UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

FINAL EXAMINATION

CHEMISTRY 351

December 10th 2013 Time: 3 Hours

READ THE INSTRUCTIONS CAREFULLY

PLEASE WRITE YOUR **NAME**, **STUDENT I.D. NUMBER** ON ***BOTH*** **YOUR ANSWER BOOKLET** AND **COMPUTER ANSWER SHEET**.
ENTER **VERSION NUMBER 1** ON THE **COMPUTER ANSWER SHEET**

The examination consists of Parts 1 - 9, each of which should be attempted. Note that some Parts provide you with a choice of questions, *i.e*. answer 4 out of 5. These will be graded in numerical order until the required number have been completed, regardless of whether they are right or wrong. Parts 1 - 5 will be computer graded, and Parts 6 - 9 are to be answered in the answer booklet provided. A periodic table with atomic numbers and atomic weights, and spectroscopic tables are appended to this examination paper.

Parts 1 - 5 consist of a series of multiple choice questions numbered 1 - 40, which are to be answered on your computer answer sheet. Indicate your answer by blackening out the appropriate space, A, B, C, D or E on the answer sheet (this must be completed within the 3hrs). Use a pencil only ***not ink*** to completely fill the circle(s). In some cases it is required that you indicate ***multiple*** items for a complete and/or correct answer by blackening out more than one space. In some other cases more than five options are available and some of these also require more than one space to be blackened out. For an example, an option specified as AB requires that you blacken out ***both*** space A and space B. Part marks may be awarded in some of the questions. Incorrect answers must be erased ***cleanly***.

Molecular models are permitted during the exam; calculators are also permitted, ***but NOT programmable calculators***.

Absolutely no other electronic devices are allowed

Cont'd -->

15% PART 1: RELATIVE PROPERTIES

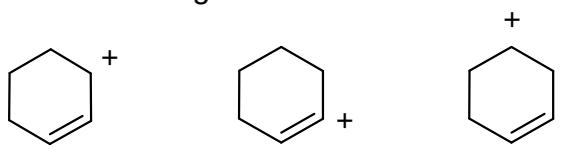
ANSWER ANY TEN (10) OF QUESTIONS 1 TO 12.

Arrange the items in questions 1-12 in DECREASING ORDER (i.e. greatest, most etc. first) with respect to the indicated property.

Use the following code to indicate your answers.

A.	**i** > **ii** > **iii**	**D**.	**ii** > **iii** > **i**
B.	**i** > **iii** > **ii**	**E**.	**iii** > **i** > **ii**
C.	**ii** > **i** > **iii**	**AB**.	**iii** > **ii** > **i**

1. The relative stability of the following carbocations:



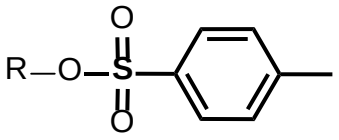
i **ii** **iii**

2. The relative nucleophilicity of the following in a polar, protic solvent:

CH_3CH_2SH $CH_3CH_2CH_3$ CH_3CH_2OH

i **ii** **iii**

3. The relative leaving group ability of the **bold group** in each of the following:



i

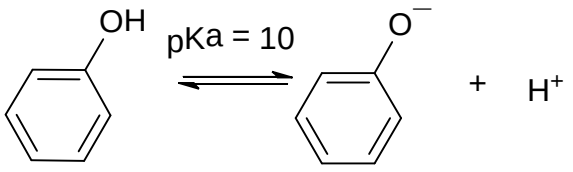
R—**OH**

ii

R—**CH_3**

iii

4. The relative amount of the conjugate base of phenol formed by the reaction of 1 mole equivalent of each of the following:



CH_3NH_2 CH_3O^- CH_3CH_3

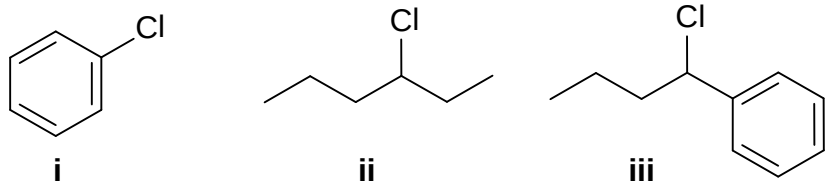
i **ii** **iii**

Cont'd -->

Use the following code to indicate your answers.

A.	**i** > **ii** > **iii**	**D**.	**ii** > **iii** > **i**
B.	**i** > **iii** > **ii**	**E**.	**iii** > **i** > **ii**
C.	**ii** > **i** > **iii**	**AB**.	**iii** > **ii** > **i**

5. The relative rate of reaction of each of the following when treated with $AgNO_3$ / aq. ethanol:

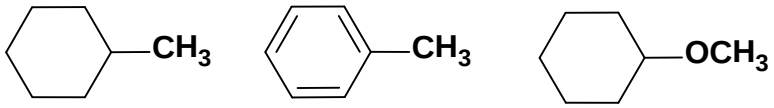


i **ii** **iii**

6. The relative rate of reaction of each of the following with HBr:

i. propan-2-ol **ii**. propan-1-ol **iii**. prop-2-en-1-ol

7. The ^{1}H-NMR chemical shifts for the groups shown in **bold** in each of the following structures:



i **ii** **iii**

8. The relative acidity of the most acidic H in each of the following:

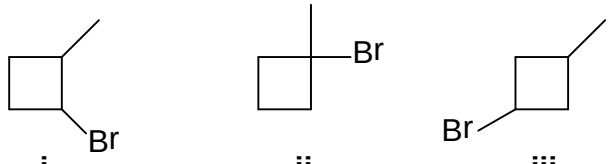
CH_3CH_2SH	HF	CH_3Cl
i	**ii**	**iii**

Cont'd -->

Use the following code to indicate your answers.

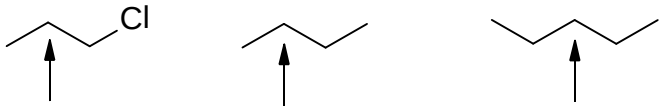
A.	**i** > **ii** > **iii**	**D**.	**ii** > **iii** > **i**
B.	**i** > **iii** > **ii**	**E**.	**iii** > **i** > **ii**
C.	**ii** > **i** > **iii**	**AB**.	**iii** > **ii** > **i**

9. The relative amount of the following products formed by the reaction methyl cyclobutane with Br_2 / uv light:



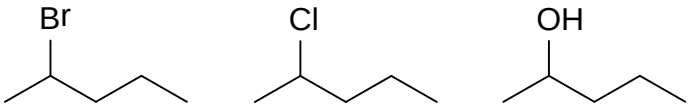
i **ii** **iii**

10. The number of lines in the H-NMR signals for the H atoms at the positions indicated in each of the following :



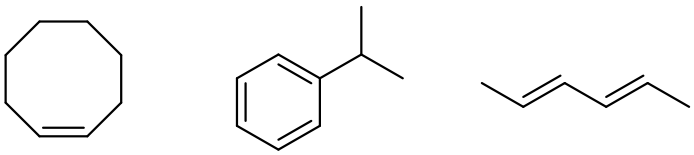
i **ii** **iii**

11. The relative yields of the Zaitsev product produced by the reaction of each of the following with hot sodium ethoxide in ethanol:



i **ii** **iii**

12. The number of types of hydrogen in each of the following:



i **ii** **iii**

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12% PART 2: MOLECULAR PROPERTIES

ANSWER ALL SIX (6) OF THE QUESTIONS 13 TO 18.

In qu 13, 14, 15, 17 &18 choose the single option that provides the best answer.

13. Which of the following is more reactive towards reaction with HCl ?

A. **I** because it forms a less stable primary carbocation

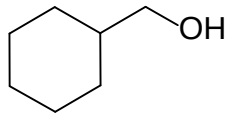
B. **II** because it forms a resonance stabilized carbocation

C. **I** because it is less sterically hindered

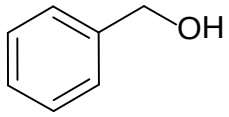
D. **II** because it is less sterically hindered

E. **I** and **II** have about equal reactivity

I



II



14. Which of the following is the strongest acid ?

I **II**

A. **I** because the C-H bond is weaker

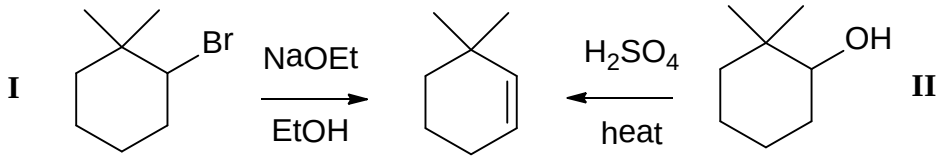
B. **II** because the C-H bond is weaker

C. **I** because the conjugate base is stablised by the positive nucleus

D. **II** because the conjugate base is further stabilized by resonance

E. **I** and **II** are about equally acidic

15. Which of the following reactions is more efficient for producing the alkene shown ?



A. **I** because the reaction is more likely to be E1

B. **II** because the reaction is more likely to be E1

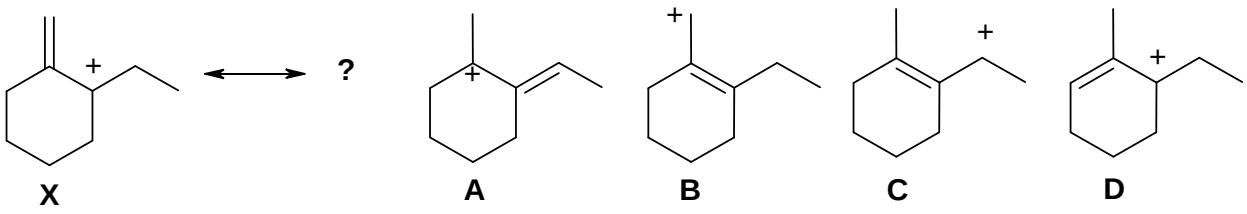
C. **I** because the reaction is more likely to be E2

D. **II** because the reaction is more likely to be E2

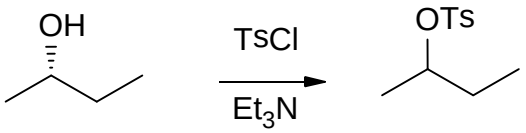
E. The routes are equally efficient at producing the alkene

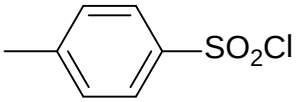
Cont'd -->

16. Which of the following is/are resonance structures of the structure **X** (**select all that apply**) ?



17. In the following reaction, the stereochemistry of the product:



TsCl = tosyl chloride = 

A. Is lost because the reaction is SN1 and takes place with inversion

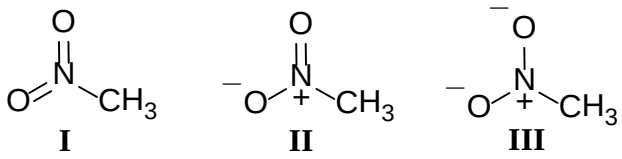
B. Is reversed because the reaction is SN2 and takes place with inversion.

C. Is lost because the reaction is SN1 and occurs via a carbocation intermediate.

D. Is retained because the reaction does not break the C-O bond.

E. Is irrelevant because the alcohol does not have a chirality center

18. Which of the following resonance structures is the major contributor to the resonance hybrid ?



A. **I** because it is has the maximum number of bonds

B. **II** because it is has complete octets

C. **III** because it is has the most delocalized charge

D. **I** because it has the least charge separation

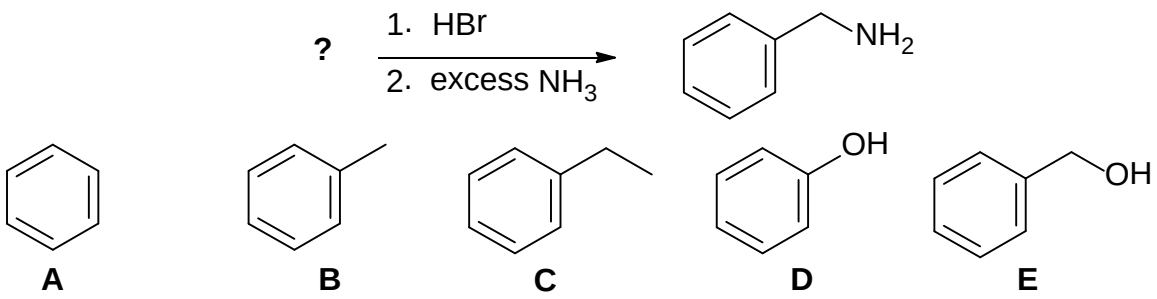
E. **III** because the charge separation is in accord with electronegativity

Cont'd -->

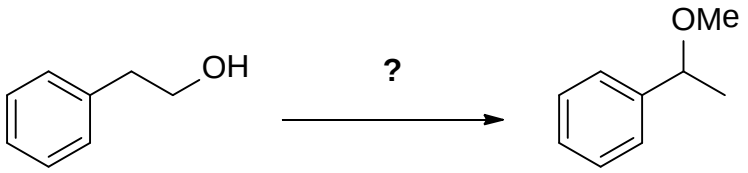
14% PART 3: REACTIONS

ANSWER ANY SEVEN (7) OF QUESTIONS 19 TO 26.
For each of questions 19-26 select the MISSING component (the best starting material, the major product or the best reagents) required in order to BEST complete each of the reaction schemes.

19.



20.



A 1. TsCl / pyridine; 2. NaOMe / cold MeOH

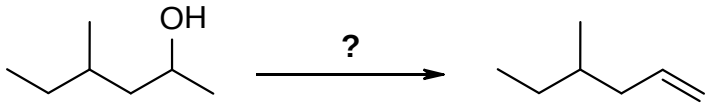
B 1. HBr; 2. NaOMe / cold MeOH

C 1. H_2SO_4 / heat; 2. Br_2; 3. MeOH

D aq. H_2SO_4

E 1. PBr_3 / pyridine; 2. MeI

21.



A conc. H_2SO_4 / heat

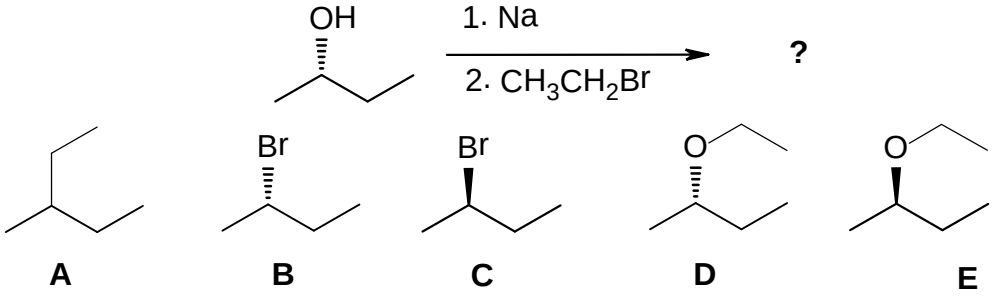
B NaOH / heat

C KO^tBu / heat

D 1. $SOCl_2$ / $N(CH_2CH_3)_3$
2. KO^tBu / heat

E 1. H_2O / H_2SO_4
2. NaOH / heat

22.



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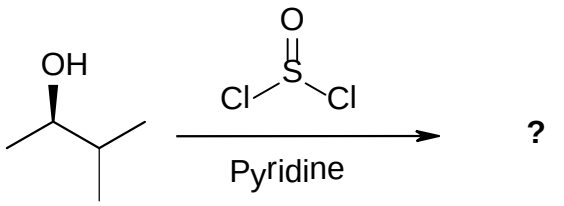
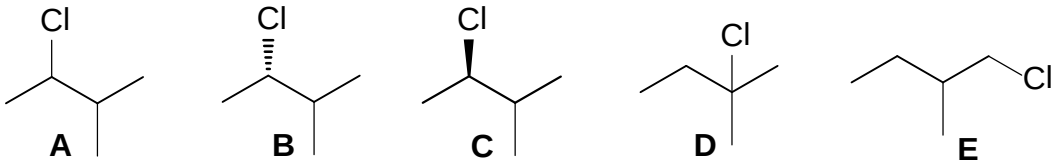
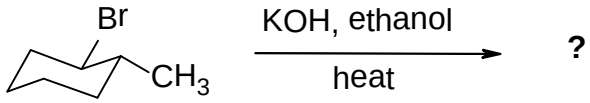
23.

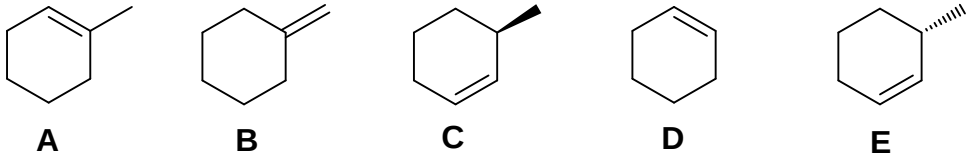


racemic

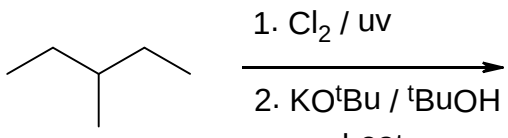


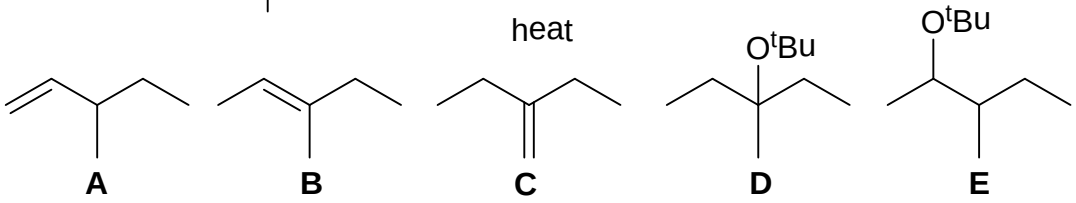
24.



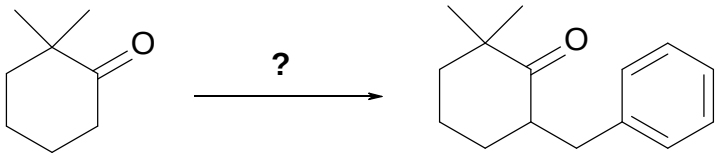


25.





26.



A 1. Na / ether; 2. benzyl alcohol

B 1. $NaNH_2$; 2. benzyl chloride

C 1. $NaNH_2$; 2. chlorobenzene

D 1. Cl_2 / uv; 2. benzyl alcohol

E 1. Cl_2 / uv; 2. bromobenzene

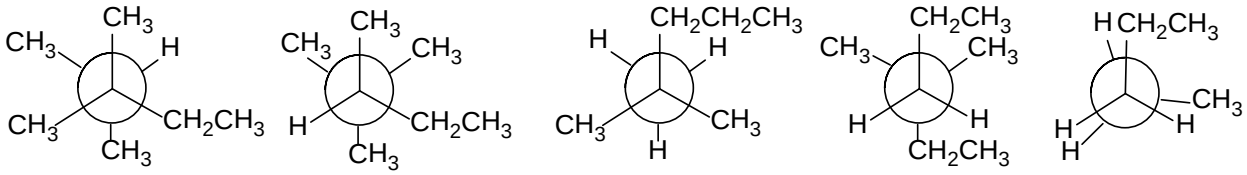
Cont'd -->

9% PART 4: CONFORMATIONAL ANALYSIS

ANSWER ANY SIX (6) OF THE QUESTIONS 27 TO 34.

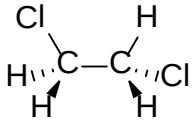
For each of the questions 27-34 select the answer(s) from those provided. In some cases more than one answer may be correct in which case all correct answers should be selected for full marks.

27. Which of the Newman projections shown represent conformations of 2,2-dimethylpentane ? (select **all that apply**)



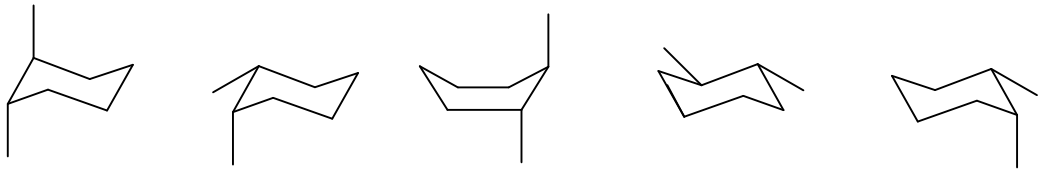
A **B** **C** **D** **E**

28. What is the **torsional** angle between the two chlorine groups in the conformation of 1,2-dichloroethane shown below ?



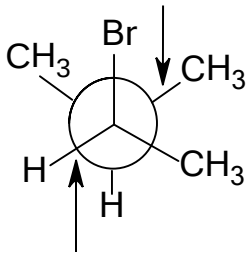
A 0^o **D** 109.5^o
B 60^o **E** 120^o
C 90^o **AB** 180^o

29. Which of the following structures represent conformations that can be adopted by *trans*-1,2-dimethylcyclohexane ? (Indicate **all that apply)**



A **B** **C** **D** **E**

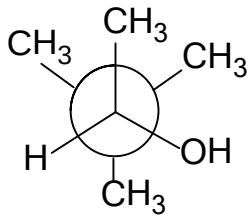
30. Which of the following terms **best** describes the relative position of the two indicated bonds in the conformation of the molecule shown below?

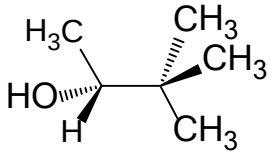


A eclipsed
B staggered
C anti
D syn
E gauche
AB trans
AC cis

Cont'd -->

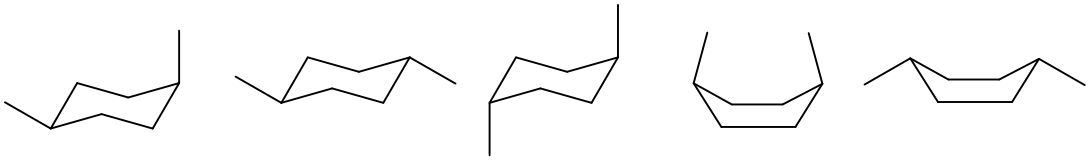
31. Which of the following terms **best** describes the relationship between the two molecules shown below ?





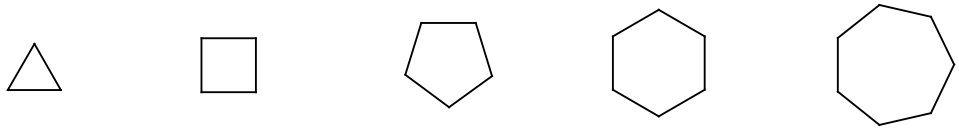
A constitutional isomers
B identical
C conformational isomers
D enantiomers
E diastereomers
AB meso
AC not isomers

32. Which of the following structures (as shown) has the lowest energy ?



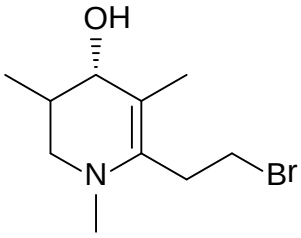
A **B** **C** **D** **E**

33. Which of the following molecules would have the most angle strain?



A **B** **C** **D** **E**

34. Which of the following terms describes the configurations of the stereocenters in the molecule shown below ?



A. R, E
B. R, Z
C. S, E
D. S, Z

Cont'd -->

12% PART 5: SPECTROSCOPY

ANSWER ALL SIX (6) OF QUESTIONS 35 TO 40.

For each of questions 35-40 select the compound from the list provided that corresponds BEST with the spectroscopic data provided. The following common abbreviations have been used s = singlet, d = doublet, t = triplet, q = quartet, p = pentet, h = hextet, *etc.* m = multiplet.

35. **^{1}H NMR** : δ/ppm 1.4 (d, 3H), 3.3 (q, 1H), 3.8 (s, 6H)
^{13}C-NMR: δ/ppm 15, 41, 52, 170
IR: 1737, 1200 cm^{-1}

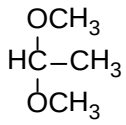
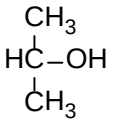
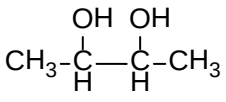
36. **^{1}H-NMR**: δ/ppm 3.3 (s, 3H), 3.7 (s, 2H)
^{13}C-NMR: δ/ppm 59, 72

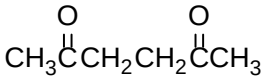
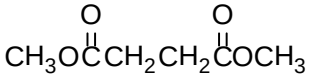
37. **^{1}H-NMR**: δ/ppm 2.1 (s, 3H), 2.4 (s, 2H)
^{13}C-NMR: δ/ppm 30, 37, 207
IR: 1713 cm^{-1}

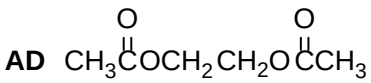
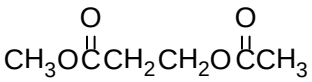
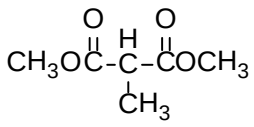
38. **^{1}H-NMR**: δ/ppm 1.0 (d, 3H), 3.3 (s, 6H), 4.5 (q, 1H)
^{13}C-NMR: δ/ppm 19, 52, 102

39. **^{1}H-NMR**: δ/ppm 1.0 (d, 6H), 1.8 (broad s, 1H, D_2O exchange), 3.7 (septet, 1H)
^{13}C-NMR: δ/ppm 25, 64
IR: 3350 cm^{-1}

40. **^{1}H-NMR**: δ/ppm 0.9 (t, 3H), 1.6 (h, 2H), 2.3 (broad s, 1H, D_2O exchange), 3.6 (t, 2H)
^{13}C-NMR: δ/ppm 10, 26, 64
IR: 3340 cm^{-1}

A $CH_3OCH_2CH_2OCH_3$ **B**  **C**  **D** 

E $CH_3CH_2CH_2OH$ **AB**  **AC** 

AD  **AE**  **BC** 

Cont'd -->

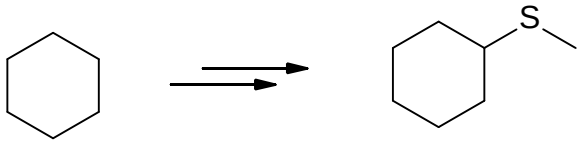
8% **PART 6: SYNTHESIS**

DESIGN EFFICIENT SYNTHESES OF ANY TWO (2) of the following target molecules from the indicated starting material. In addition, you are allowed to use any hydrocarbon with three or fewer carbon atoms, any solvents or inorganic reagents, and any organic reagents that do not contribute carbon atoms to the carbon skeleton in the product. More than one step will be required for each synthesis. Clearly show the required reagents and the product of each step.

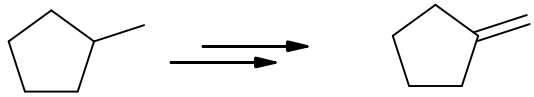
WRITE YOUR ANSWERS IN THE EXAM BOOKLET PROVIDED.

DO NOT SHOW MECHANISMS.

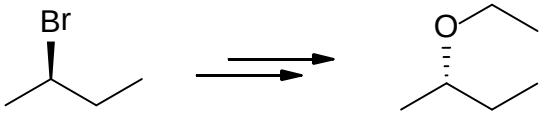
A.



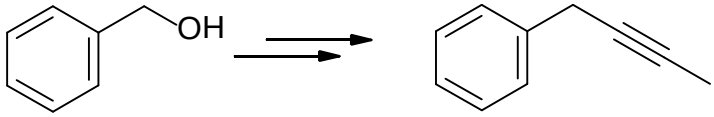
B.



C.



D.



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10% PART 7: MECHANISMS

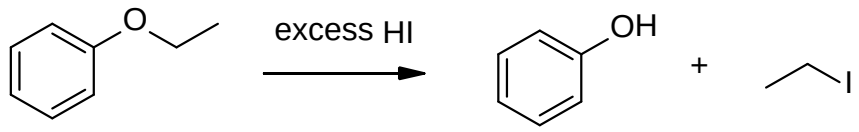
WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED

ANSWER TWO (2) QUESTIONS, ONE from PART A and ONE from PART B.

NO REAGENTS OTHER THAN THOSE ALREADY SHOWN ARE REQUIRED.

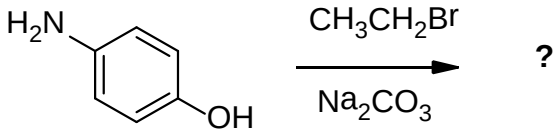
(5%) PART A: Use a curly arrow mechanism to explain ONE of the following reactions:

i. Draw the reaction mechanism for the reaction of ethoxybenzene to give phenol and ethyl iodide:



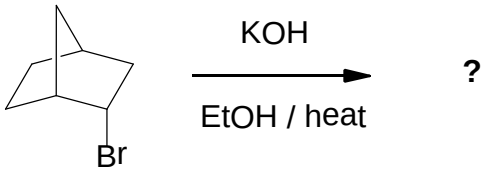
OR

ii. Predict the major product of this reaction by showing the mechanism. Briefly justify your choice.



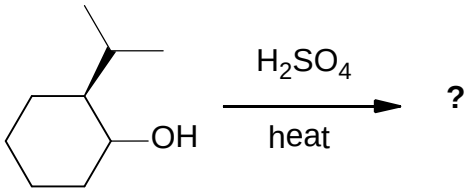
(5%) PART B: Use a curly arrow mechanism to explain ONE of the following reactions:

i. Predict the major product of this reaction by showing the mechanism. Briefly justify your choice.



OR

iii. Predict the major product of this reaction by showing the mechanism. Briefly justify your choice.



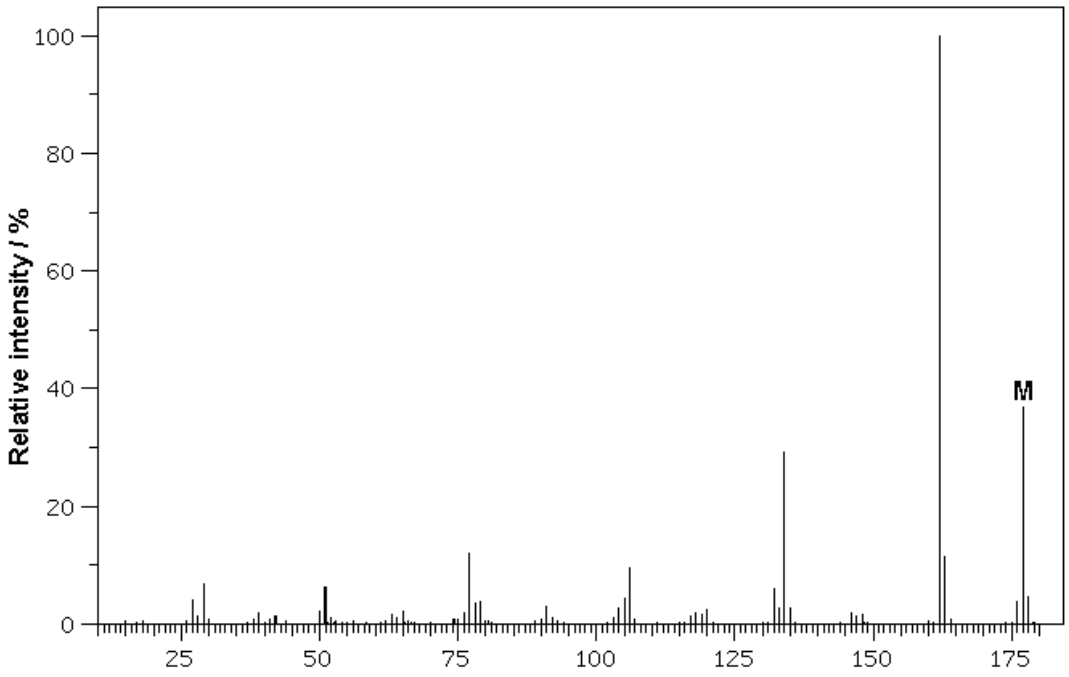
Cont'd -->

10% PART 8: SPECTROSCOPY

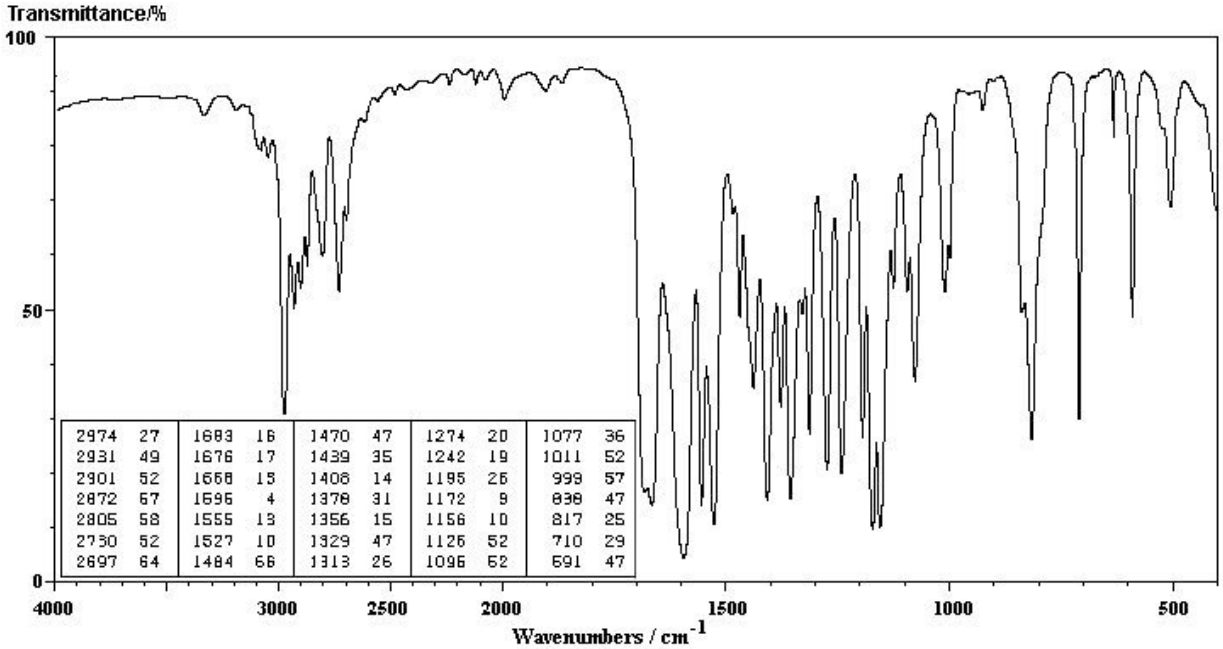
WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED. Show your workings as PARTIAL marks will be given.

From the spectral data provided below, identify the structure of the "unknown" molecule.

Mass Spectrum:



IR Spectrum:



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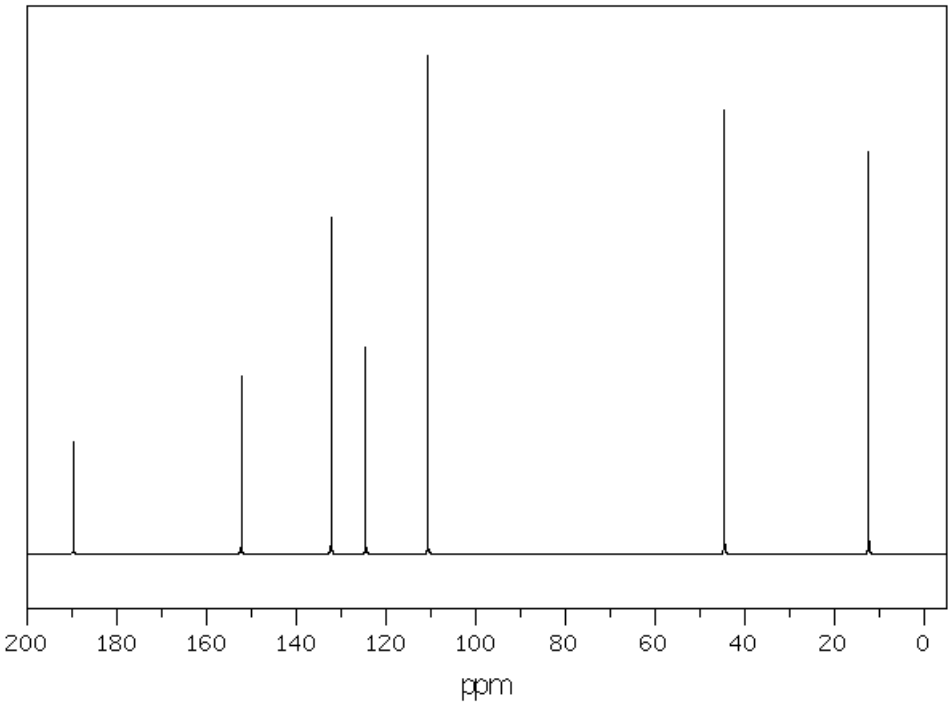
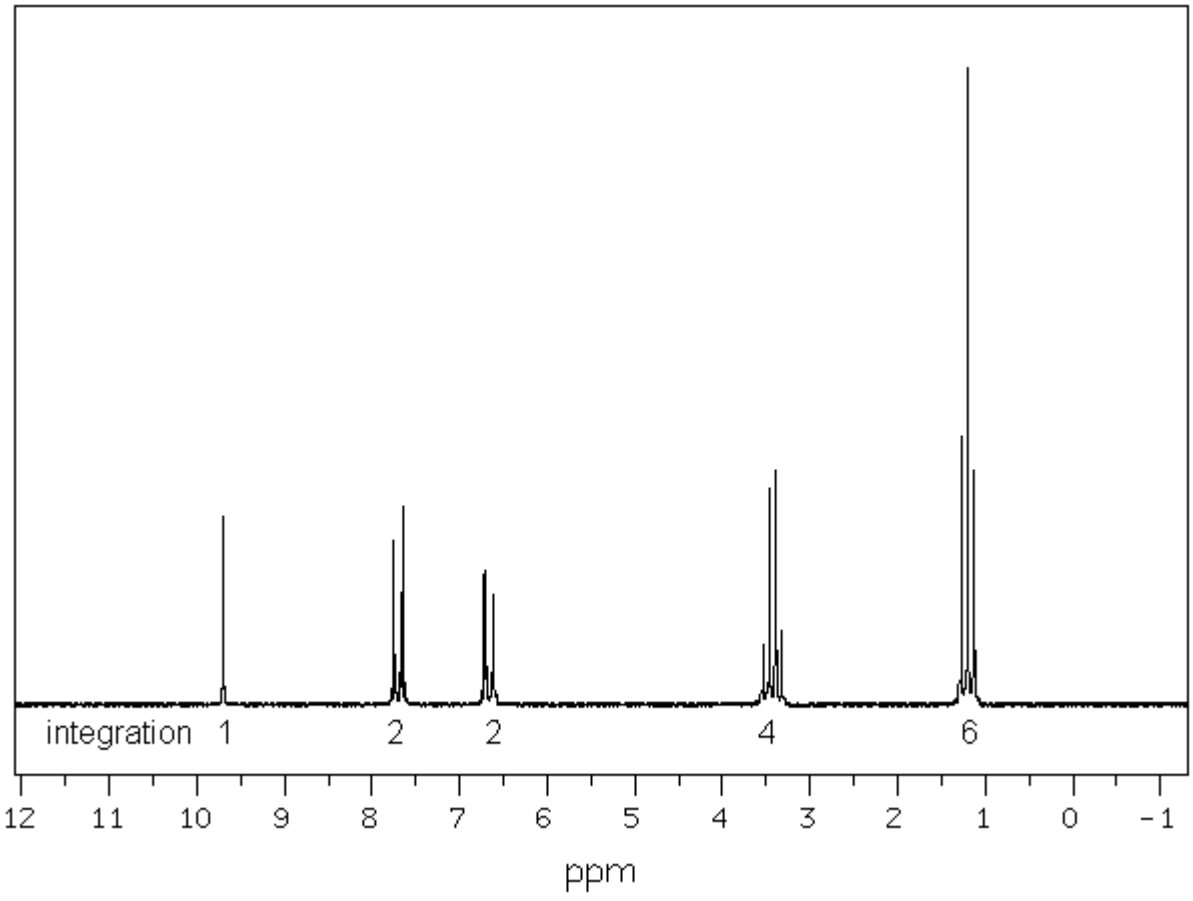
^{13}C-NMR:



^{1}H-NMR:



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10% PART 9: STRUCTURE DETERMINATION

WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED

An achiral compound **A** with molecular formula $C_7H_{13}Br$ reacted rapidly with aq. ethanolic silver nitrate. When **A** was heated with ethanolic KOH to give a hydrocarbon **B**, molecular formula C_7H_{12}. When **A** was heated with KO*t*Bu in DMSO, it gave hydrocarbon **C**, a constitutional isomer of **B**. The 13C-NMR of **C** showed only 5 peaks: 150, 107, 35, 28 and 26 ppm.

Chiral compound **D**, a constitutional isomer of **A**, was heated in ethanol to give **B** as the major product. Compound **D** could be synthesized directly by reacting (1*S*, 2*R*)-2-methylcyclohexanol with PBr_3 and triethylamine.

Achiral compound **E**, with molecular formula $C_7H_{14}O$ (IR: 3500cm^{-1}, broad), was reacted with tosyl chloride and triethylamine to give compound **F**. Heating compound **F** with ethanolic KOH gave compound **C** as the only product. Reaction of compound **E** with HBr gave compound **A** as the major product, whereas reaction of compound **E** with PBr_3 and triethylamine produced compound **G**, a constitutional isomer of **A** and **D**. Compound **G** could also be produced by reacting compound **F** with KBr in acetone. **G** was found to react rapidly with NaI in acetone.

Identify A-G (only structures are needed)

****** THE END ******

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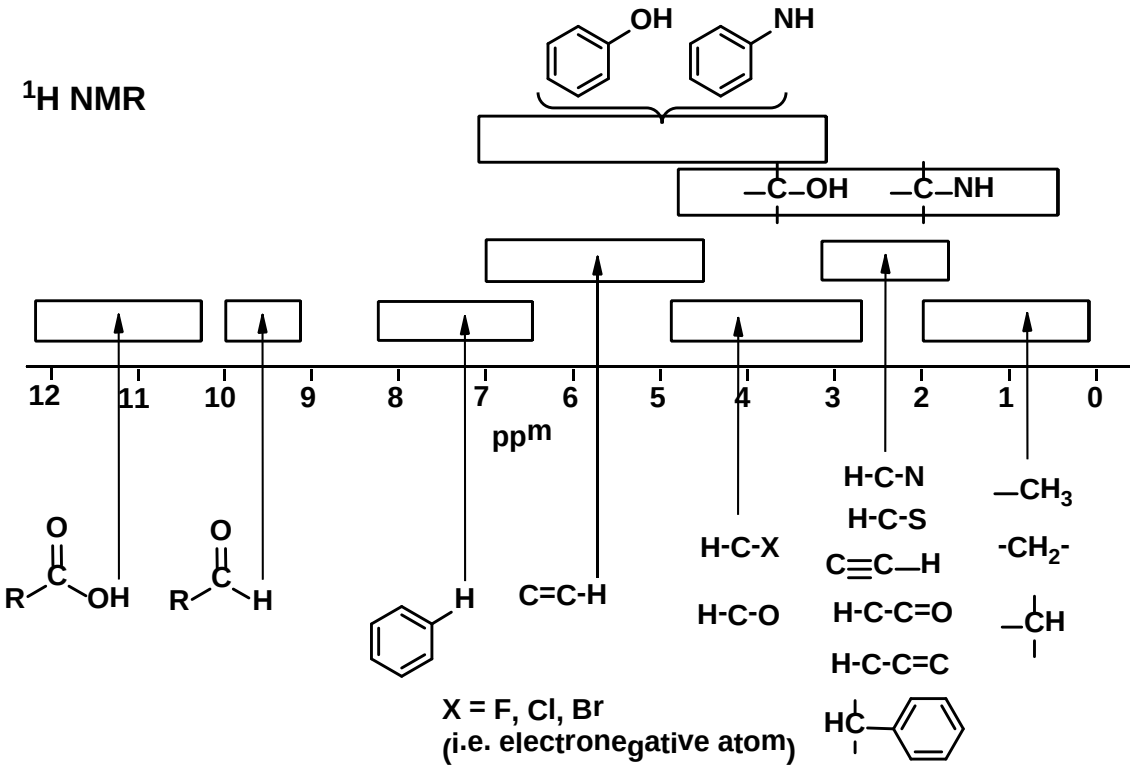
SPECTROSCOPIC TABLES

^{1}H NMR

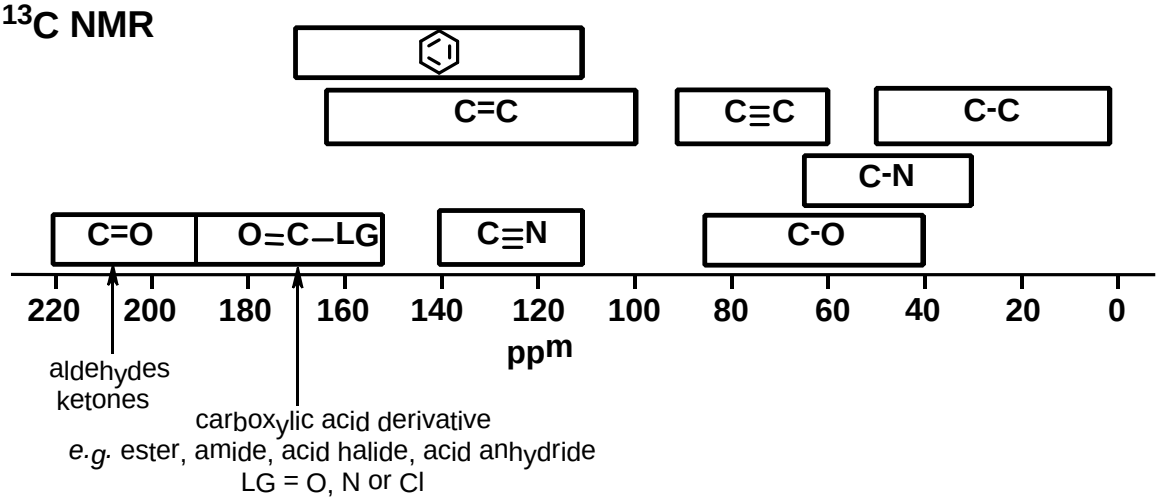


^{1}H NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm

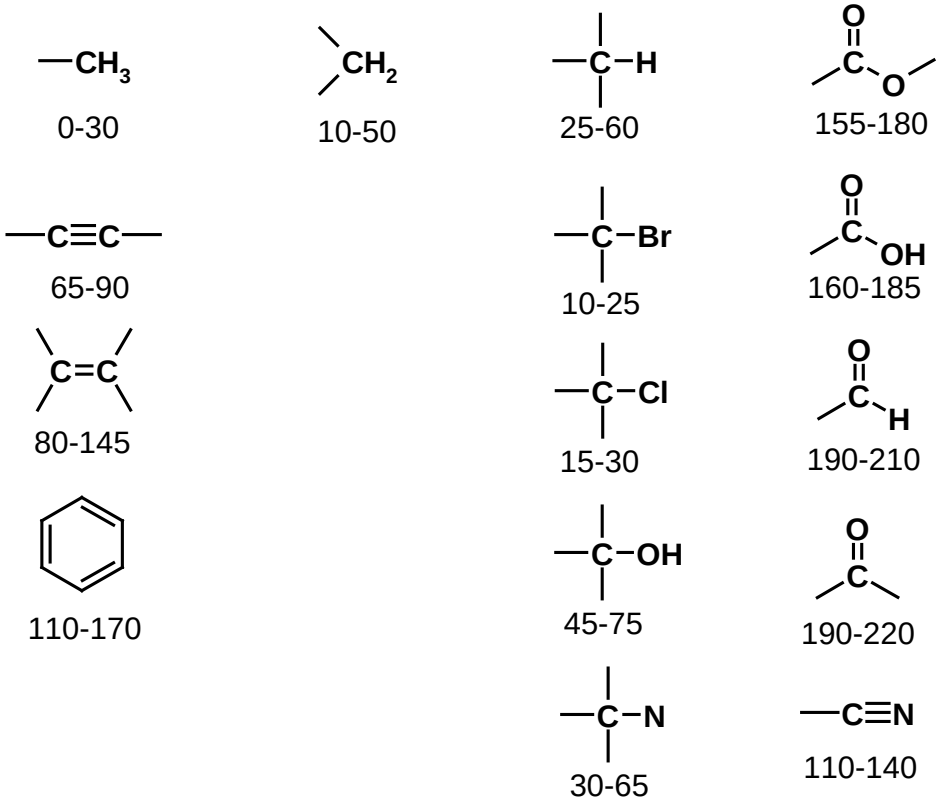
R =	methyl —CH_3	methylene -CH_2-	methyne —CH	other	
R—C(R)—	0.9	1.4	1.5	sp^3C-OH	1-5
R, R, C=C	1.6	2.3	2.6	sp^3C-NH	1-3
R—C(=O)—	2.1	2.4	2.5	C≡CH	2.5
R—N	2.2	2.5	2.9	H, C=C	4.5-6.5
R—C$_6$H$_5$	2.3	2.7	3.0	H—C$_6$H$_5$	6.5-8
R—Br	2.7	3.3	4.1	R—C(=O)—H	9-10
R—Cl	3.1	3.4	4.1	R—C(=O)—OH	9-12
R—O—	3.3	3.4	3.7		

Cont'd -->

^{13}C NMR



^{13}C NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm



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INFRA-RED GROUP ABSORPTION FREQUENCIES

		TYPE OF VIBRATION	FREQUENCY (cm^{-1})	WAVELENGTH (μ)	INTENSITY (1)
C–H	Alkanes	(stretch)	3000-2850	3.33-3.51	s
	$-CH_3$	(bend)	1450 and 1375	6.90 and 7.27	m
	$-CH_2-$	(bend)	1465	6.83	m
	Alkenes	(stretch)	3100-3000	3.23-3.33	m
		(bend)	1700-1000	5.88-10.0	s
	Aromatics	(stretch)	3150-3050	3.17-3.28	s
		(out-of-plane bend)	1000-700	10.0-14.3	s
	Alkyne	(stretch)	ca. 3300	ca.3.03	s
	Aldehyde		2900-2800	3.45-3.57	w
			2800-2700	3.57-3.70	w
C–C	Alkane	not usually useful			
C=C	Alkene		1680-1600	5.95-6.25	m-w
	Aromatic		1600-1400	6.25-7.14	m-w
C≡C	Alkyne		2250-2100	4.44-4.76	m-w
C=O	Aldehyde		1740-1720	5.75-5.81	s
	Ketone		1725-1705	5.80-5.87	s
	Carboxylic acid		1725-1700	5.80-5.88	s
	Ester		1750-1730	5.71-5.78	s
	Amide		1700-1640	5.88-6.10	s
	Anhydride		ca. 1810	ca. 5.52	s
			ca. 1760	ca. 5.68	s
	Acyl chloride		1800	5.55	s
C–O	Alcohols, Ethers, Esters,				
	Carboxylic acids		1300-1000	7.69-10.0	s
O–H	Alcohols, Phenols				
	Free		3650-3600	2.74-2.78	m
	H-Bonded		3400-3200	2.94-3.12	m
	Carboxylic acids (2)		3300-2500	3.03-4.00	m
N–H	Primary and secondary amines		ca. 3500	ca. 2.86	m
C≡N	Nitriles		2260-2240	4.42-4.46	m
N=O	Nitro ($R-NO_2$)		1600-1500	6.25-6.67	s
			1400-1300	7.14-7.69	s
C–X	Fluoride		1400-1000	7.14-10.0	s
	Chloride		800-600	12.5-16.7	s
	Bromide, Iodide		<600	>16.7	s

(1) s = strong, m = medium and w = weak

(2) note that the -OH absorption of solid carboxylic acids which run as a nujol mull can be difficult to see as they maybe very broad

Cont'd -->

PERIODIC TABLE

1 1A																	18 8A
1 **H** 1.008	**2** 2A											**13** 3A	**14** 4A	**15** 5A	**16** 6A	**17** 7A	2 **He** 4.003
3 **Li** 6.941	4 **Be** 9.012											5 **B** 10.81	6 **C** 12.01	7 **N** 14.01	8 **O** 16.00	9 **F** 19.00	10 **Ne** 20.18
11 **Na** 22.99	12 **Mg** 24.31	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	13 **Al** 26.98	14 **Si** 28.09	15 **P** 30.97	16 **S** 32.07	17 **Cl** 35.45	18 **Ar** 39.95
19 **K** 39.10	20 **Ca** 40.08	21 **Sc** 44.96	22 **Ti** 47.88	23 **V** 50.94	24 **Cr** 52.00	25 **Mn** 54.94	26 **Fe** 55.85	27 **Co** 58.93	28 **Ni** 58.69	29 **Cu** 63.55	30 **Zn** 65.38	31 **Ga** 69.72	32 **Ge** 72.59	33 **As** 74.92	34 **Se** 78.96	35 **Br** 79.90	36 **Kr** 83.80
37 **Rb** 85.47	38 **Sr** 87.62	39 **Y** 88.91	40 **Zr** 91.22	41 **Nb** 92.91	42 **Mo** 95.94	43 **Tc** (98)	44 **Ru** 101.1	45 **Rh** 102.9	46 **Pd** 106.4	47 **Ag** 107.9	48 **Cd** 112.4	49 **In** 114.8	50 **Sn** 118.7	51 **Sb** 121.8	52 **Te** 127.6	53 **I** 126.9	54 **Xe** 131.3
55 **Cs** 132.9	56 **Ba** 137.3	57* **La** 138.9	72 **Hf** 178.5	73 **Ta** 180.9	74 **W** 183.9	75 **Re** 186.2	76 **Os** 190.2	77 **Ir** 192.2	78 **Pt** 195.1	79 **Au** 197.0	80 **Hg** 200.6	81 **Tl** 204.4	82 **Pb** 207.2	83 **Bi** 209.0	84 **Po** (209)	85 **At** (210)	86 **Rn** (222)
87 **Fr** (223)	88 **Ra** 226.0	89** **Ac** (227)	104 **Rf** (261)	105 **Ha** (262)	106 **Sg** (263)	107 **Ns** (262)	108 **Hs** (265)	109 **Mt** (266)	110 **Uun** (269)	111 **Uuu** (272)							

Lanthanides *	58 **Ce** 140.1	59 **Pr** 140.9	60 **Nd** 144.2	61 **Pm** (145)	62 **Sm** 150.4	63 **Eu** 152.0	64 **Gd** 157.3	65 **Tb** 158.9	66 **Dy** 162.5	67 **Ho** 164.9	68 **Er** 167.3	69 **Tm** 168.9	70 **Yb** 173.0	71 **Lu** 175.0
Actinides **	90 **Th** 232.0	91 **Pa** 231.0	92 **U** 238.0	93 **Np** 237.0	94 **Pu** (244)	95 **Am** (243)	96 **Cm** (247)	97 **Bk** (247)	98 **Cf** (251)	99 **Es** (252)	100 **Fm** (257)	101 **Md** (258)	102 **No** (259)	103 **Lr** (260)