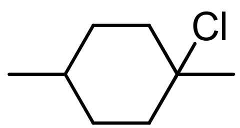
(b)



$6 \times 1.0 = 6.0, \quad \frac{6.0}{46.4} = 12.9\%$



$8 \times 3.8 = 30.4, \quad \frac{30.4}{46.4} = 65.5\%$



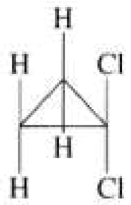
$2 \times 5.0 = 10.0, \quad \frac{10.0}{46.4} = 21.6\%$

Total = 46.4

20. Provide all structures of isomers for the compound “dichlorocyclopropane”, then predict the sets of signal(s) would be shown in ^{1}H NMR spectrum. (15 point)

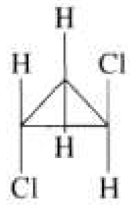
Prob. 6:

a.



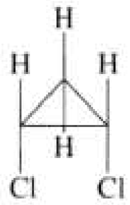
All the Hs are equivalent.

b.



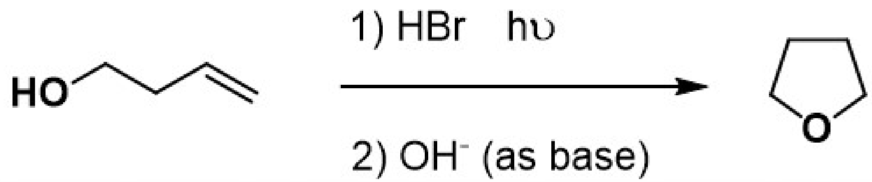
The Hs attached to the front of the molecule are equivalent, and the methylene Hs are equivalent.

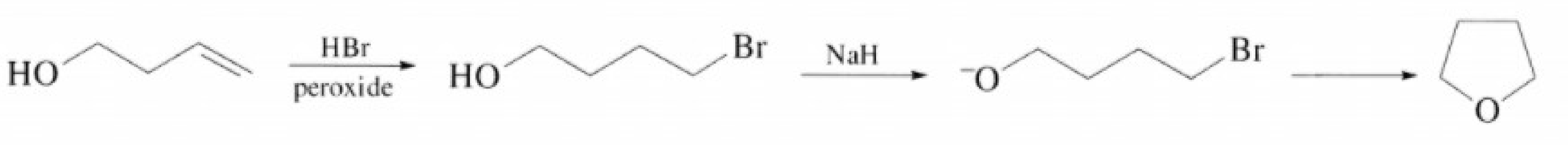
c.

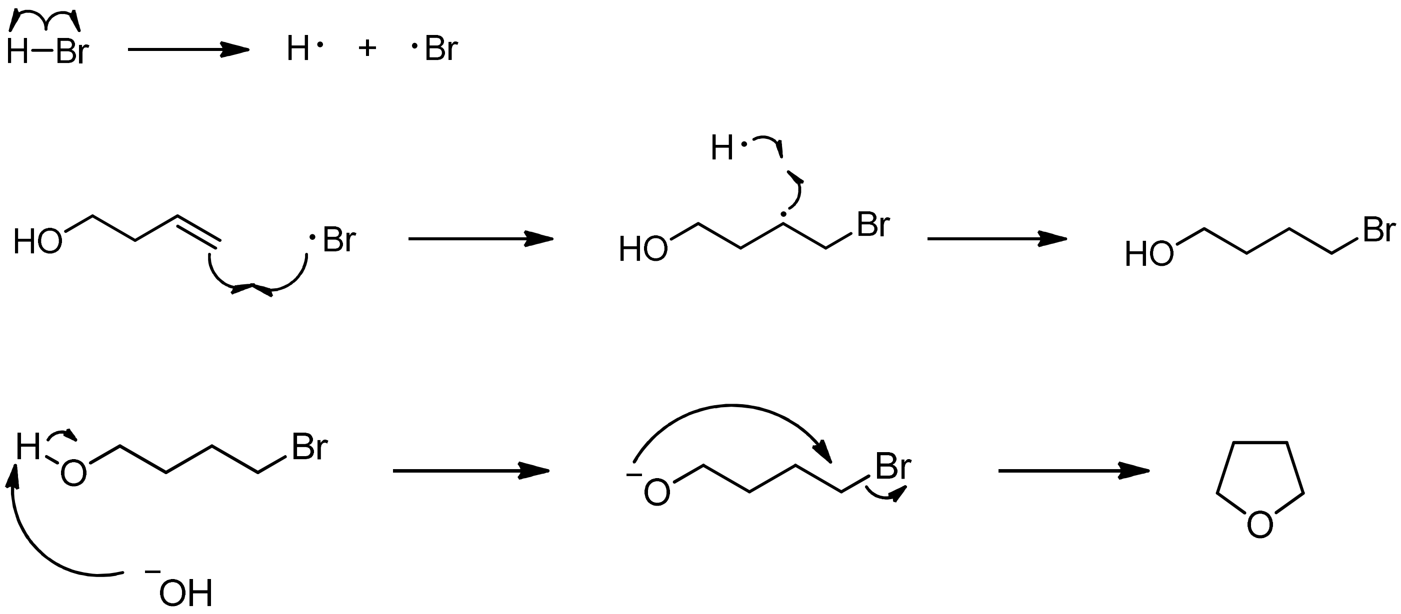


The Hs attached to the front of the molecule are equivalent, and the methylene Hs are not equivalent.

21. Propose a reasonable mechanism for the following reaction. (15 point)

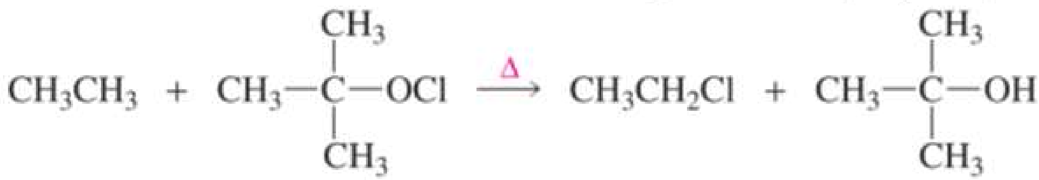






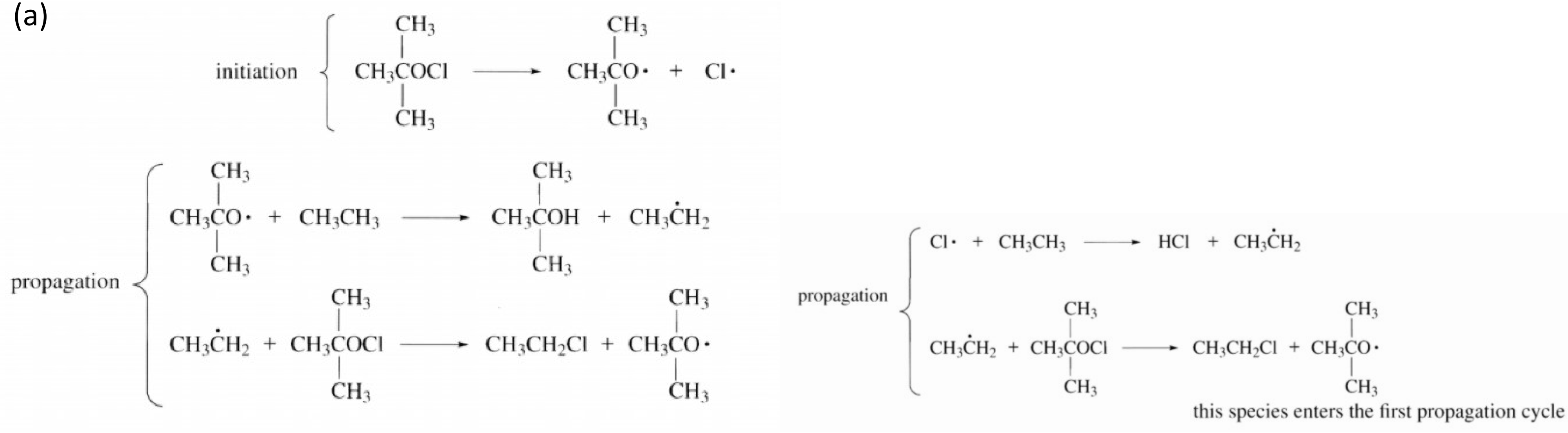
22.

(a) Propose a reasonable mechanism for the following reaction. (15 point)



(b) Predict the byproducts (副產物) and describe how they are formed. (as much as possible, assume that once product form, it will not react with a radical second time) (10 point)

(a)



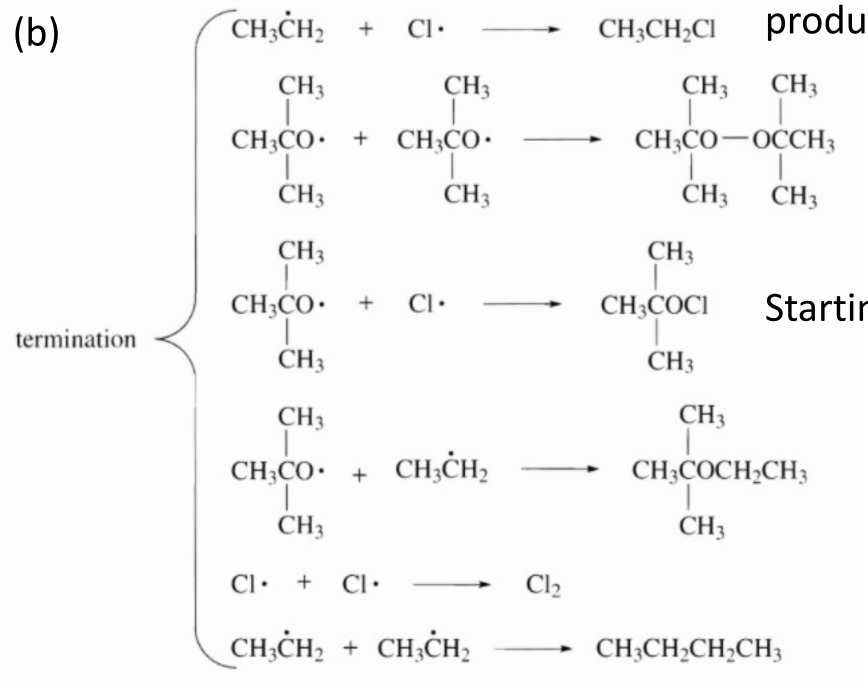
22.

(a) Propose a reasonable mechanism for the following reaction. (15 point)

$$CH_3CH_3 \ + \ CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-OCl \ \xrightarrow{\Delta} \ CH_3CH_2Cl \ + \ CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-OH$$

(b) Predict the byproducts (副產物) and describe how they are formed. (as much as possible, assume that once product form, it will not react with a radical second time) (10 point)

(b)



product

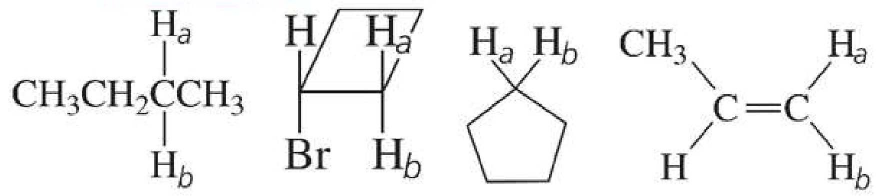
Starting material

H-Cl would also form

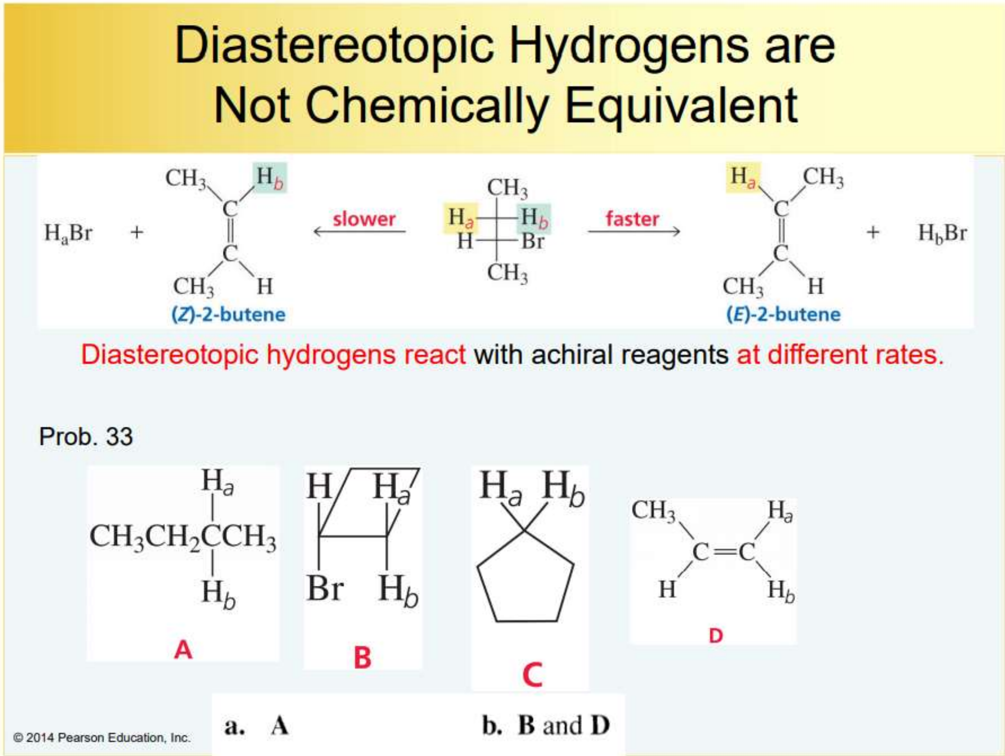
23. For the following compounds,

(a) which pair of hydrogens (H_a and H_b) are enantiotopic hudrogens? (5 point)

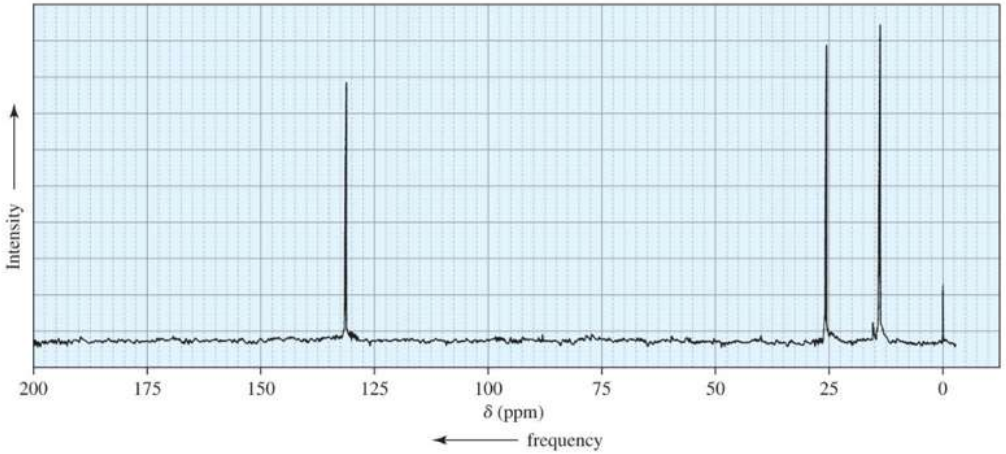
(b) Which pairs are diastereotopic hydrogens? (5 point)



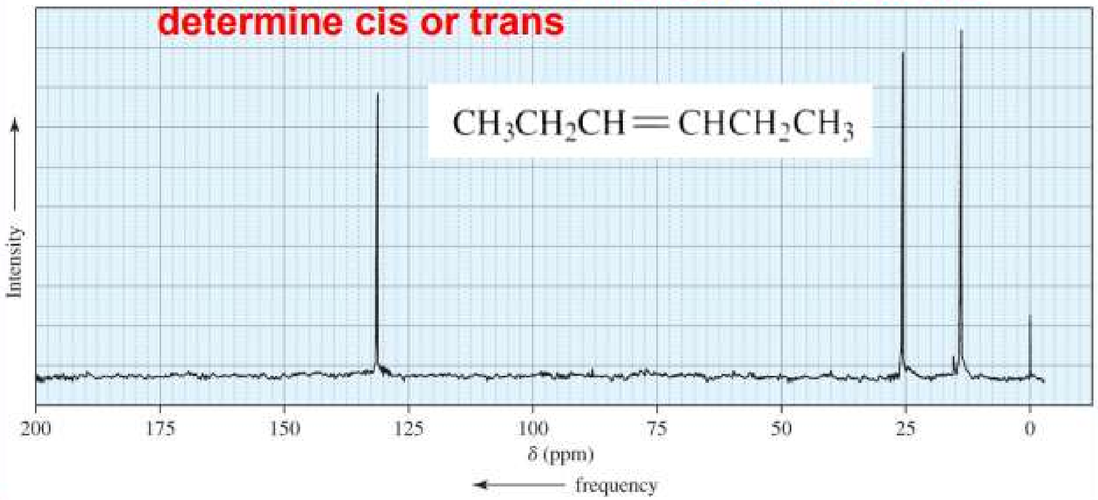
A B C D



24. Identify the following compound from its molecular formula (C_6H_{12}) and its ^{13}C NMR spectrum. (10 point)

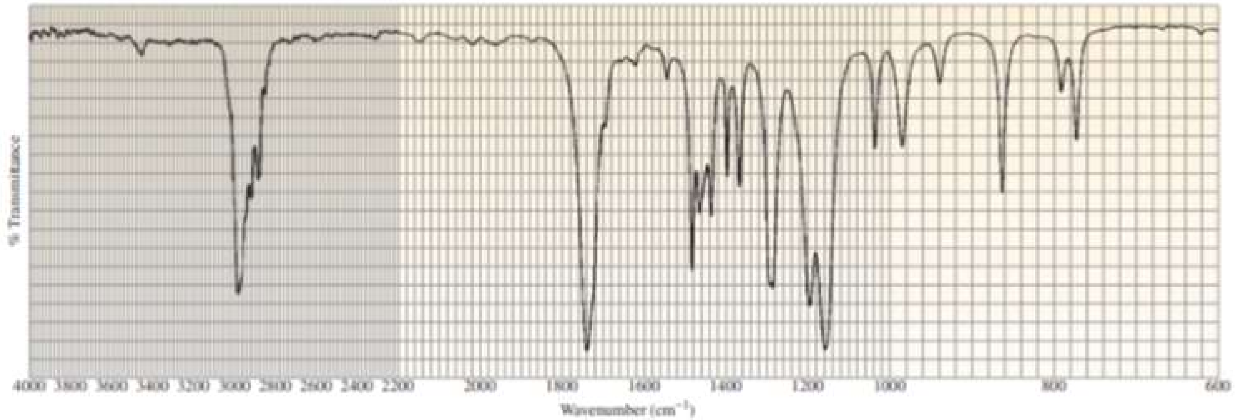


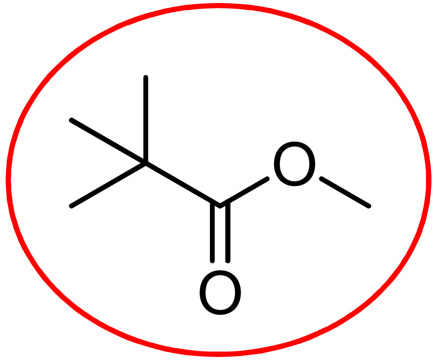
d. C_6H_{12} : deg. of unsat.: 1; C=C and sym.; ^1H NMR to determine cis or trans

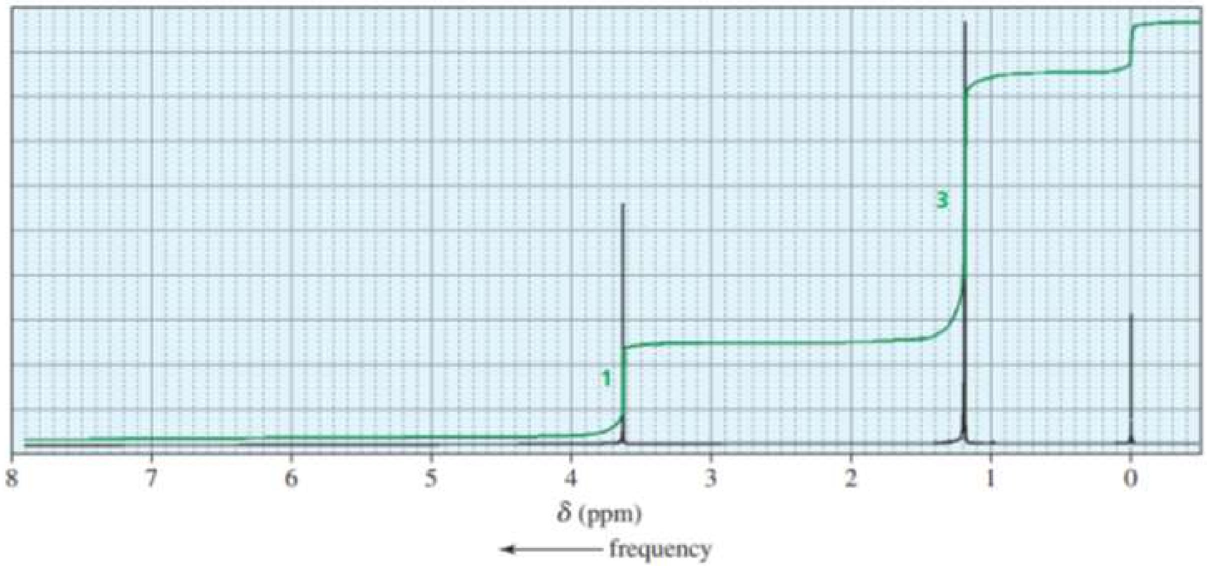


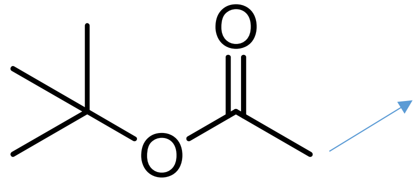
25. Please identify each compound by the following spectrum. (10 point each)

(a) $C_6H_{12}O_2$ (IR and ^1H NMR spectrum)



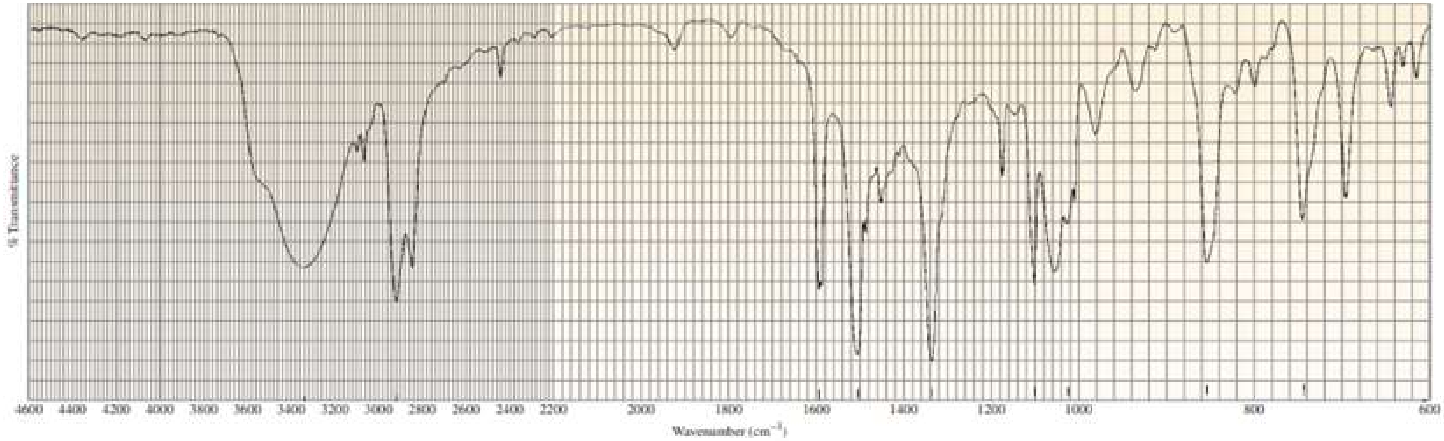


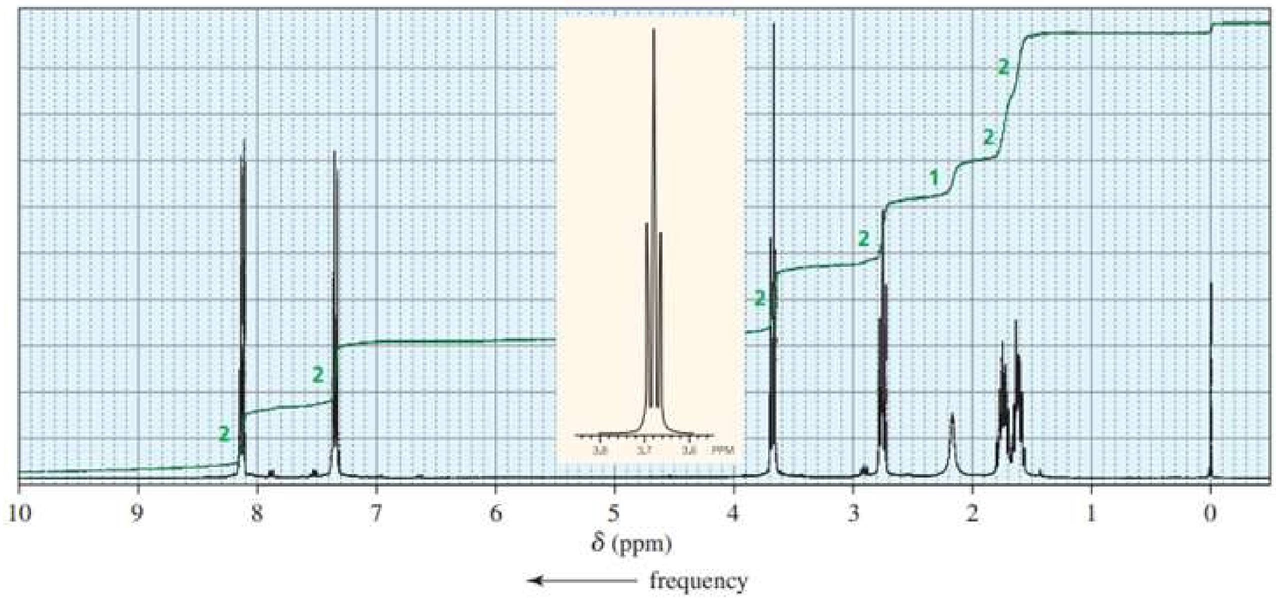


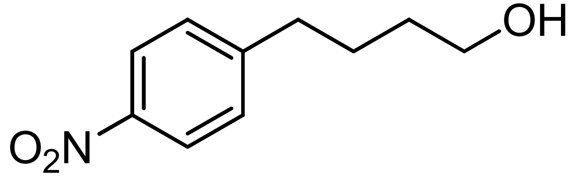


Peak will show at ~2.0 ppm

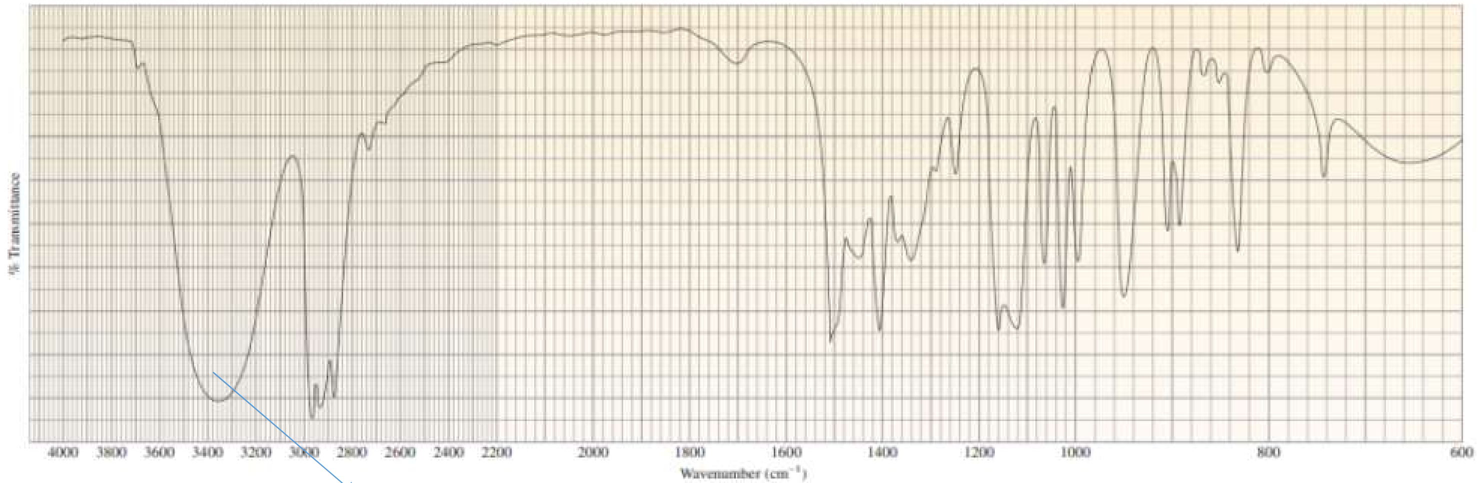
(b) $C_{10}H_{13}NO_3$ (IR and ^1H NMR spectrum)



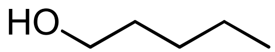


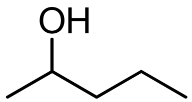


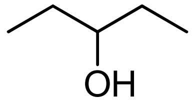
26. The IR spectrum of compound **A** with a molecular formula of $C_5H_{12}O$ is shown below. Compound **A** is oxidized to give compound **B**, a ketone with a molecular formula of $C_5H_{10}O$. When compound **A** is heated with H_2SO_4, compounds **C** and **D** are obtained. Much more **D** is obtained than **C**. Reaction of compound **C** with O_3, followed by treatment with dimethyl sulfide, gives two products: formaldehyde and compound **E**, with a molecular formula of C_4H_8O. Reaction of compound **D** with O_3, followed by treatment with dimethyl sulfide, gives two products: compound **F**, with a molecular formula of C_3H_6O, and compound **G**, with a molecular formula of C_2H_4O. What are the structures of compounds **A** through **G**? (hint: if alkene is treated with ozone followed by DMS, two carbonyl products will obtain) (35 point)

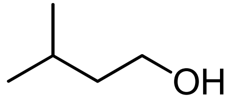


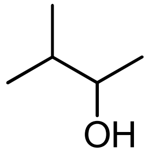
O-H > alcohol not ether

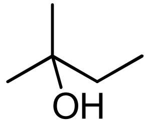

1°

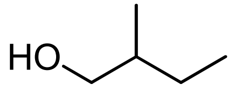

2°

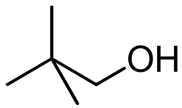

2°


1°


2°

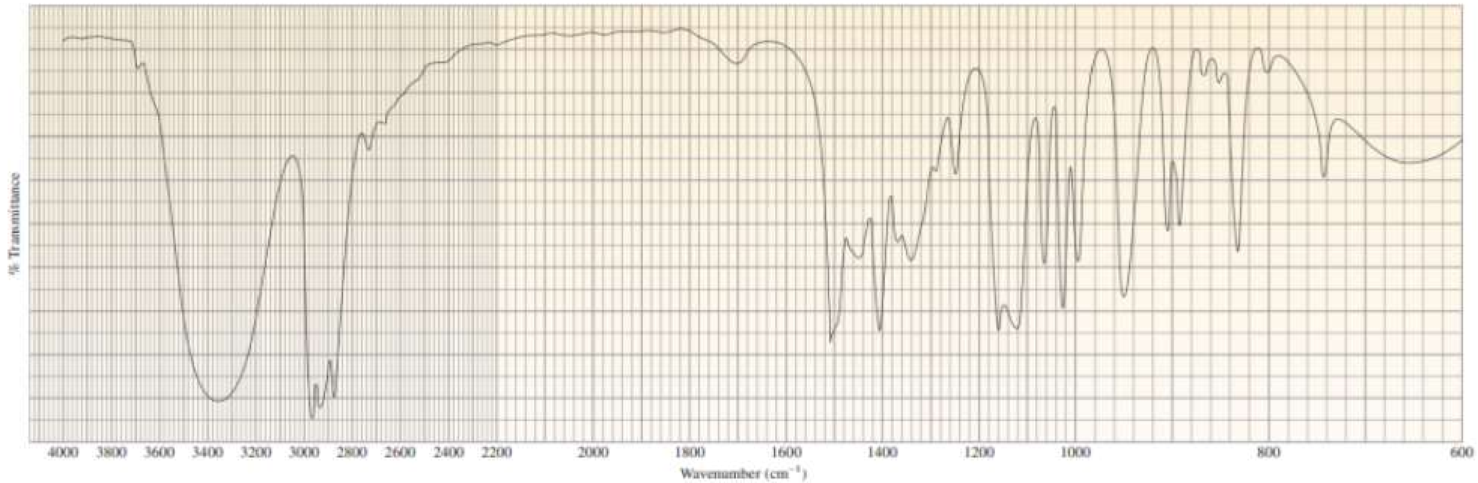

3°

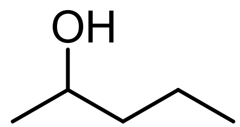

1°

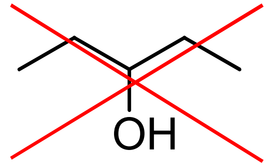

1°

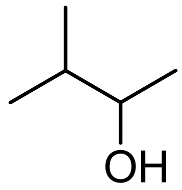
Oxidate to ketone > 2°

26. The IR spectrum of compound **A** with a molecular formula of $C_5H_{12}O$ is shown below. Compound **A** is oxidized to give compound **B**, a ketone with a molecular formula of $C_5H_{10}O$. When compound **A** is heated with H_2SO_4, compounds **C** and **D** are obtained. Much more **D** is obtained than **C**. Reaction of compound **C** with O_3, followed by treatment with dimethyl sulfide, gives two products: formaldehyde and compound **E**, with a molecular formula of C_4H_8O. Reaction of compound **D** with O_3, followed by treatment with dimethyl sulfide, gives two products: compound **F**, with a molecular formula of C_3H_6O, and compound **G**, with a molecular formula of C_2H_4O. What are the structures of compounds **A** through **G**? (hint: if alkene is treated with ozone followed by DMS, two carbonyl products will obtain) (35 point)



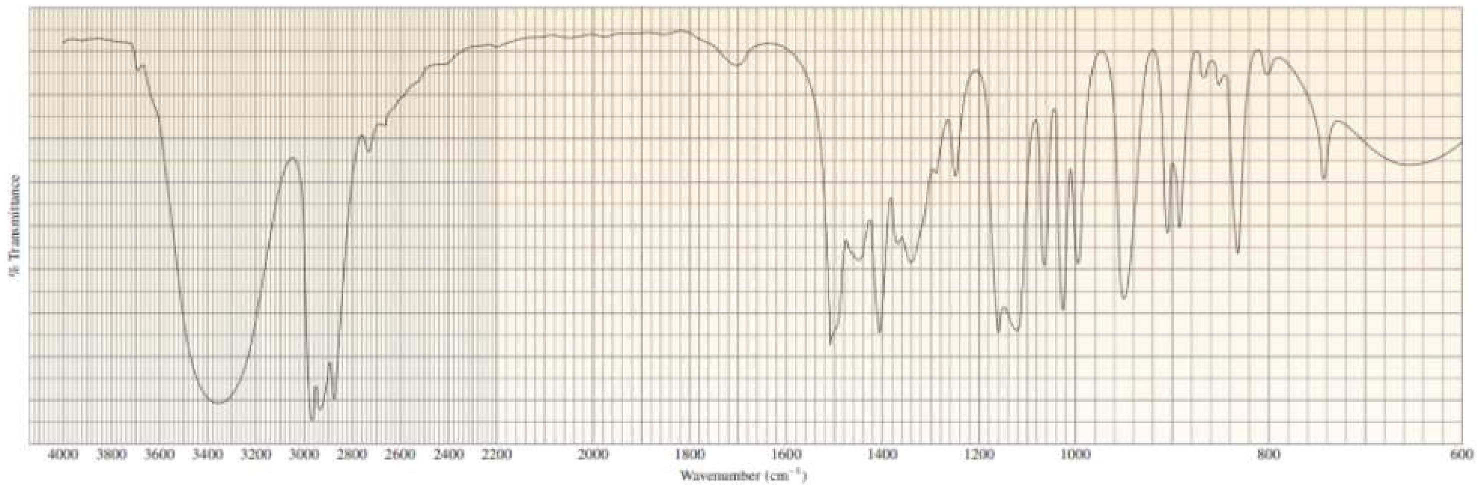


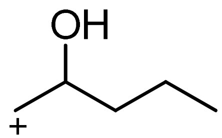




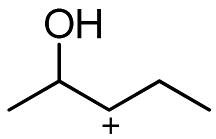
Treat with H_2SO_4 to get two product
> asymetric

26. The IR spectrum of compound **A** with a molecular formula of $C_5H_{12}O$ is shown below. Compound **A** is oxidized to give compound **B**, a ketone with a molecular formula of $C_5H_{10}O$. When compound **A** is heated with H_2SO_4, compounds **C** and **D** are obtained. Much more **D** is obtained than **C**. Reaction of compound **C** with O_3, followed by treatment with dimethyl sulfide, gives two products: formaldehyde and compound **E**, with a molecular formula of C_4H_8O. Reaction of compound **D** with O_3, followed by treatment with dimethyl sulfide, gives two products: compound **F**, with a molecular formula of C_3H_6O, and compound **G**, with a molecular formula of C_2H_4O. What are the structures of compounds **A** through **G**? (hint: if alkene is treated with ozone followed by DMS, two carbonyl products will obtain) (35 point)

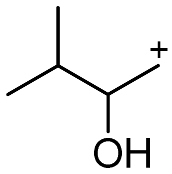




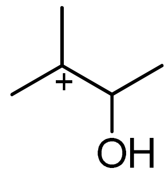
1°



2°



1°

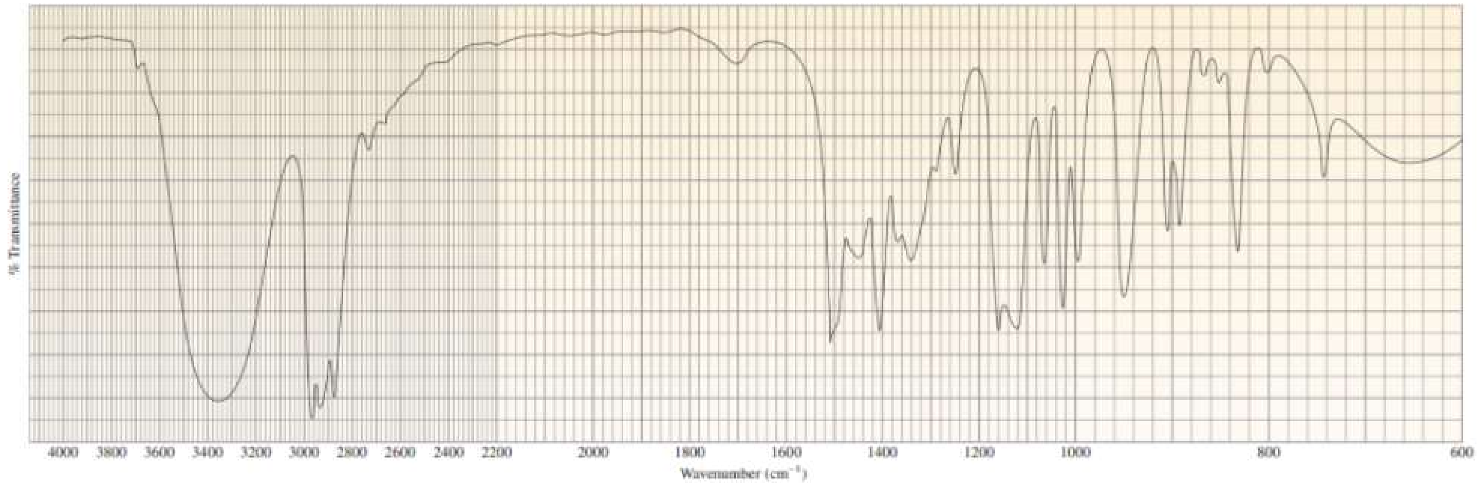


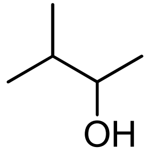
3°

"much more"

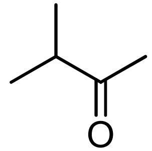
- Higher selective
- Lower one is correct

26. The IR spectrum of compound **A** with a molecular formula of $C_5H_{12}O$ is shown below. Compound **A** is oxidized to give compound **B**, a ketone with a molecular formula of $C_5H_{10}O$. When compound **A** is heated with H_2SO_4, compounds **C** and **D** are obtained. Much more **D** is obtained than **C**. Reaction of compound **C** with O_3, followed by treatment with dimethyl sulfide, gives two products: formaldehyde and compound **E**, with a molecular formula of C_4H_8O. Reaction of compound **D** with O_3, followed by treatment with dimethyl sulfide, gives two products: compound **F**, with a molecular formula of C_3H_6O, and compound **G**, with a molecular formula of C_2H_4O. What are the structures of compounds **A** through **G**? (hint: if alkene is treated with ozone followed by DMS, two carbonyl products will obtain) (35 point)

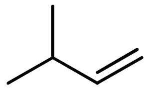




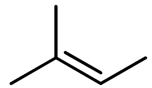
A



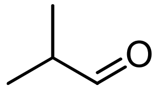
B



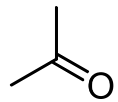
C



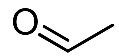
D



E



F



G