UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

FINAL EXAMINATION

CHEMISTRY 351

December 13th 2010 Time: 3 Hours

READ ALL THE INSTRUCTIONS CAREFULLY

PLEASE WRITE YOUR NAME, STUDENT I.D. NUMBER ON ***BOTH*** YOUR EXAM ANSWER BOOKLET AND 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 - 42, 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. Use a pencil only and ***not ink***. 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.

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15% PART 1: RELATIVE PROPERTIES

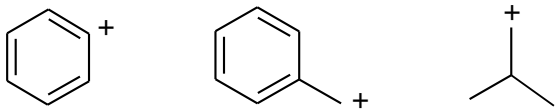
ANSWER ANY TEN (10) OF QUESTIONS 1 TO 12.

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.

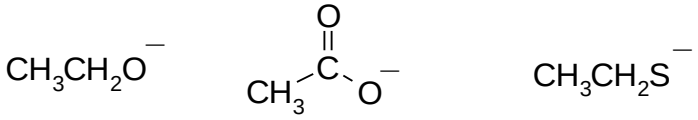
A.	**i > ii > iii**	**D**.	**ii > iii > i**
B.	**i > iii > ii**	**E**.	**iii > i > ii**
C.	**ii > i > iii**	**AB**.	**iii > ii > i**

1. The relative stability of the following carbocations:



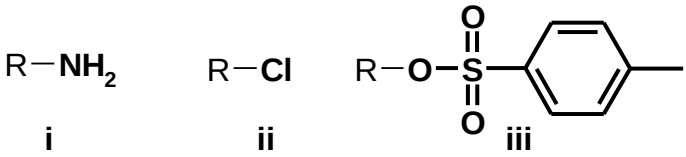
i **ii** **iii**

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



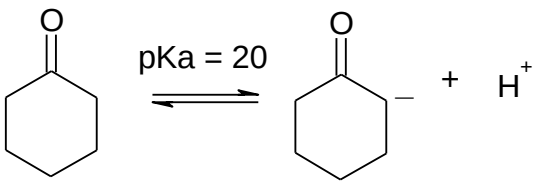
i **ii** **iii**

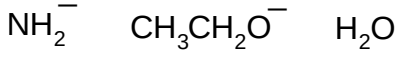
3. The relative leaving group ability of the **bold group** in each of the following:



i **ii** **iii**

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



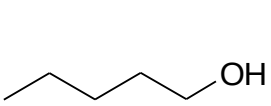


i **ii** **iii**

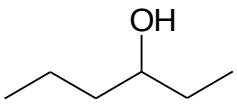
Use the following code to indicate your answers.

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

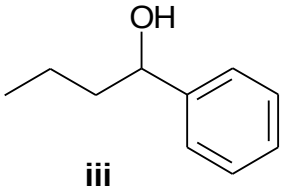
5. The relative rate of reaction of each of the following when heated with sulfuric acid:



i



ii

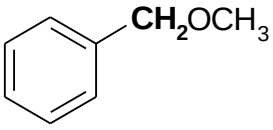


iii

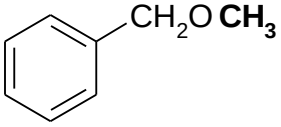
6. The relative rate of reaction of each of the following with NaI / acetone (2-propanone):

i 2-Bromo-2-methylpropane
ii 2-Bromopropane
iii Bromobenzene

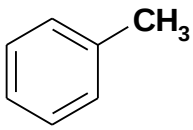
7. The ^{1}H-NMR chemical shifts for the groups shown in **bold** in each of the following structures:



i

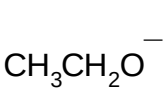


ii

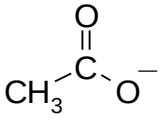


iii

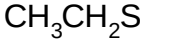
8. The relative basicity of the following:



i



ii

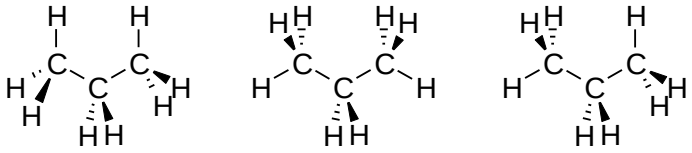


iii

Use the following code to indicate your answers.

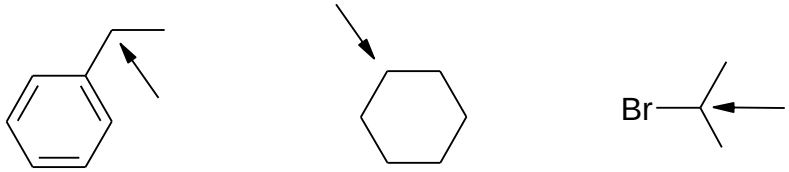
A.	**i** > **ii** > **iii**	**D**.	**ii** > **iii** > **i**
B.	**i** > **iii** > **ii**	**E**.	**iii** > **i** > **ii**
C.	**ii** > **i** > **iii**	**AB**.	**iii** > **ii** > **i**

9. The relative energies of the conformations shown below:



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 :

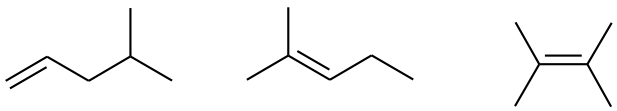


i **ii** **iii**

11. The relative yields of the Zaitsev product produced by the reaction of 2-bromo-2,3-dimethylbutane with each of the following:

$NaOCH_2CH_3$	$NaOCH_3$	$NaOC(CH_3)_3$
i	**ii**	**iii**

12. The relative stability of the following alkenes:



i **ii** **iii**

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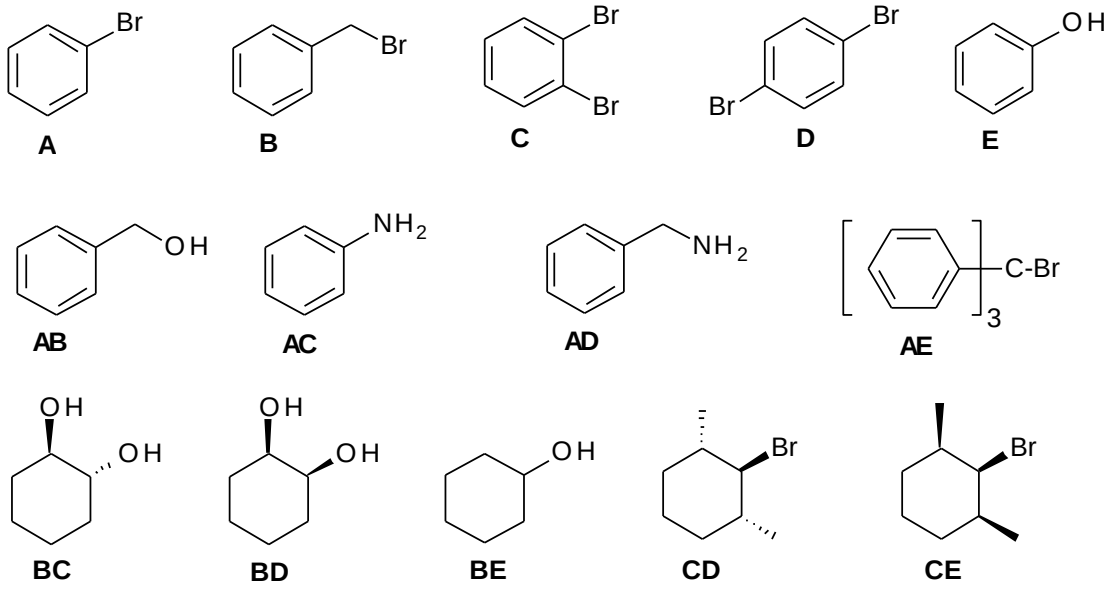
9% **PART 2: MOLECULAR PROPERTIES**

ANSWER ANY SIX (6) OF THE QUESTIONS 13 TO 20.

Use the structures below to answer questions 13-20.



13. Which of the above structures would undergo the fastest S_N1 reaction when treated with water ?

14 Which of the above structures would undergo the fastest S_N2 reaction when treated with NaOH/water ?

15. Which of the above structures would undergo the fastest E2 reaction when heated with potassium t-butoxide in t-butanol ?

16. Which of the above structures is the most acidic compound ?

17. Which of the above structures is the most basic compound ?

18. Which of the above structures would have the smallest dipole moment ?

19. Which of the above structures would have the simplest ^{1}H-NMR spectrum (*i.e.* fewest number of peaks)?

20. Which of the above structures would have the same energy as its ring-flip form?

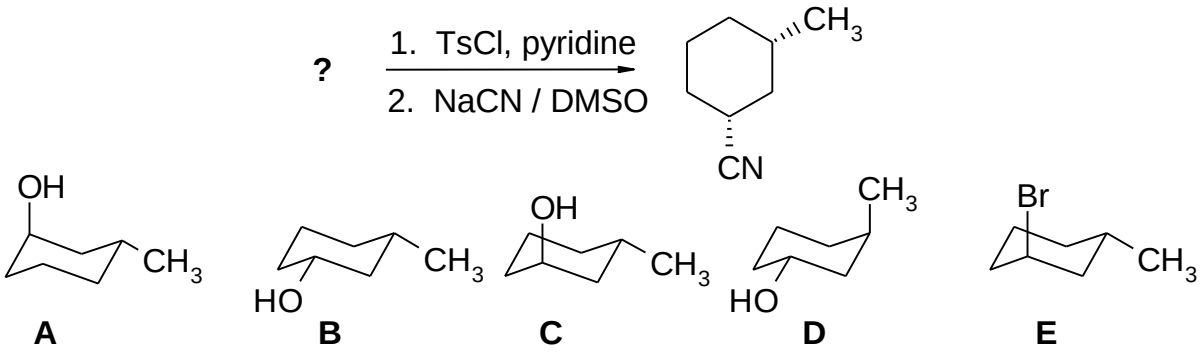
Cont'd -->

14% PART 3: REACTIONS

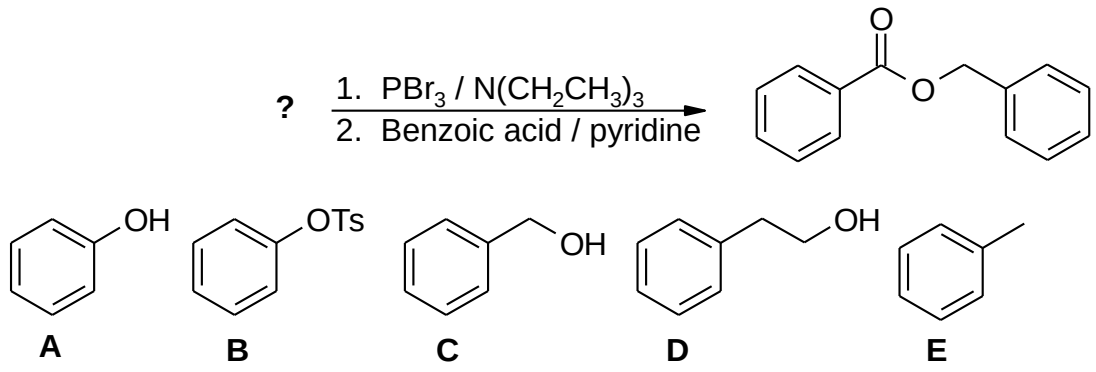
ANSWER ANY SEVEN (7) OF QUESTIONS 21 TO 28.

For each of questions 21-28 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.

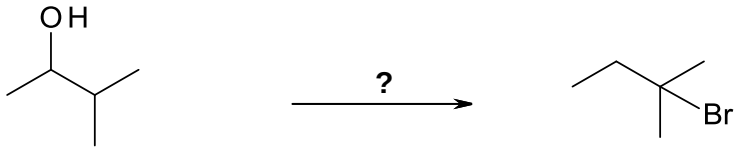
21.



22.



23.



A PBr_3 / $N(CH_2CH_3)_3$

B HBr

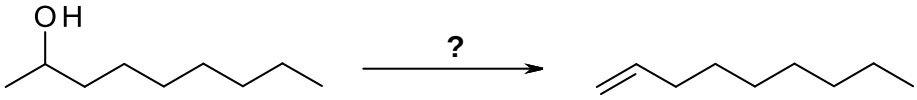
C 1. conc. H_2SO_4
2. PBr_3 / $N(CH_2CH_3)_3$

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

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

Cont'd -->

24.



A conc. H_2SO_4 / heat

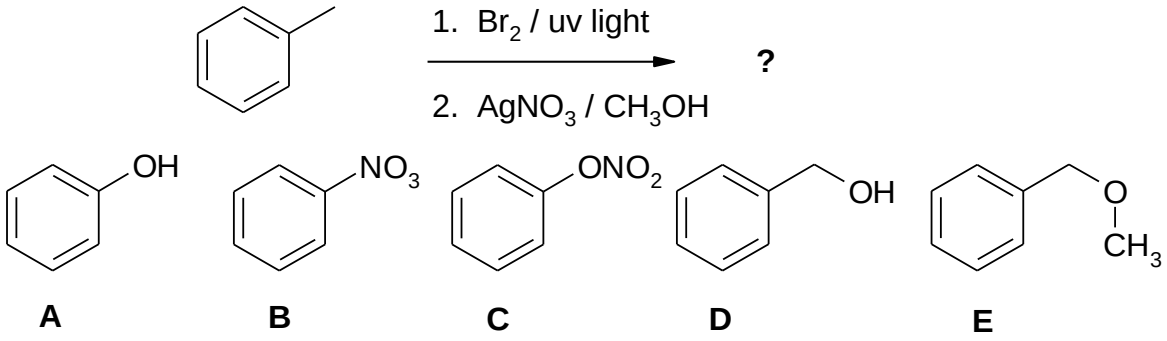
B HBr / heat

C NaOH / heat

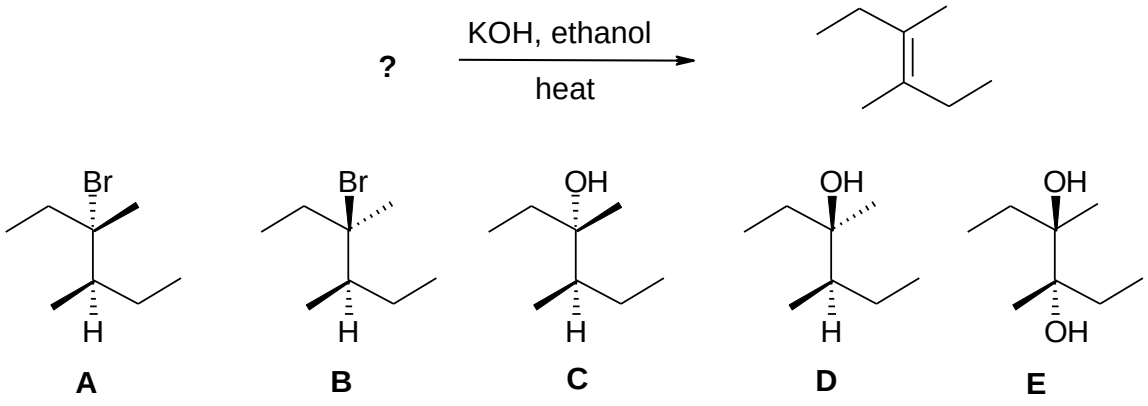
D 1. H_2O / H_2SO_4
2. NaOH / heat

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

25.



26. Select the starting material that reacts at the fastest rate to give the indicated product:



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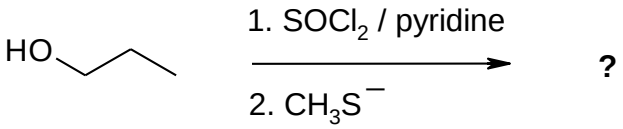
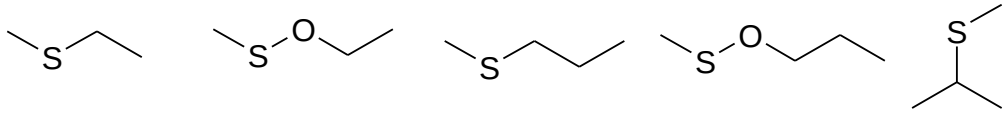
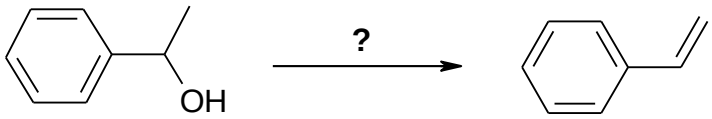
27.





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

28.



A Conc. H_2SO_4 / heat

B NaOH / EtOH / heat

C KO^tBu / EtOH / heat

D $AgNO_3$ / EtOH / heat

E 1. $SOCl_2$/ NEt_3
2. Conc. H_2SO_4 / heat

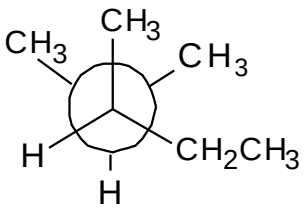
Cont'd -->

12% PART 4: CONFORMATIONAL ANALYSIS

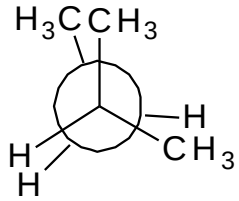
ANSWER SIX (6) OF THE QUESTIONS 29 TO 36.

For each of the questions 29-36 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.

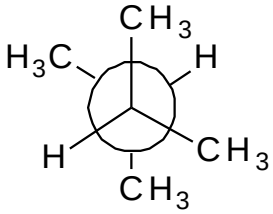
29. Which of the following Newman projections represent conformations of 2,3-dimethylbutane ?



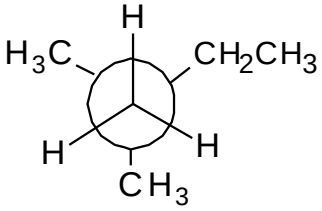
A



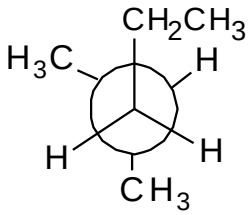
B



C

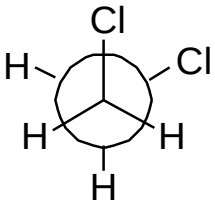


D



E

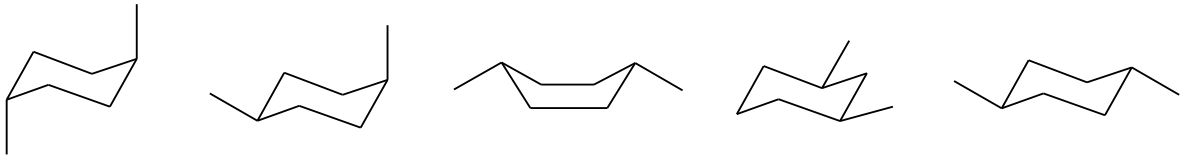
30. What is the **Cl-C-C-Cl** torsional (dihedral) angle in the molecule that is represented by the Newman projection shown below ?



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

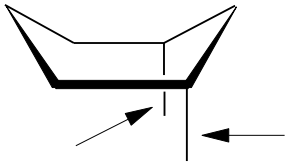
Cont'd -->

31. Which of the following represents **<u>any</u>** conformation that can be adopted by cis-1,4-dimethylcyclohexane ?



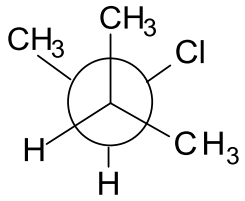
A **B** **C** **D** **E**

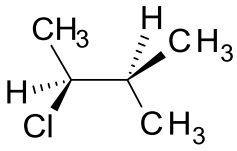
32. Which of the following terms **best** describes the relative position of the two indicated bonds in the cyclohexane conformation shown below?



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

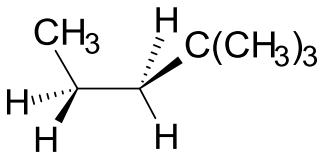
33. Which of the following terms **best** describes the relationship between the two molecules shown below ?





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

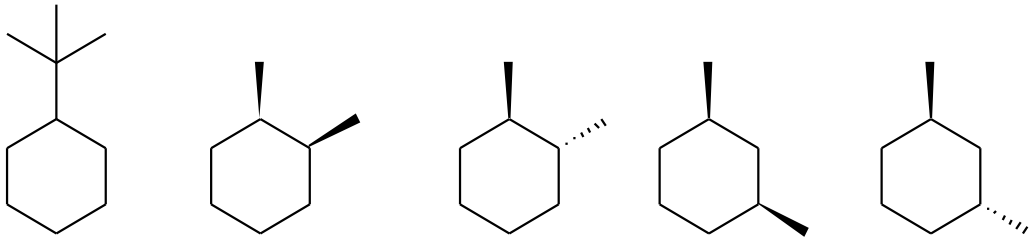
34. What term(s) associated with types of strain can be used to describe the following ?



A Van der Waals
B Torsional (eclipsing)
C 1,3-Diaxial
D Flagpole
E Ring

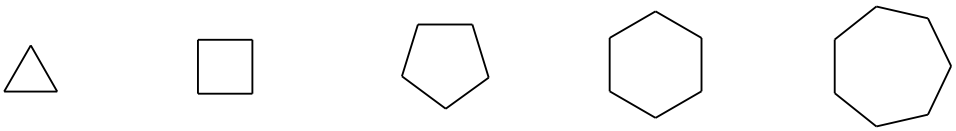
Cont'd -->

35. Which of the following molecules would have the least exothermic heat of combustion ?



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

36. Which of the following structures has the most angle strain per methylene (-CH_2-) unit in its most stable conformation?



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

Cont'd -->

12% PART 5: SPECTROSCOPY

ANSWER ALL SIX (6) OF QUESTIONS 37 TO 42.

For each of questions 37-42 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, m = multiplet.

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

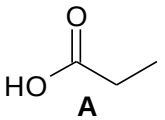
38. **^{1}H NMR** : δ/ppm 1.0 (t, 3H), 2.4 (q, 2H)
^{13}C-NMR: δ/ppm 12, 46
IR : 2974 cm^{-1}

39. **^{1}H NMR** : δ/ppm 0.7 (t, 3H), 0.8 (s, 3H), 1.2 (q, 2H)
^{13}C-NMR: δ/ppm 8, 26, 33, 34
IR : 2964 cm^{-1}

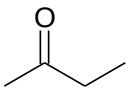
40. **^{1}H NMR** : δ/ppm 1.2 (t, 3H), 2.9 (q, 2H)
^{13}C-NMR: δ/ppm 10, 41, 175
IR : 1792 cm^{-1}

41. **^{1}H NMR** : δ/ppm 1.1 (t, 3H), 2.4 (q, 2H), 11.7 (s, 1H, D_2O exchange)
^{13}C-NMR: δ/ppm 9, 27, 181
IR : ~3400 cm^{-1} (broad), 1716 cm^{-1}.

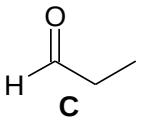
42. **^{1}H-NMR**: δ/ppm 1.2 (t, 3H), 2.6 (s, 1H, D_2O exchange), 3.7 (q, 2H)
^{13}C-NMR: δ/ppm 18, 58
IR : ~3300 cm^{-1} (broad)



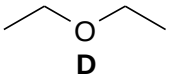
A



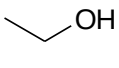
B



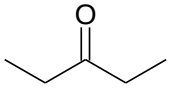
C



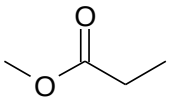
D



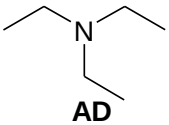
E



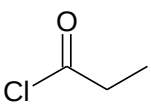
AB



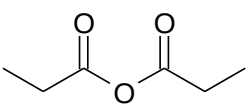
AC



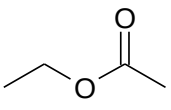
AD



AE



BC



BD


BE

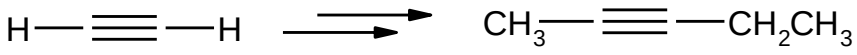
Cont'd -->

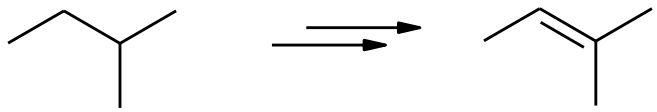
8% PART 6: SYNTHESIS

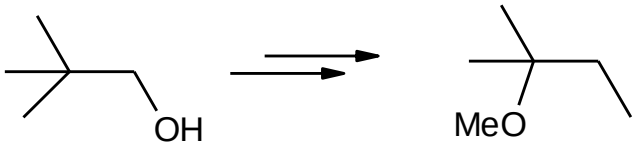
DESIGN EFFICIENT SYNTHESES OF ANY TWO (2) of the following target molecules from the indicated starting materials. In addition, you are allowed to use any alkane with three or fewer carbon atoms, any solvent or inorganic reagent, and any organic reagent that does not become part of the carbon skeleton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

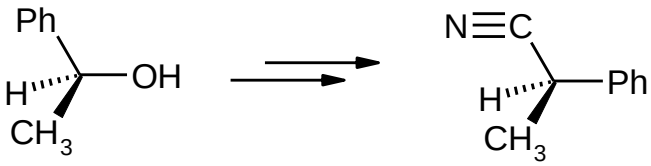
WRITE YOUR ANSWERS IN THE EXAM BOOKLET PROVIDED.

DO NOT SHOW MECHANISMS.

A. 

B. 

C. 

D. 

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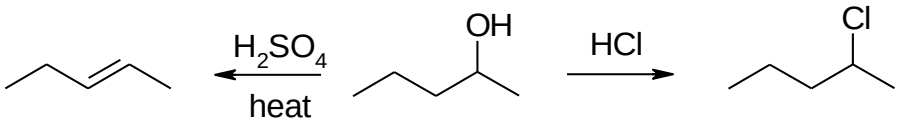
9% PART 7: MECHANISMS

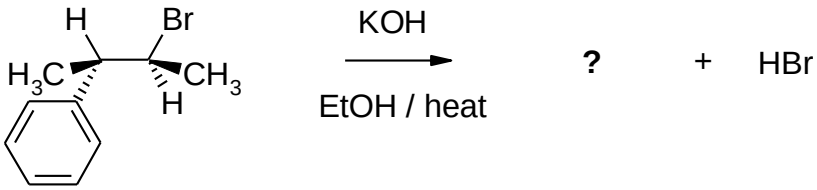
WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED

Use curly arrows to show the mechanism in order to explain **ANY TWO** of the following:

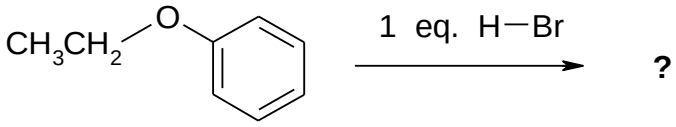
A Draw the reaction mechanism for the reactions of pentan-2-ol shown below. Briefly explain the difference.



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



C Based on the reactions of alcohols with HBr, predict the major product of this reaction by showing the mechanism. Briefly justify your choice.



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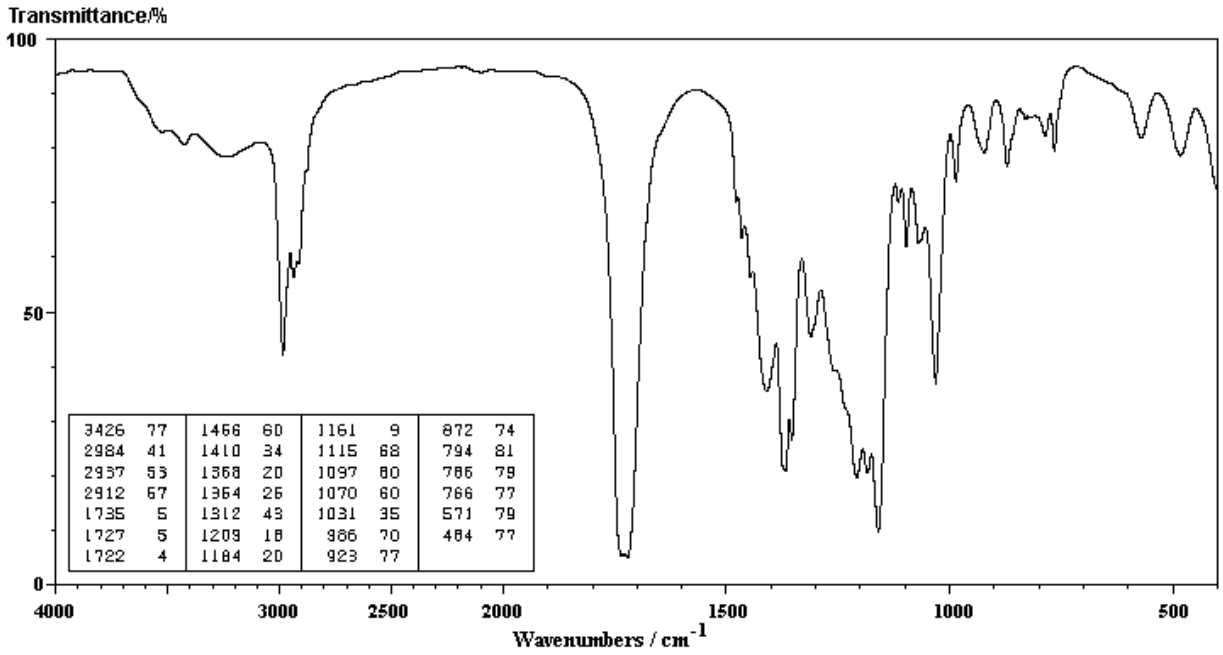
10% **PART 8: SPECTROSCOPY**

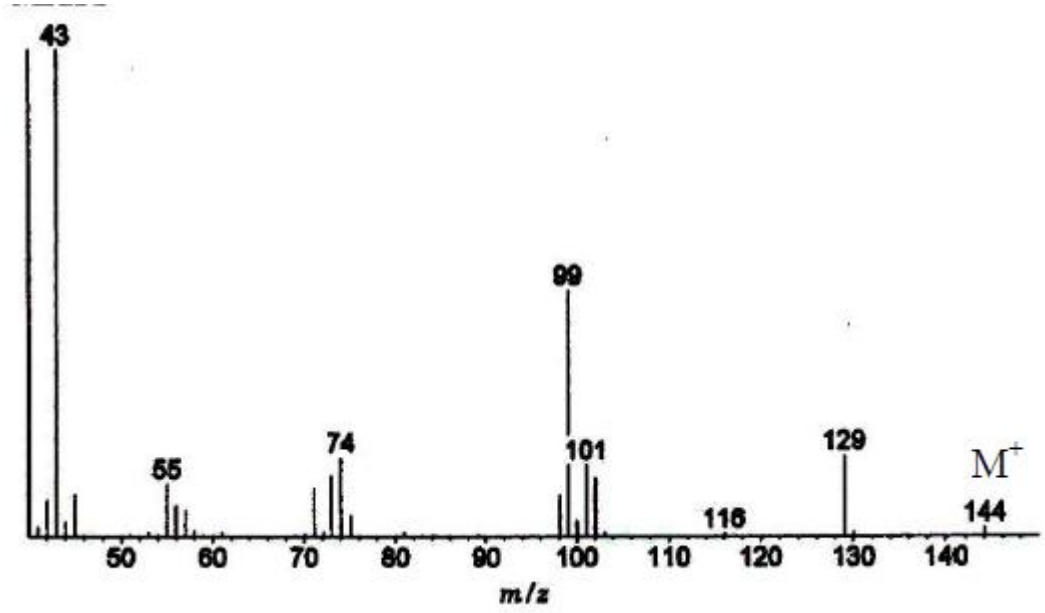
WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED. Show your workings as PARTIAL marks will be given.

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

IR Spectrum:



Mass Spectrum:



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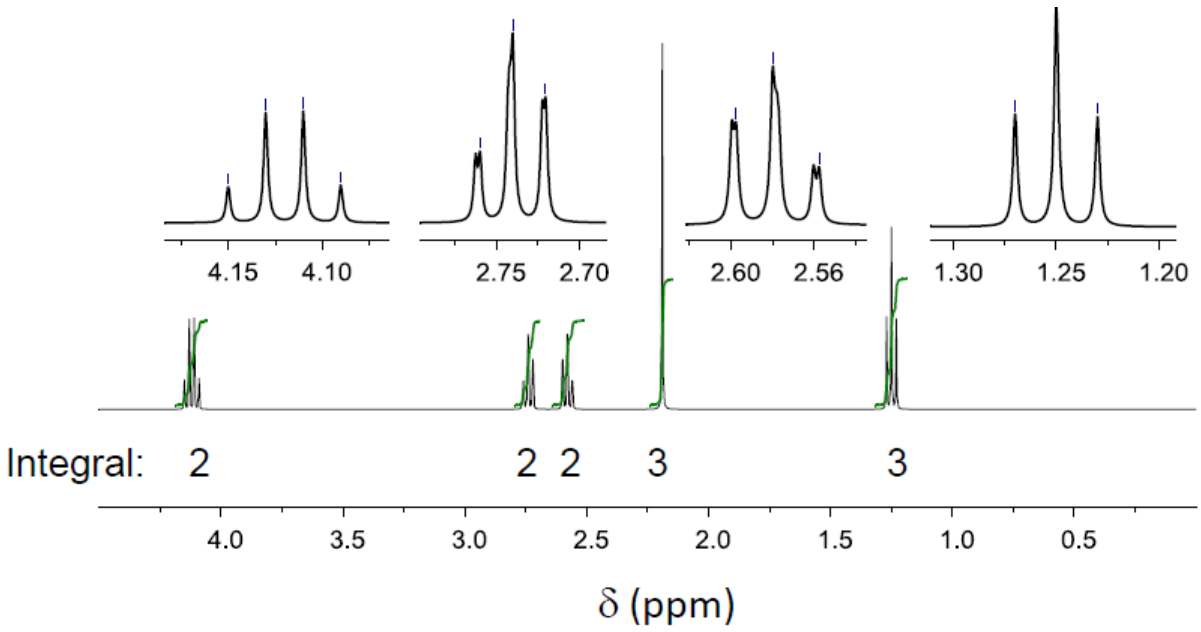
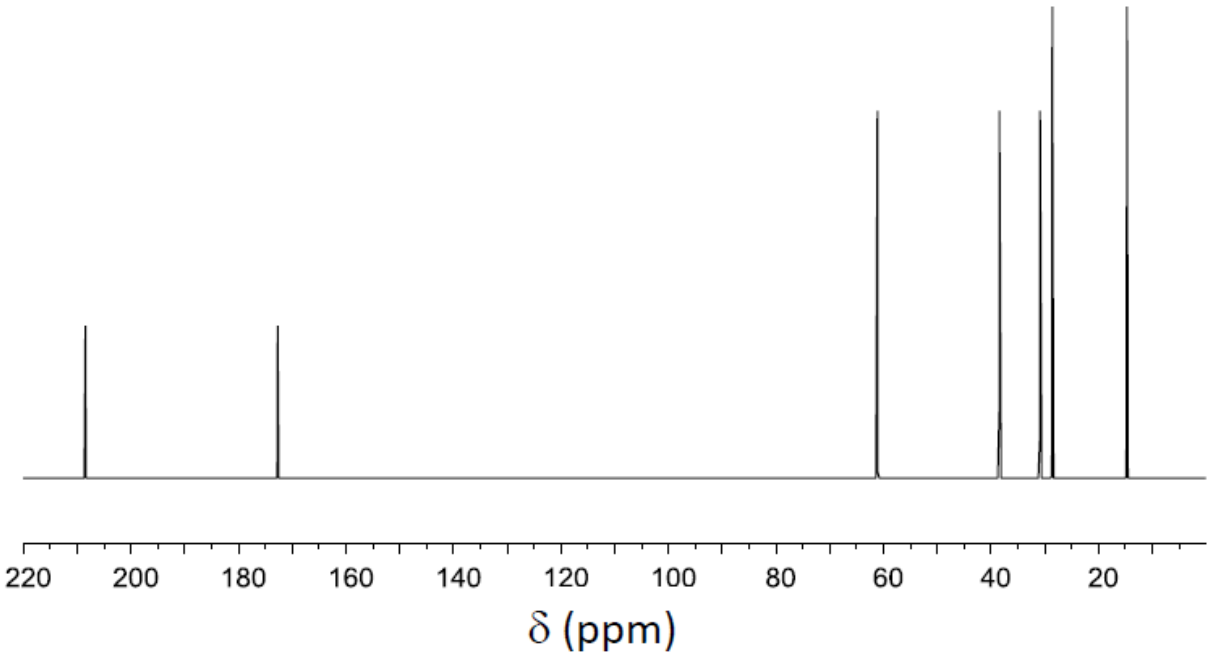
^{1}H-NMR: NOTE: There are no peaks above 4.5ppm. This spectrum includes an enlarged representation of some of the peaks to show more detail.



^{13}C-NMR:



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11% PART 9: STRUCTURE DETERMINATION

WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED

Compound **A** has a molecular formula of $C_9H_{12}O$. The ^{13}C-NMR of **A** has 7 peaks. The IR spectrum of **A** has a broad peak at ~3500 cm^{-1}. If **A** is treated with PBr_3/Et_3N, **B** is formed directly. **B** reacts with hot NaOEt in HOEt to give compound **C** as the major product, and its geometric isomer (diastereomer) **D** as the minor product. When both **C** and **D** are reacted with H_2 using a catalyst (a reaction that converts an alkene into an alkane) they both give 1-phenylpropane as the product.

When **A** is treated with concentrated HBr, compound **E** is formed. **E** reacts rapidly with $CH_3OH/AgNO_3$ to give **F** which has a molecular formula of $C_{10}H_{14}O$. **E** can also react with aqueous Na_2CO_3 to give compound **G** which is a constitutional isomer of **A**. When **G** is treated with concentrated HBr, and when 1-phenylpropane is treated with Br_2 under UV light, **E** is obtained as the major product.

Molecules **A**, **B**, **E**, **F**, **G** are chiral.

1. Identify **A**-**G** (only structures are needed).
2. Draw the structure of 1-phenylpropane.
3. Draw a constitutional isomer of 1-phenylpropane.
4. Give the <u>complete</u> IUPAC names for the structures you draw for **C** and **D**.

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

ASC / TGB / IRH 2010

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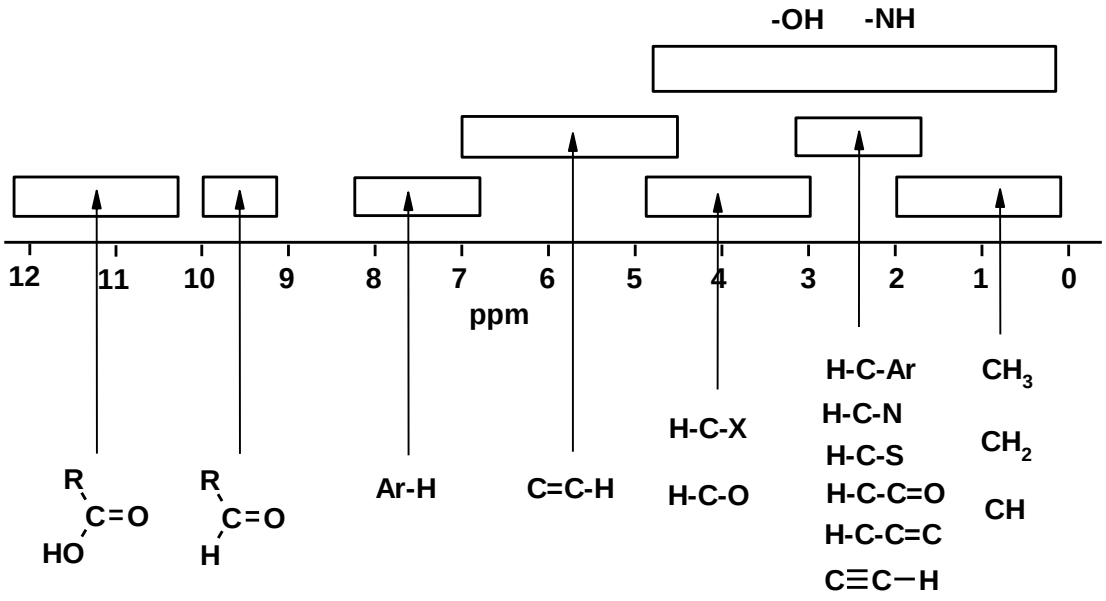
SPECTROSCOPIC TABLES

^{1}H NMR



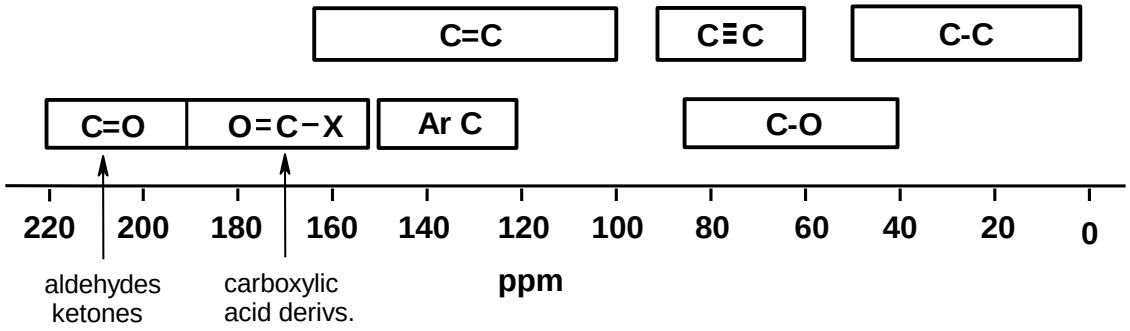
^{1}H NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm

	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
O C R	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

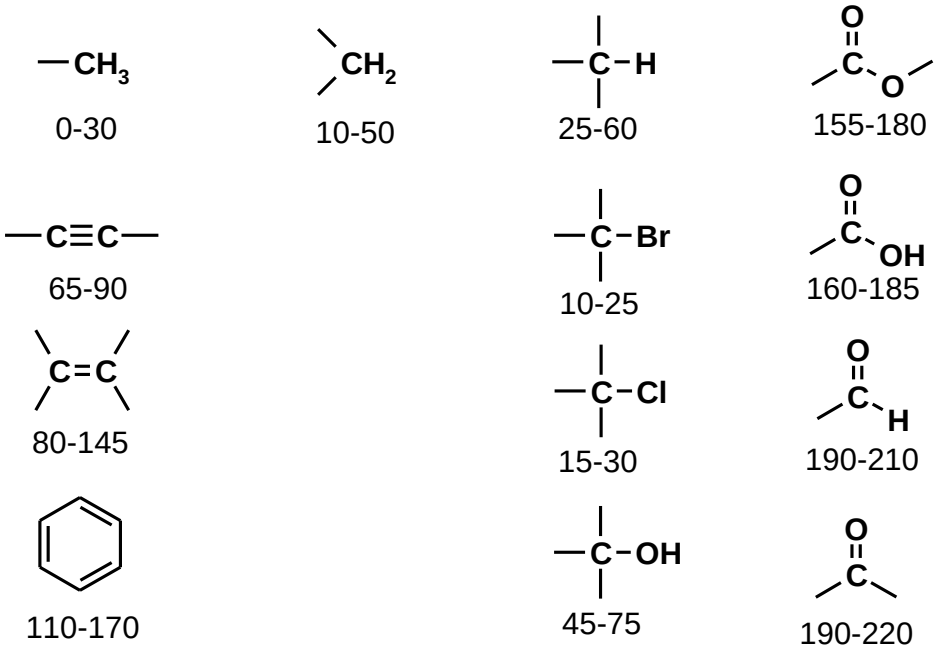
other	
-OH	1-5
-NH	1-3
C≡CH	2.5
C=C H	5.5
Ar-H	7.3
O C R H	10
O C R OH	9-12

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)