UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

FINAL EXAMINATION

CHEMISTRY 351

Version 1

December 12th, 2015 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

15% PART 1: RELATIVE PROPERTIES

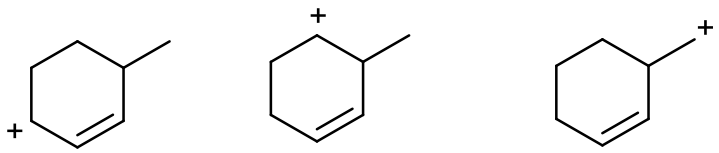
ANSWER ANY TEN (10) OF QUESTIONS 1 TO 12.

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.

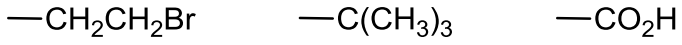
A.	**i > ii > iii**	**D**.	**ii > iii > i**
B.	**i > iii > ii**	**E**.	**iii > i > ii**
C.	**ii > i > iii**	**AB**.	**iii > ii > i**

1. The relative stability of the following carbocations:



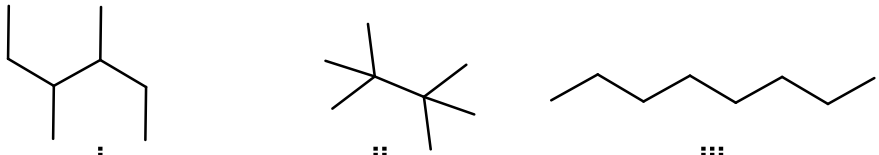
i **ii** **iii**

2. The relative Cahn-Ingold-Prelog priority rule ranking (used for assigning E/Z or R/S stereochemistry) of each of the following :



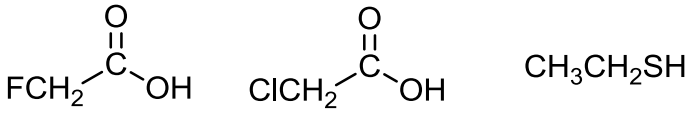
i **ii** **iii**

3. The heats of combustion of each of the following (least negative to most negative):



i **ii** **iii**

4. The relative acidity of each of the following:



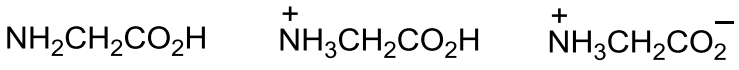
i **ii** **iii**

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 amounts of each of the following species of glycine (also known as 2-aminoethanoic acid) present in an aqueous solution of pH=2 :

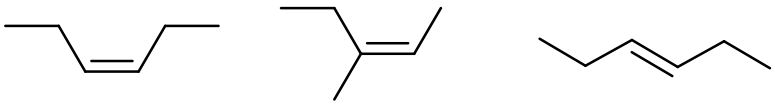


i **ii** **iii**

6. The relative rate of reaction of each of the following with H_2SO_4 :

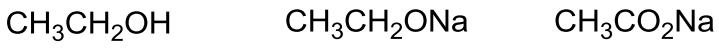
i. n-propanol **ii**. i-propanol **iii**. t-butanol

7. The relative stability of each of the following alkenes:



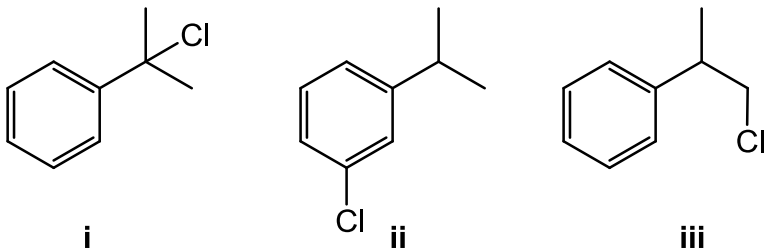
i **ii** **iii**

8. The relative nucleophilicity in a polar protic solvent of each of the following:



i **ii** **iii**

9. The relative amount of the following products formed by the reaction of isopropylbenzene with Cl_2 / uv light:



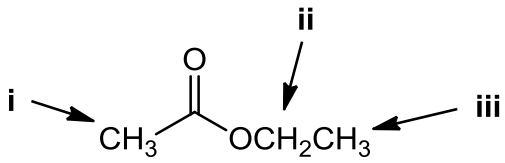
i **ii** **iii**

Cont'd -->

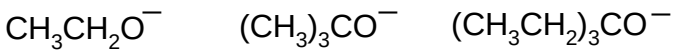
Use the following code to indicate your answers.

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

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

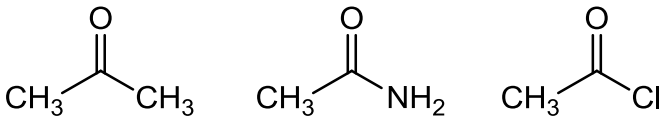


11. The relative yield of the Zaitsev product from the reaction of 2-bromohexane with each of the following:



i ii iii

12. The relative stretching frequency of the C=O bonds in each of the following :



i **ii** **iii**

12% PART 2: MOLECULAR PROPERTIES

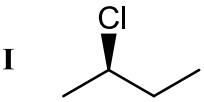
ANSWER ALL SIX (6) OF THE QUESTIONS 13 TO 18.

In questions 13-17 choose the single option that provides the best answer.

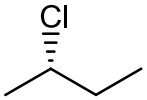
13. Which of the following is the major product of the reaction of (R)-butan-2-ol with $SOCl_2$ / Et_3N ?

A. **I** because an SN2 reaction with inversion occurs
B. **II** because an SN2 reaction with inversion occurs
C. **I** because an SN1 reaction with inversion occurs
D. **II** because an SN1 reaction with inversion occurs
E. **I** and **II** are formed in equal amounts via an SN1 reaction

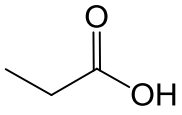
I



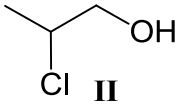
II



14. Which of the following is the strongest acid ?



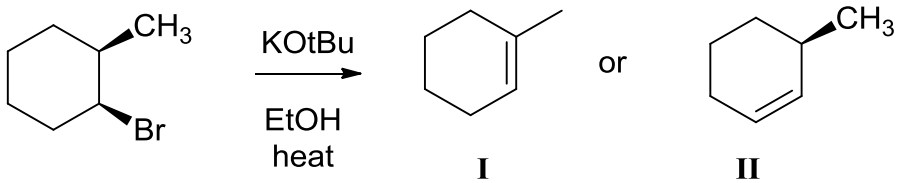
I



II

A. **I** because there is less of a steric effect
B. **II** because there is a greater steric effect due to the large Cl atom
C. **I** because the Cl atom destablises the conjugate base of **II**
D. **II** because of the inductive effect due to the electronegativity of the Cl atom
E. **I** because it is a carboxylic acid

15. In the reaction shown below, which alkene **I** or **II** is the major product and why ?



I **II**

A. **I** because it is the Zaitsev product (the more stable, more highly substituted)
B. **I** because the anti arrangement controls the outcome of the E2 reaction
C. **I** because the more stable tertiary carbocation is formed via a 1,2-hydride shift
D. **II** because the anti arrangement controls the outcome of the E2 reaction
E. **II** because steric effects control the outcome due to the bulky base

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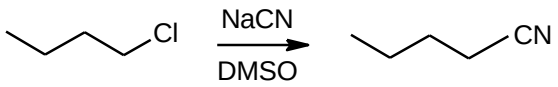
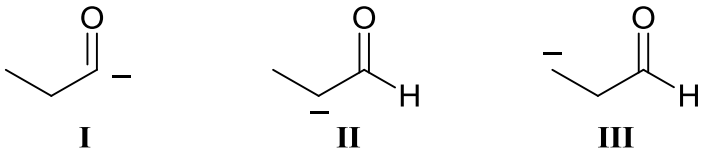
16. In the reaction shown below, the rate of reaction is markedly increased when catalytic amounts of NaI are added to the reaction mixture. This is because:



A. NaI is a polar aprotic solvent
B. NaI is a stronger nucleophile than NaCN
C. NaI is a weaker nucleophile than NaCN
D. NaI in DMSO favours SN2 reactions that are faster than SN1 reactions
E. NaI reacts with the alkyl chloride to introduce a better leaving group

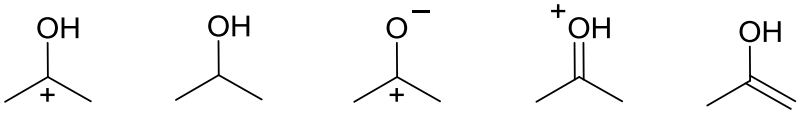
17. Which of the following structures is the most stable and why ?



I **II** **III**

A. **I** because of the anion electrons proximity to both an electronegative atom and a π bond.
B. **II** because the anion electrons sit in an orbital that aligns parallel with the π bond
C. **I** because the anion electrons are held closest to a positively charged carbon atom nucleus
D. **II** because the anion electrons are held closest to a positively charged carbon atom nucleus
E. **III** because the anion electrons are held closest to a positively charged carbon atom nucleus

18. Which of the following is/are resonance structures of the conjugate acid of propan-2-one (**select all that apply**) ?



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

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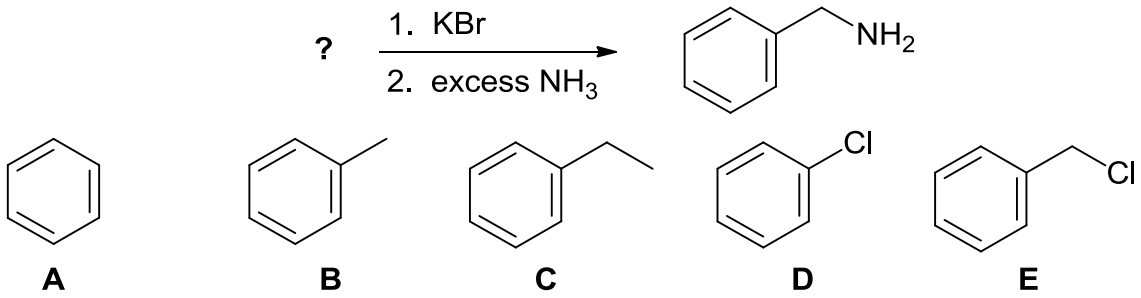
14% PART 3: REACTIONS

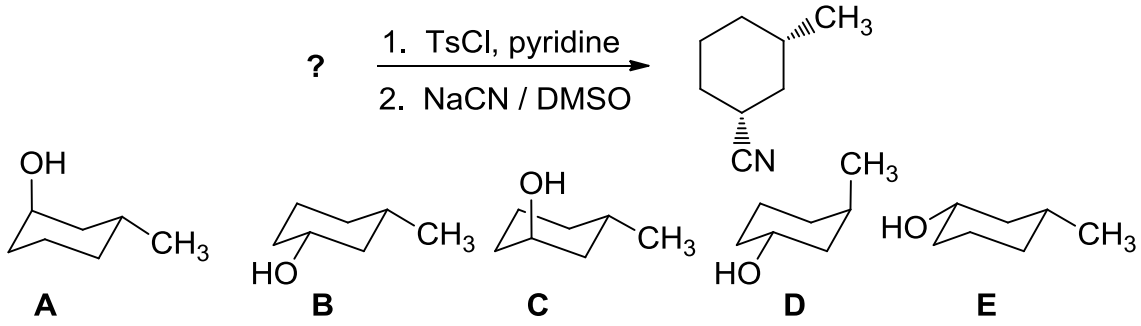
ANSWER ANY SEVEN (7) OF QUESTIONS 19 TO 26.

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.

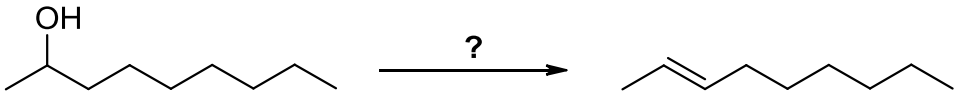
19.



20.



21.



A conc. H_2SO_4 / heat

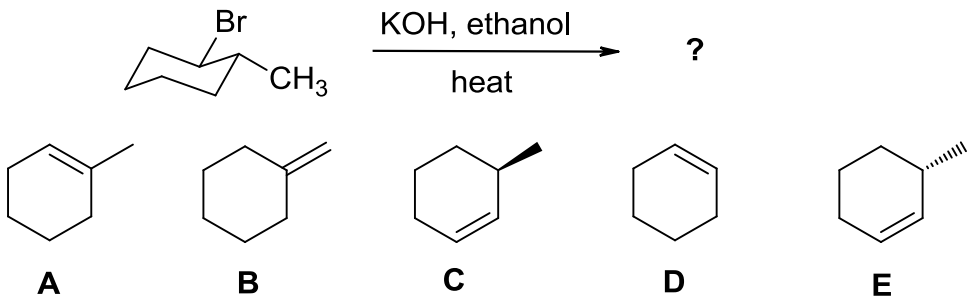
B HBr / heat

C NaOH / heat

D 1. H_2O / H_2SO_4
2. NaOH / heat

E 1. PBr_3 / $N(CH_2CH_3)_3$
2. KO^tBu / heat

22.



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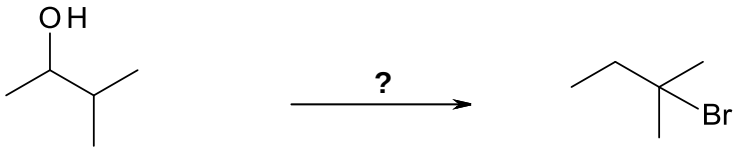
23.



A PBr_3 / $N(CH_2CH_3)_3$

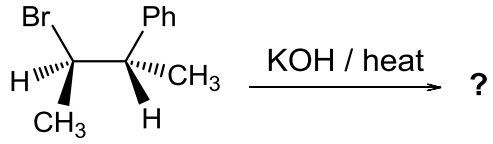
B HBr

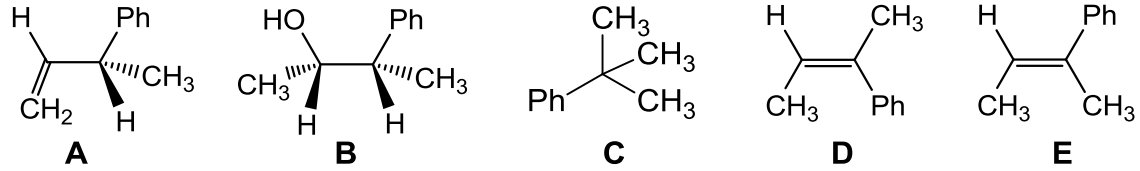
C 1. conc. H_2SO_4
2. PBr_3 / $N(CH_2CH_3)_3$

D 1. H_2O / H_2SO_4
2. PBr_3 / $N(CH_2CH_3)_3$

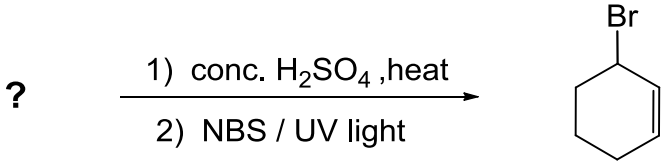
E 1. NaOH / heat
2. PBr_3 / $N(CH_2CH_3)_3$

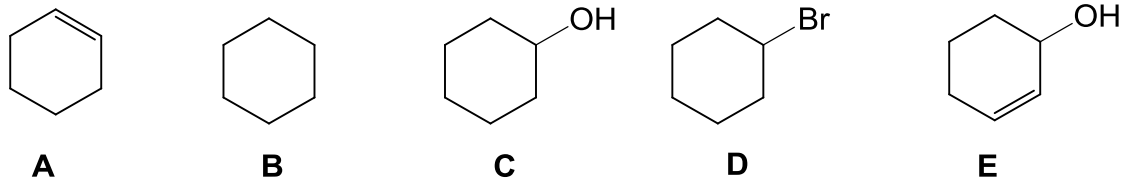
24.



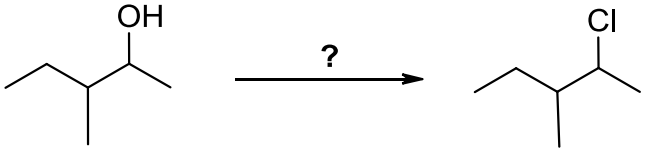


25.





26.



A conc. HCl

B Cl_2

C NaCl / DMSO

D tosyl chloride / Et_3N

E $SOCl_2$ / Et_3N

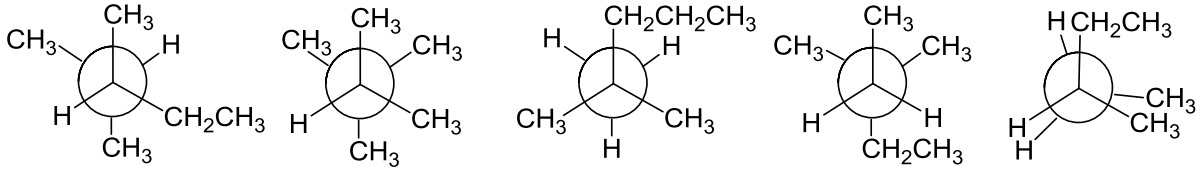
Cont'd -->

9% PART 4: CONFORMATIONAL ANALYSIS

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

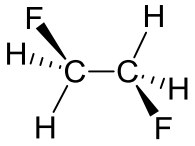
For each of the questions 27-34 select the answer(s) from those provided. In some cases more than one answer may be correct in which case all correct answers should be selected for full marks.

27. Which of the Newman projections shown represent conformations of 2,3-dimethylpentane ? (select **all that apply**)



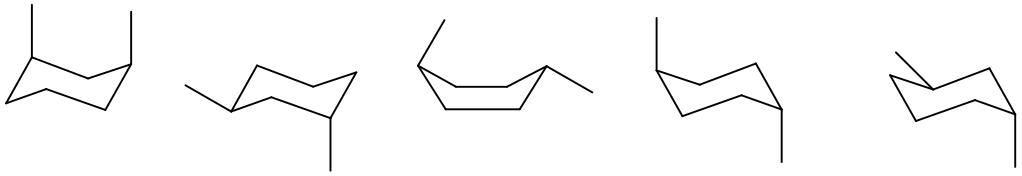
A **B** **C** **D** **E**

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



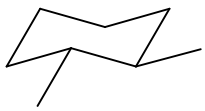
A 0° **D** 109.5°
B 60° **E** 120°
C 90° **AB** 180°

29. Which of the following structures represent conformations that can be adopted by *trans*-1,3-dimethylcyclohexane ? (select **all that apply**)



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

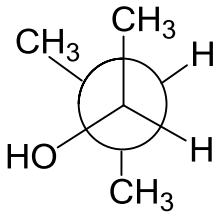
30. Which of the following terms **best** describes the relative position of the two methyl groups in the conformation of the molecule shown below?

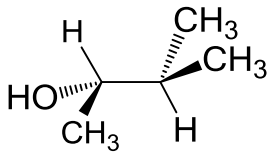


A eclipsed
B staggered
C anti
D syn
E gauche

Cont'd -->

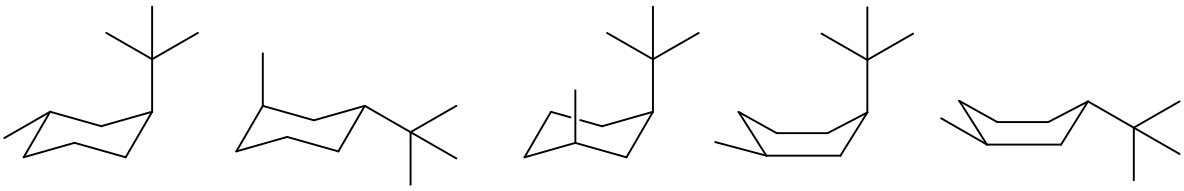
31. Which of the following terms **best** describes the relationship between the two molecules shown below ?





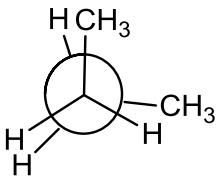
A constitutional isomers
B identical
C conformational isomers
D enantiomers
E diastereomers
AB meso
AC not isomers

32. Which of the following conformations is the **most** stable ?

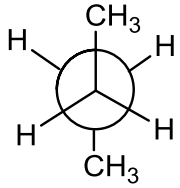


A **B** **C** **D** **E**

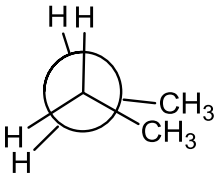
33. Which of the following conformations of butane is the **most** stable?



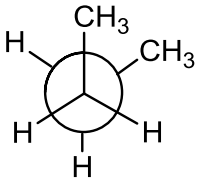
A



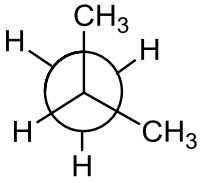
B



C

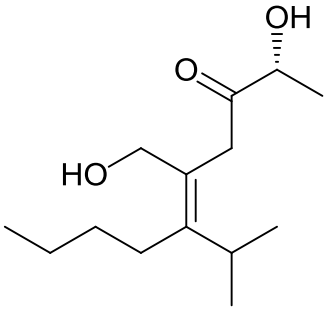


D



E

34. Which of the following terms describes the configuration(s) of the stereocenter(s) in the molecule shown below ? (select **<u>all that apply</u>**)



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

35. **^{1}H NMR** : δ/ppm 1.1 (triplet, 3H), 2.1 (singlet, 3H), 2.5 (quartet, 2H)
^{13}C-NMR: δ/ppm 8, 29, 37, 209
IR : 1718 cm^{-1}

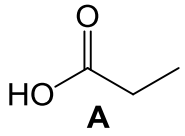
36. **^{1}H NMR** : δ/ppm 1.0 (triplet, 3H), 2.4 (quartet, 2H)
^{13}C-NMR: δ/ppm 12, 46
IR : 2974 cm^{-1}

37. **^{1}H NMR** : δ/ppm 0.7 (triplet, 3H), 0.8 (singlet, 3H), 1.2 (quartet, 2H)
^{13}C-NMR: δ/ppm 8, 26, 33, 34
IR : 2964 cm^{-1}

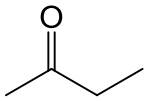
38. **^{1}H NMR** : δ/ppm 1.2 (triplet, 3H), 2.9 (quartet, 2H)
^{13}C-NMR: δ/ppm 10, 41, 175
IR : 1792 cm^{-1}

39. **^{1}H NMR** : δ/ppm 1.1 (triplet, 3H), 2.4 (quartet, 2H), 11.7 (singlet, 1H, D_2O exchange)
^{13}C-NMR: δ/ppm 9, 27, 181
IR : ~3400 cm^{-1} (broad), 1716 cm^{-1}.

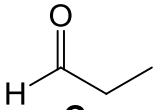
40. **^{1}H-NMR**: δ/ppm 1.2 (triplet, 3H), 2.6 (singlet, 1H, D_2O exchange), 3.7 (quartet, 2H)
^{13}C-NMR: δ/ppm 18, 58
IR : ~3300 cm^{-1} (broad)



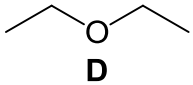
A



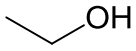
B



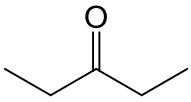
C



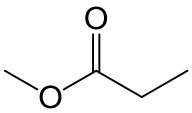
D



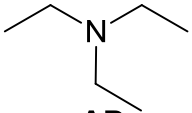
E



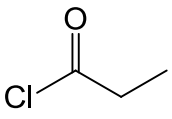
AB



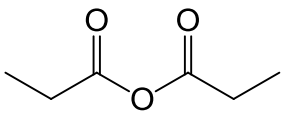
AC



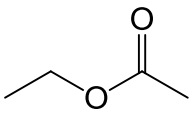
AD



AE



BC



BD


BE

Cont'd -->

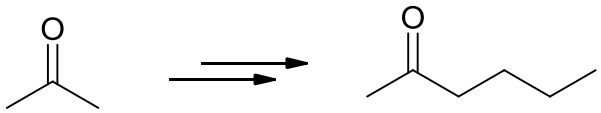
8% **PART 6: SYNTHESIS**

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.

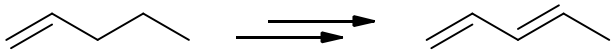
WRITE YOUR ANSWERS IN THE EXAM BOOKLET PROVIDED.

DO NOT SHOW MECHANISMS.

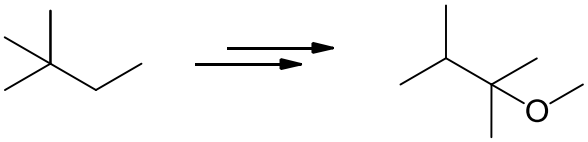
A.



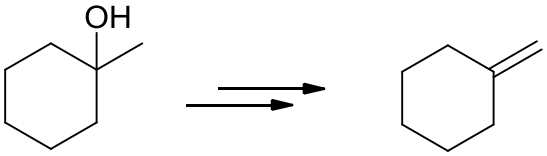
B.



C.



D.



10% PART 7: MECHANISMS

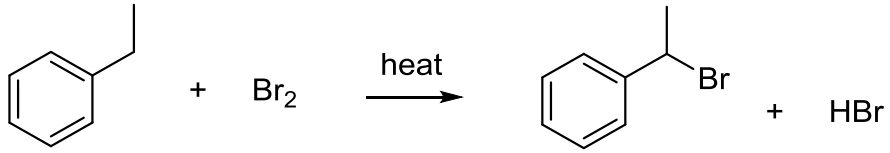
WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED

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

NO REAGENTS OTHER THAN THOSE ALREADY SHOWN ARE REQUIRED.

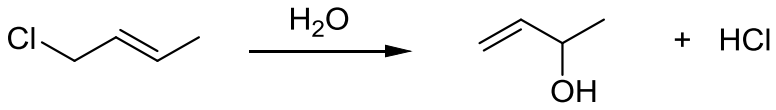
(5%) PART A: Use a curly arrow mechanism to explain ONE of the following reactions:

i.



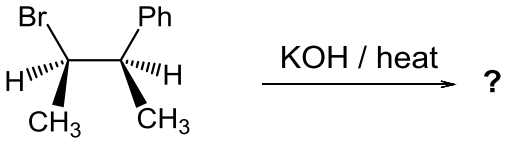
OR

ii.



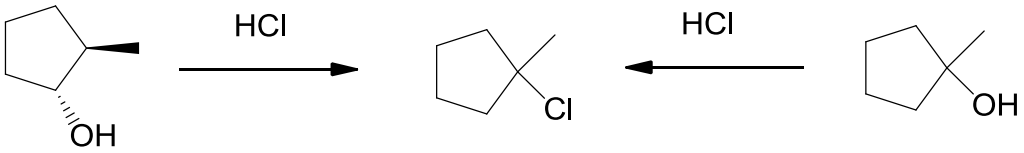
(5%) PART B: Use a curly arrow mechanism to explain ONE of the following reactions:

i. Predict the major product of the following reaction by showing the mechanism.



OR

ii. The two isomeric alcohols shown below both react with HCl to form the alkyl chloride shown. Draw curly arrow mechanisms to show how each alcohol reacts to give the product shown. Briefly justify your choice.



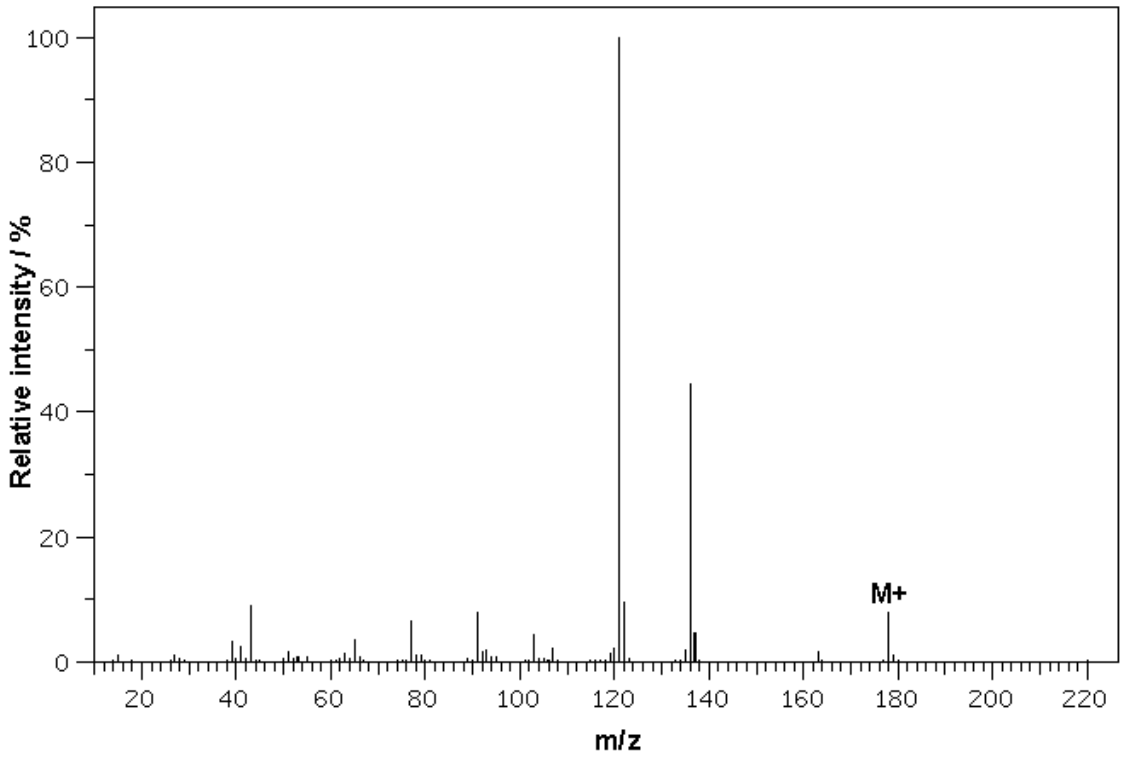
Cont'd -->

10% PART 8: SPECTROSCOPY

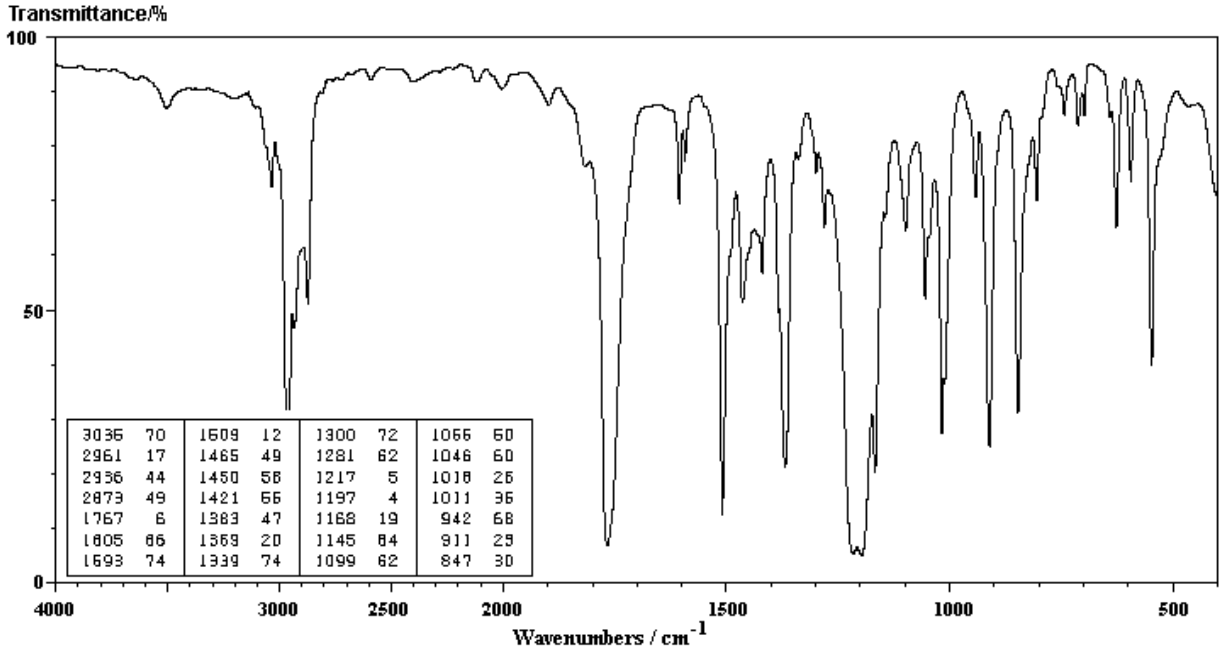
WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED. Show your workings as PARTIAL marks will be given.

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

Mass Spectrum:



IR Spectrum:



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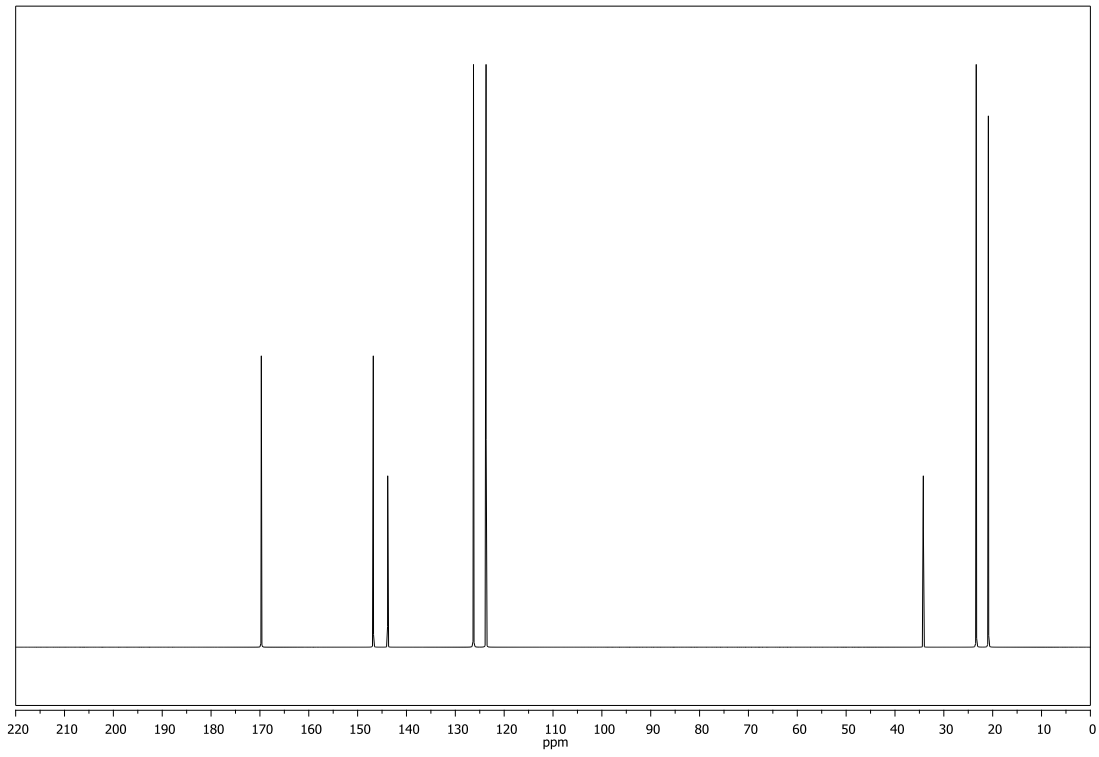
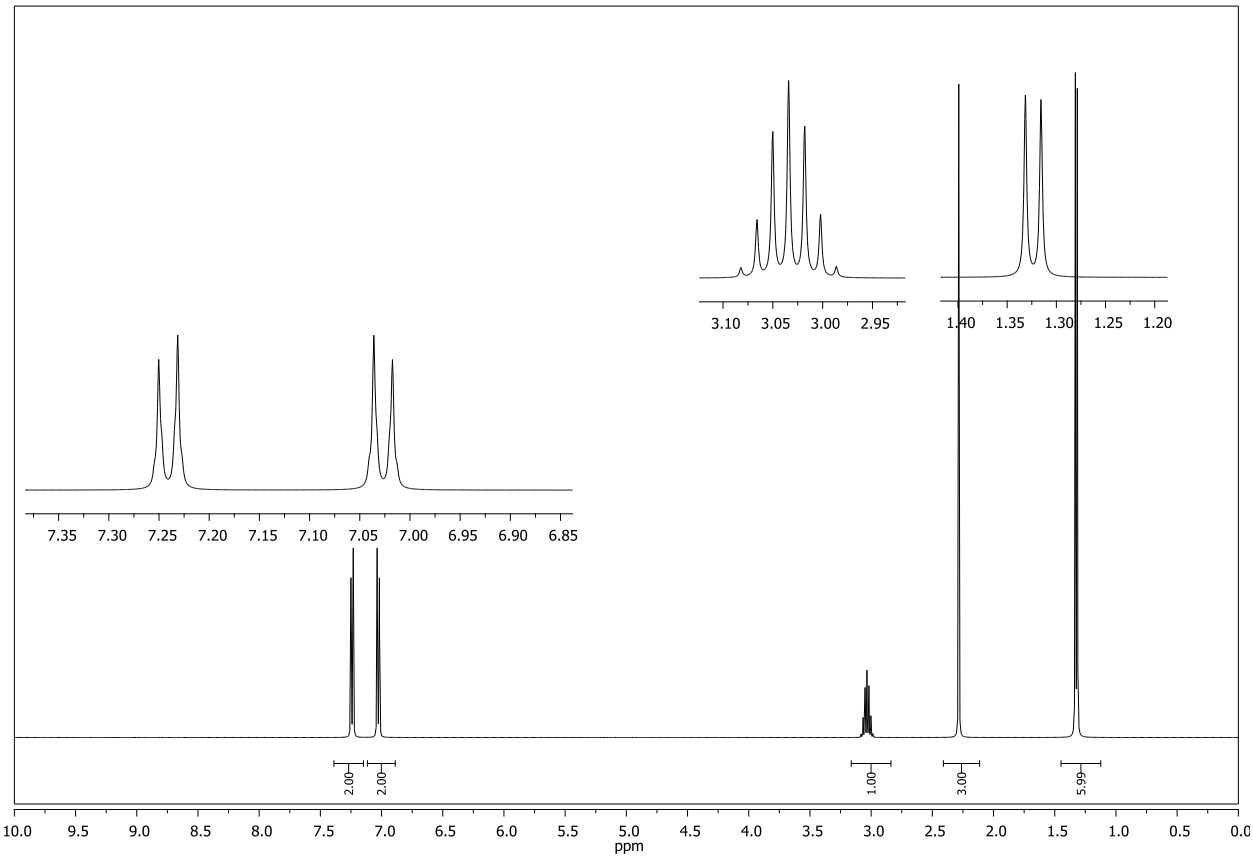
^{13}C-NMR:



^{1}H-NMR:



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10% PART 9: STRUCTURE DETERMINATION

WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED

Hydrocarbon, **H**, C_5H_{12}, was photochlorinated using Cl_2 and u.v. light. This gave four isomeric monochlorinated compounds **A**, **B**, **C** and **D**. The percentage yield of these products was such that **A** > **B** > **C** > **D**. Of these four compounds, **A** and **B** were chiral.

The four alkyl chlorides were then tested under two sets of reaction conditions for comparison a) NaI in acetone and, b) $AgNO_3$ in aqueous ethanol.

With NaI in acetone the relative rates of reaction were **D** > **B** > **A** > **C**

With $AgNO_3$ in aqueous ethanol, the relative rates of reaction were **C** > **A** > **B** ≈ **D**

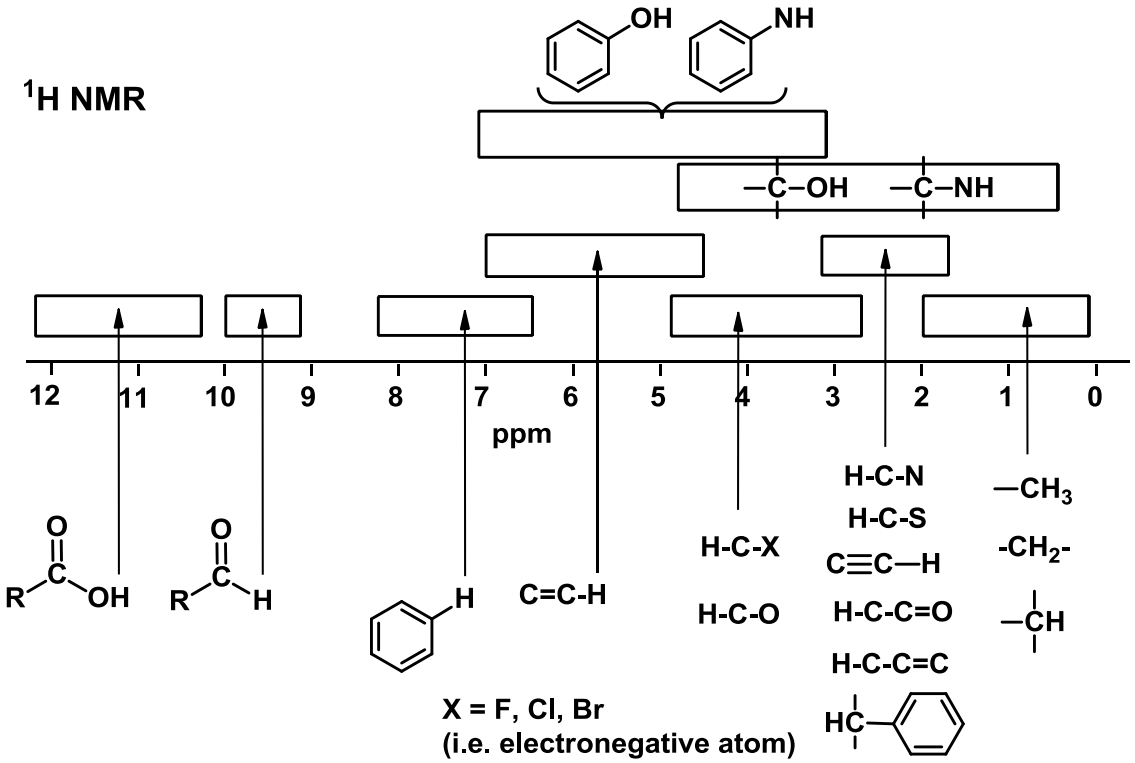
The proton decoupled C13 NMR of the original hydrocarbon **H** was obtained and was found to contain the following peaks: 36, 30, 19 and 12 ppm.

- **Identify A, B, C, D and H (only structures are needed)**
- **Draw a 3D representation of the structure of A and give its IUPAC systematic name.**

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

Cont'd -->

SPECTROSCOPIC TABLES



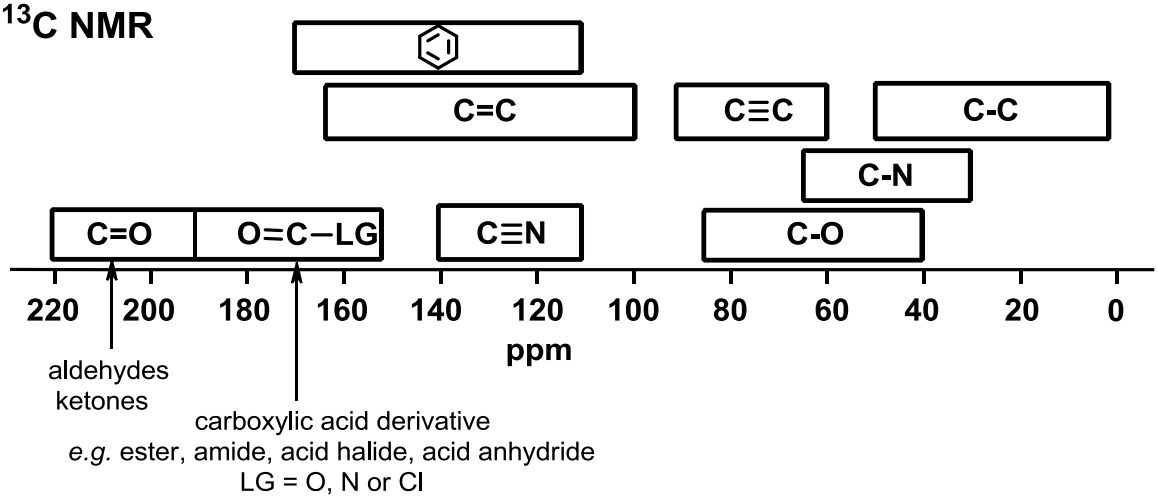
^{1}H NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm

R =	methyl $-CH_3$	methylene $-CH_2-$	methyne $-CH$
R–C—	0.9	1.4	1.5
R–C=C	1.6	2.3	2.6
R–C(=O)–	2.1	2.4	2.5
R–N	2.2	2.5	2.9
R–Ar	2.3	2.7	3.0
R–Br	2.7	3.3	4.1
R–Cl	3.1	3.4	4.1
R–O—	3.3	3.4	3.7

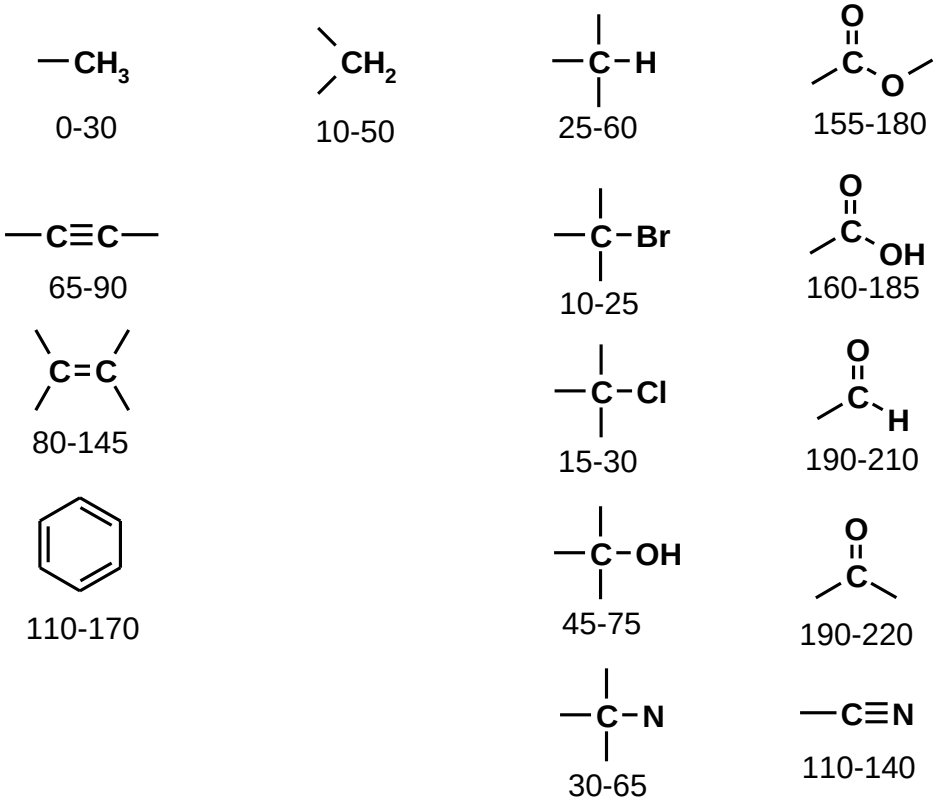
other	
sp^3C-OH	1-5
sp^3C-NH	1-3
C≡CH	2.5
C=C(H)–	4.5-6.5
H–Ar	6.5-8
R–C(=O)–H	9-10
R–C(=O)–OH	9-12

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)