UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

FINAL EXAMINATION

CHEMISTRY 351

December 19th, 2006

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 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 - 44, 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.

20% PART 1 RELATIVE PROPERTIES

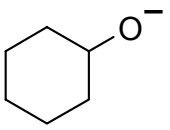
ANSWER ANY TEN (10) OF QUESTIONS 1 TO 12.

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

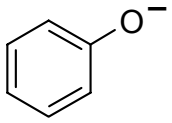
Use the following code to indicate your answers

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

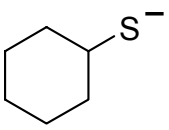
1. The relative nucleophilicity of the following :



i

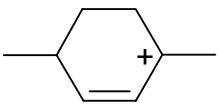


ii

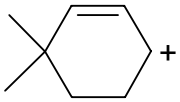


iii

2. The relative stability of the following carbocations :



i



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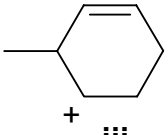
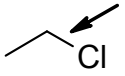
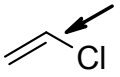


iii

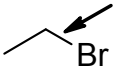
3. The stretching frequency in the infrared spectrum of the bonds indicated below:



i

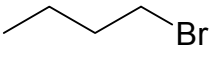


ii

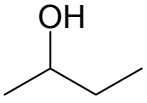


iii

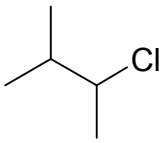
4. The relative rates of reaction of each of the following with NaN_3 in acetone:



i



ii



iii

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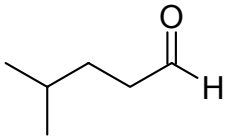
Use the following code to indicate your answers

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 number of peaks expected in the normal proton decoupled ^{13}C NMR spectrum for each of the following:



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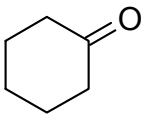

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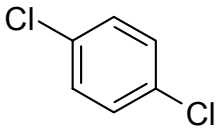
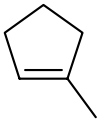
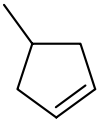


iii

6. The relative stability of following substituted cyclopentenes :



i



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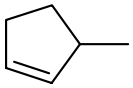
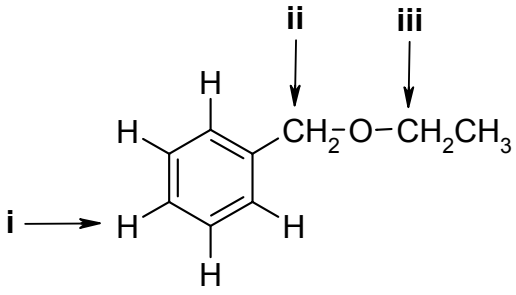
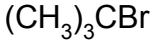


iii

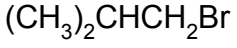
7. The ^{1}H-NMR chemical shifts for the groups indicated in the following structure :



8. The relative rates of reaction of each of the following when heated with KOH in ethanol :



i



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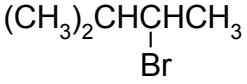
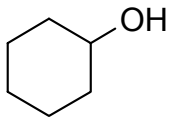


iii

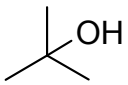
Use the following code to indicate your answers

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 rates of reaction of each of the following when heated with H_2SO_4 :



i



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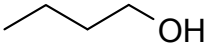
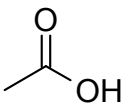


iii

10. The relative amount of the conjugate base formed when each of the following reacts with of 1 mole equivalent of sodium methoxide:

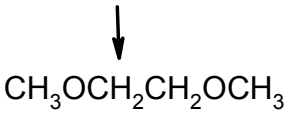


i

ii

iii

11. The number of lines in the H-nmr coupling patterns for the H atoms indicated in each of the following :



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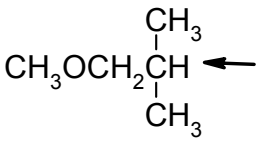
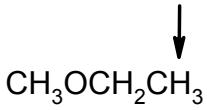
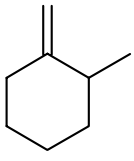


ii

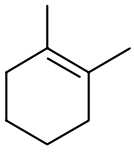


iii

12. The relative heats of combustion of the following alkenes (least exothermic to most exothermic):



i



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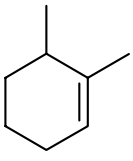


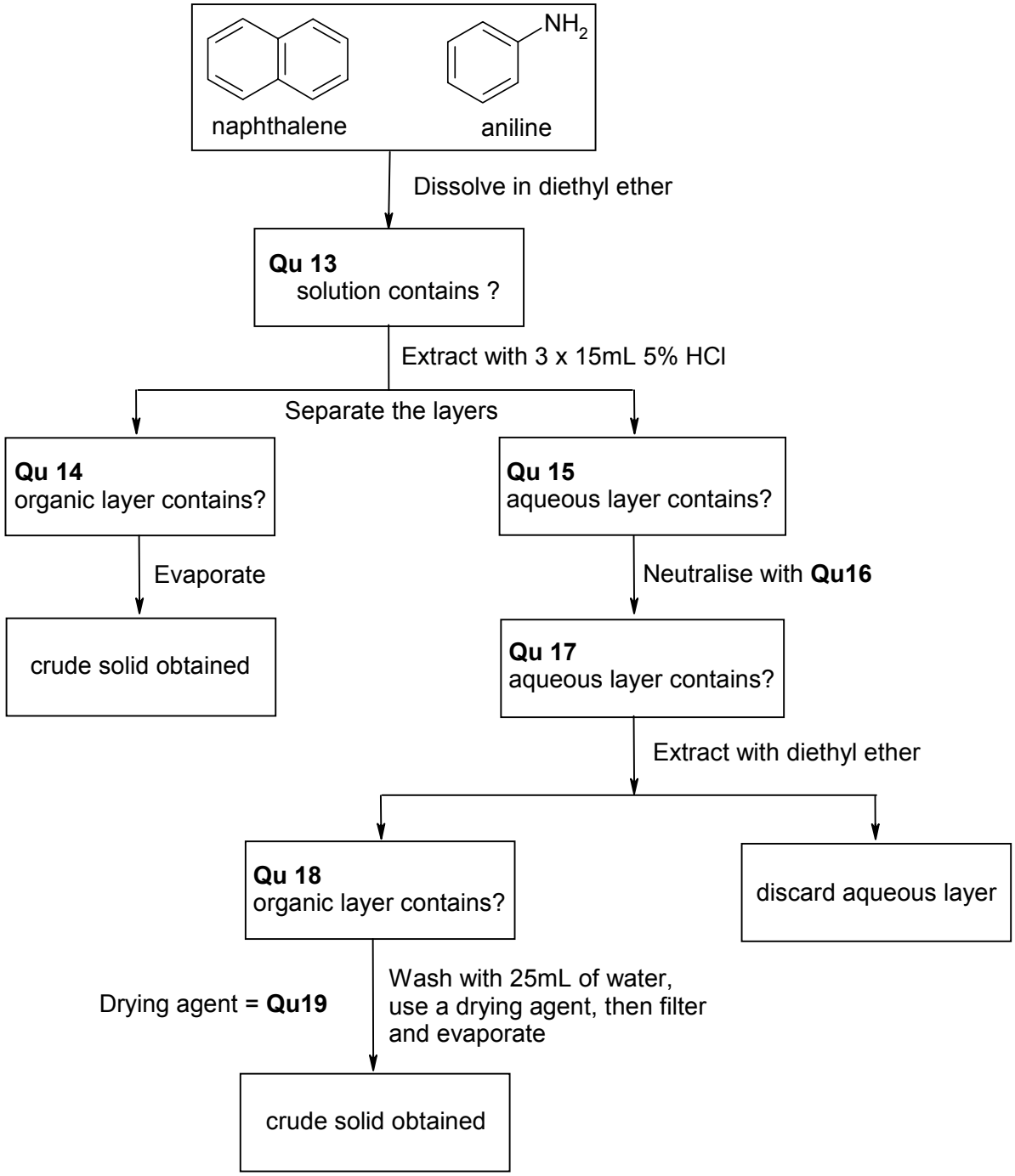
iii

9% PART 2: LABORATORY

ANSWER ALL SEVEN (7) OF THE QUESTIONS 13-19.

Questions 13-19 are based on the following scheme for the separation of an organic mixture from the laboratory component of the course.

In some questions, MORE THAN ONE ANSWER MAY BE REQUIRED FOR THE ANSWER TO BE COMPLETELY CORRECT.



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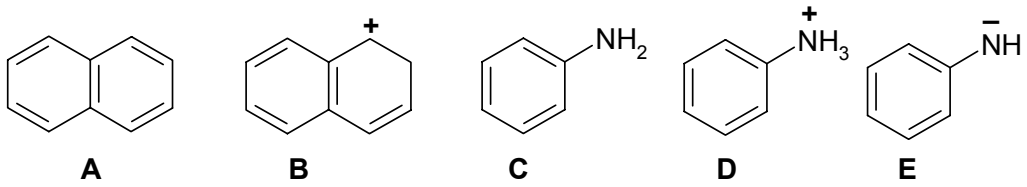


Use the key provided above to answer questions 13, 14, 15, 17, 18

13. At the point indicated in the extraction scheme **Qu 13**, which of the species would be present in the solution ?

14. At the point indicated in the extraction scheme **Qu 14**, which of the species would be present in the organic layer ?

15. At the point indicated in the extraction scheme **Qu 15**, which of the species would be present in the aqueous layer ?

16. Based on the extraction scheme, which of the following is the **best** choice to neutralise the aqueous layer ?

A. 15mL of 5% NaOH **B.** 20mL of 10% NaOH **C.** 45mL of 5% NaOH
D. 15mL of 5% HCl **E.** 20mL of 10% HCl **AB.** 45mL of 5% HCl

17. At the point indicated in the extraction scheme **Qu 17**, which of the species would be present in the aqueous layer ?

18. At the point indicated in the extraction scheme **Qu 18**, which of the species would be present in the organic layer ?

19. Which of the following is an example of a suitable drying agent ?

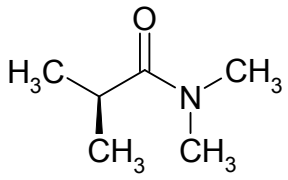
A. charcoal **B.** silver nitrate **C.** sodium iodide
D. magnesium sulfate **E.** sulfuric acid **AB.** iodine

Cont'd -->

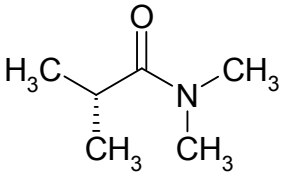
10% PART 3: MOLECULAR PROPERTIES

ANSWER ALL TEN (10) of the questions 20-29.
In some questions, MORE THAN ONE ANSWER MAY BE REQUIRED FOR THE ANSWER TO BE COMPLETELY CORRECT.

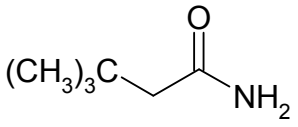
Use the following information and structures A-E to answer questions 20 - 23



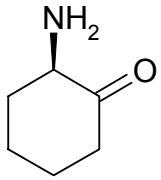
A



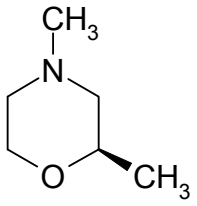
B



C



D



E

20. Which structure(s) has / have an sp^3 hybridized nitrogen ?

21. Which structure(s) has / have a chirality center ?

22. Which structure(s) is / are **not** an isomer of N,N-diethylaminoethanal ?

23. Which structure(s) is / are protonated to greater than 50% when reacted with one mole equivalent with CH_3CO_2H ?

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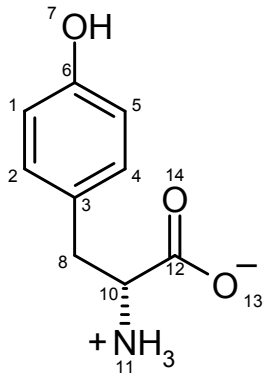
For each of the questions 24-29 about the amino acid TYROSINE (right), select the answer from those provided.



24. What is the index of hydrogen deficiency (IHD) of **TYROSINE** ?

A. 2 **B**. 3 **C**. 4 **D**. 5 **E**. 6

25. How many types of hydrogen are there in **TYROSINE** ?

A. 5 **B**. 6 **C**. 7 **D**. 8 **E**. 9

26. In **TYROSINE**, what are the hydridisations of **C10, N11 and O13** respectively ?

A. sp^3, sp^2, sp^2 **B**. sp^2, sp^3, sp^3 **C**. sp^2, sp^2, sp^3
D. sp^3, sp^3, sp^2 **E**. sp^2, sp^3, sp^2 **AB**. sp^2, sp^2, sp^2

27. In **TYROSINE**, what is the oxidation state of **C6**?

A. -3 **B**. -2 **C**. 1- **D**. 0 **E**. +1 **AB**. +2 **AC**. +3

28. In **TYROSINE**, what is the oxidation state of **N11** ?

A. -3 **B**. -1 **C**. 0 **D**. +1 **E**. +2 **AB**. +3 **AC**. +4

29. In **TYROSINE**, what is the approximate pK_a for the loss of the first proton from **N11** ?

A. 0 **B**. 5 **C**. 10 **D**. 20 **E**. 35

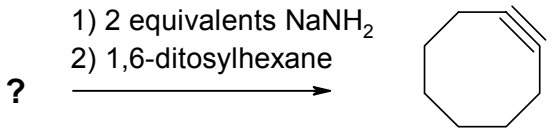
Cont'd -->

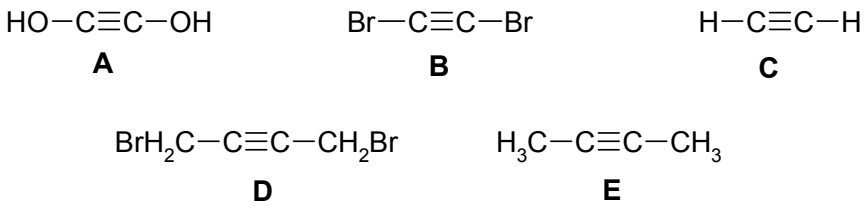
12% PART 4: REACTIONS

ANSWER ANY EIGHT (8) OF QUESTIONS 30-38.

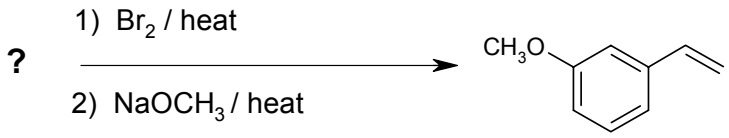
For each of questions 30-38 select the MISSING component (the starting material, the product or the reagents) required in order to BEST complete each of the reaction schemes.

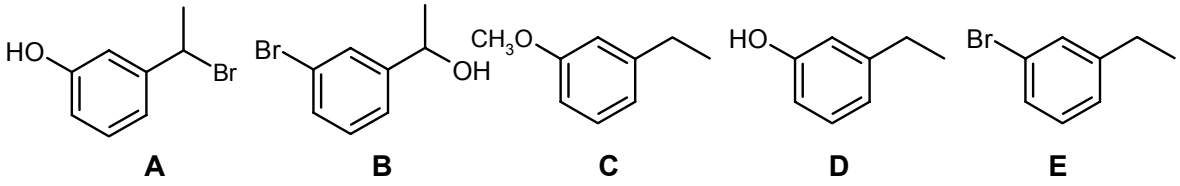
30.



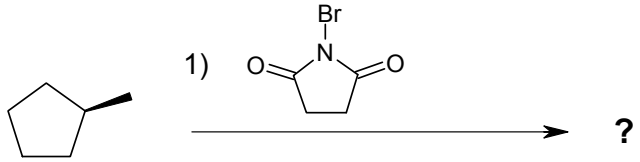


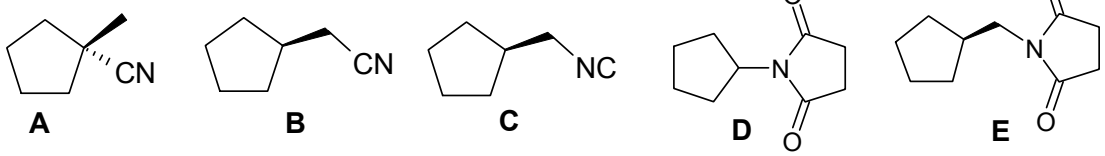
31.





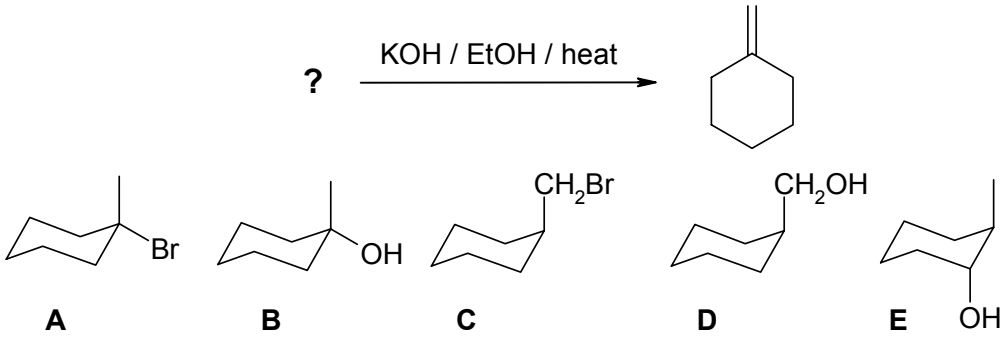
32.



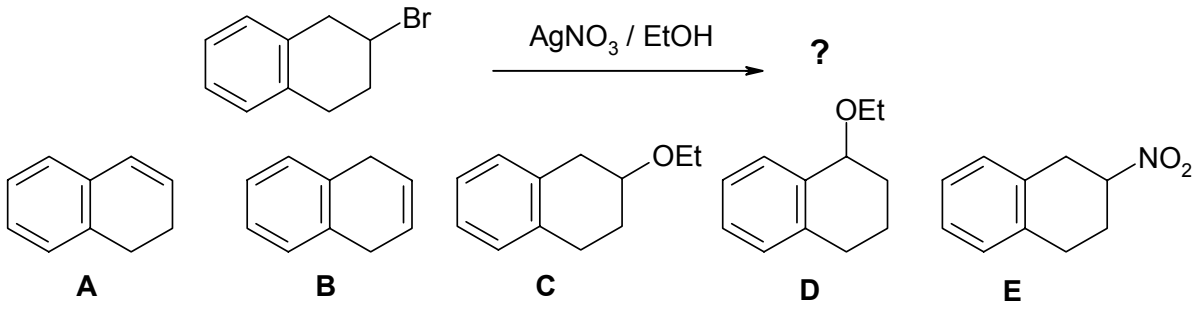


Cont'd -->

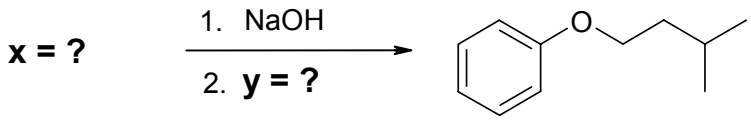
33.



34.



35.



A **x** = phenol **y** = 1-bromo-2-methylbutane

B **x** = benzyl alcohol **y** = 1-bromo-2-methylbutane

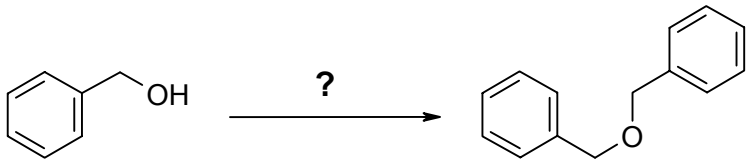
C **x** = phenol **y** = 1-bromo-3-methylbutane

D **x** = benzyl alcohol **y** = 1-bromo-3-methylbutane

E **x** = 3-methylbutanol **y** = bromobenzene

Cont'd -->

36.



A. 1. HBr 2. benzylmethanol

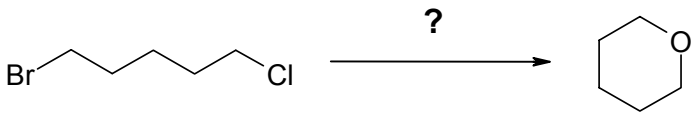
B. 1. HBr 2. phenol, pyridine

C. 1. HBr 2. diphenyl ether, pyridine

D. 1. HBr 2. benzyl bromide

E. 1. KO^tBu 2. benzyl bromide

37.



A. NaOH

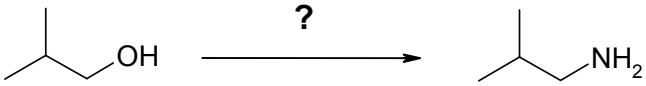
B. CH_3OCH_3, heat

C. Na, H_2O, heat

D. 1. NaSH 2. TsCl, pyridine 3. NaOH, H_2O

E. 1. TsCl, pyridine 2. NaOH, H_2O

38.



A. 1. PBr_3, NEt_3 2. excess NH_3

B. 1. N-bromosuccinimide 2. excess NH_3

C. 1. NaBr 2. excess NH_3

D. H_3O^+, NH_3, heat

E. H_3O^+, $NaNH_2$, heat

Cont'd -->

12% PART 5: SPECTROSCOPY

ANSWER ALL SIX (6) OF QUESTIONS 39 - 44.

For each of questions 39-44 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, dd = doublet of doublets, ex = exchangeable

39. **^{1}H-NMR**: δ/ppm 1.1 (t, 3H), 2.4 (q, 2H)
^{13}C-NMR: δ/ppm 7.9, 36, 212
IR: 1716 cm^{-1}

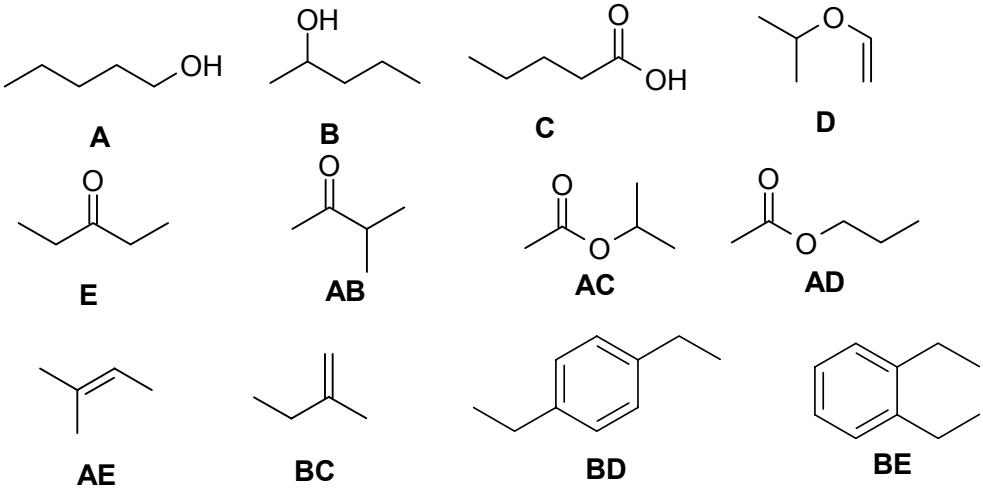
40. **^{1}H-NMR**: δ/ppm 1.0 (t, 3H), 1.7 (s, 3H), 2.0 (q, 2H), 4.7 (m, 2H)
^{13}C-NMR: δ/ppm 12.4, 22.4, 30.7, 109, 148
IR: 1650 cm^{-1}

41. **^{1}H-NMR**: δ/ppm 1.2 (d, 6H), 4.0 (dd, 1H), 4.1 (septet, 1H), 4.2 dd, 1H), 6.3 (dd, 1H)
^{13}C-NMR: δ/ppm 22.0, 71.7, 88.1, 151
IR: 1635, 1202, 1122 cm^{-1}

42. **^{1}H-NMR**: δ/ppm 0.9 (t, 3H), 1.4 (m, 4H), 1.6 (p, 2H), 2.4 (s, 1H, D_2O ex), 3.6 (t, 2H)
^{13}C-NMR: δ/ppm 14.1, 22.7, 28.2, 32.5, 62.7
IR: 3100-3500 cm^{-1}

43. **^{1}H-NMR**: δ/ppm 1.22 (t, 3H), 2.6 (q, 2H) 7.1 (s, 2H)
^{13}C-NMR: δ/ppm 15.7, 28.5, 127.8, 141.4
IR: 1516, 1462 cm^{-1}

44. **^{1}H NMR** : δ/ppm 1.2 (d, 6H), 2.0 (s, 3 H), 5.0 (septet, 1H)
^{13}C-NMR: δ/ppm 21.3, 21.8, 67.5, 170
IR = 1738, 1248 cm^{-1}



Cont'd -->

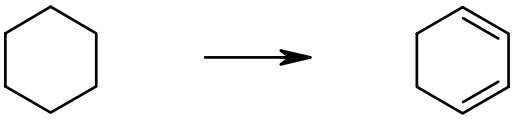
6% PART 6: SYNTHESIS

DESIGN EFFICIENT MULTISTEP SYNTHESES OF ANY TWO (2) of the following target molecules from the starting material indicated. In addition, you are allowed to use any other hydrocarbon with three or less carbon atoms and any solvent or inorganic reagent that does not become part of the carbon skeleton in the product.

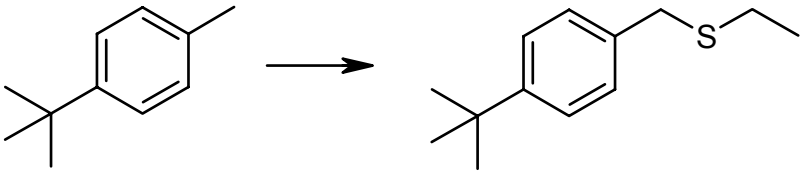
WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED.

DO NOT SHOW MECHANISMS.

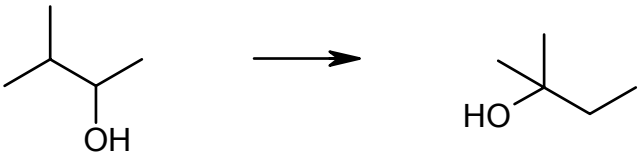
A



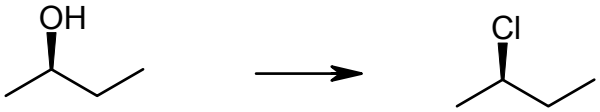
B



C



D



Cont'd -->

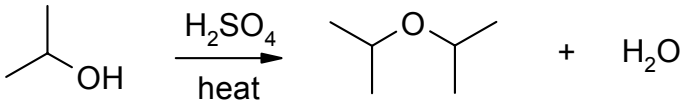
9% PART 7: MECHANISMS

WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED

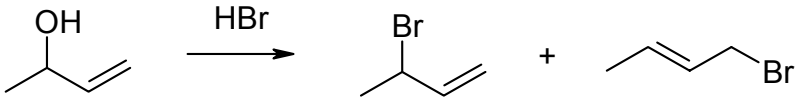
ANSWER ANY THREE (3) OF THE QUESTIONS I to IV.

Use curly arrows to show the mechanism in order to explain any THREE (3) of the following reactions / observations :

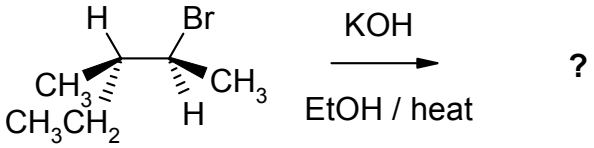
I.



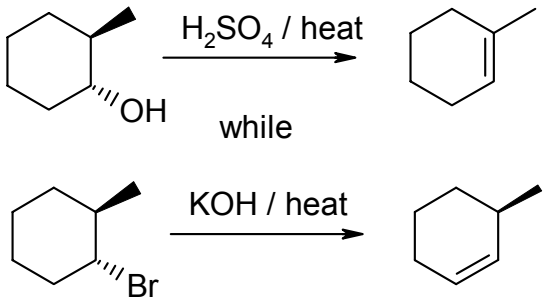
II



III. Predict the major product of this reaction and show the mechanism :



IV. Why do the following similar reactions give different alkene products ?

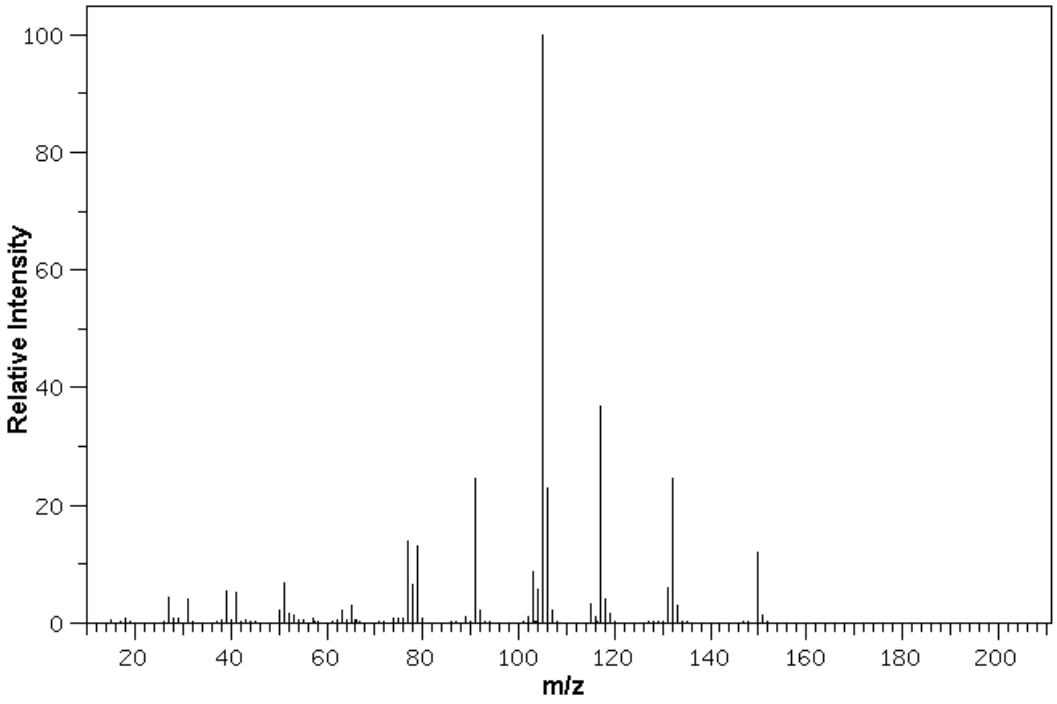


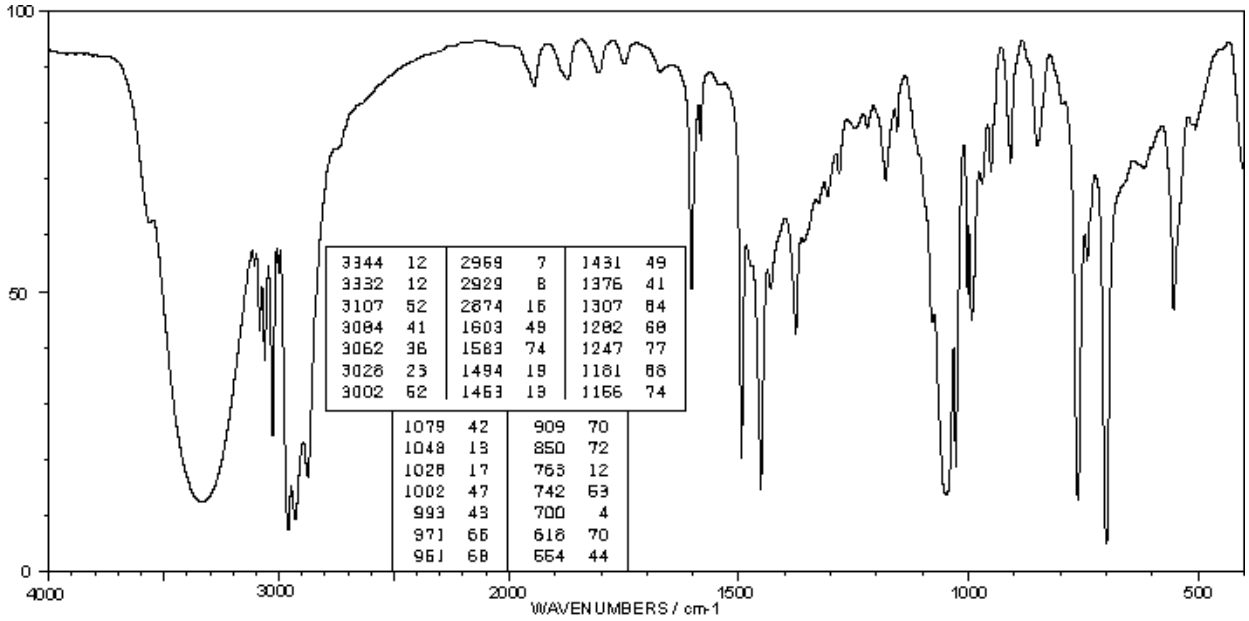
Cont'd -->

10% PART 8: SPECTROSCOPY

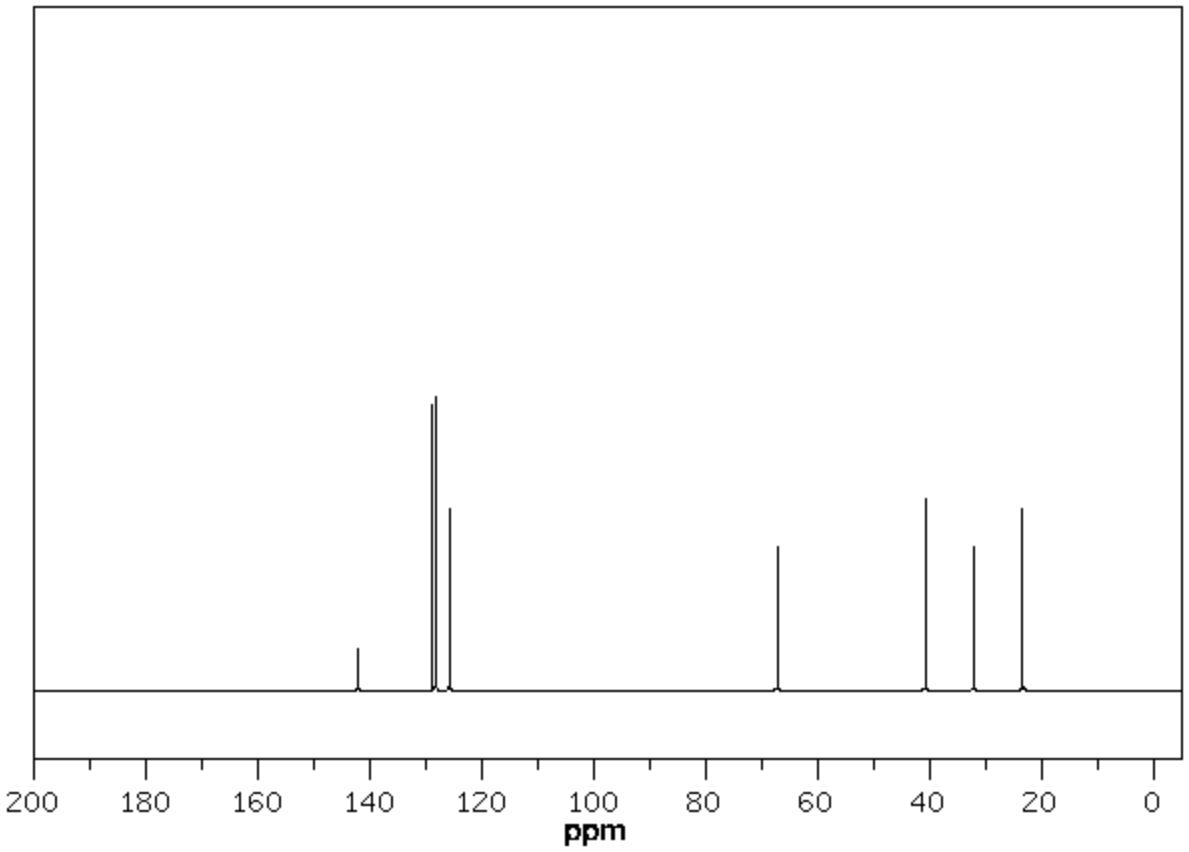
WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED. Show your workings as PARTIAL marks will be given.

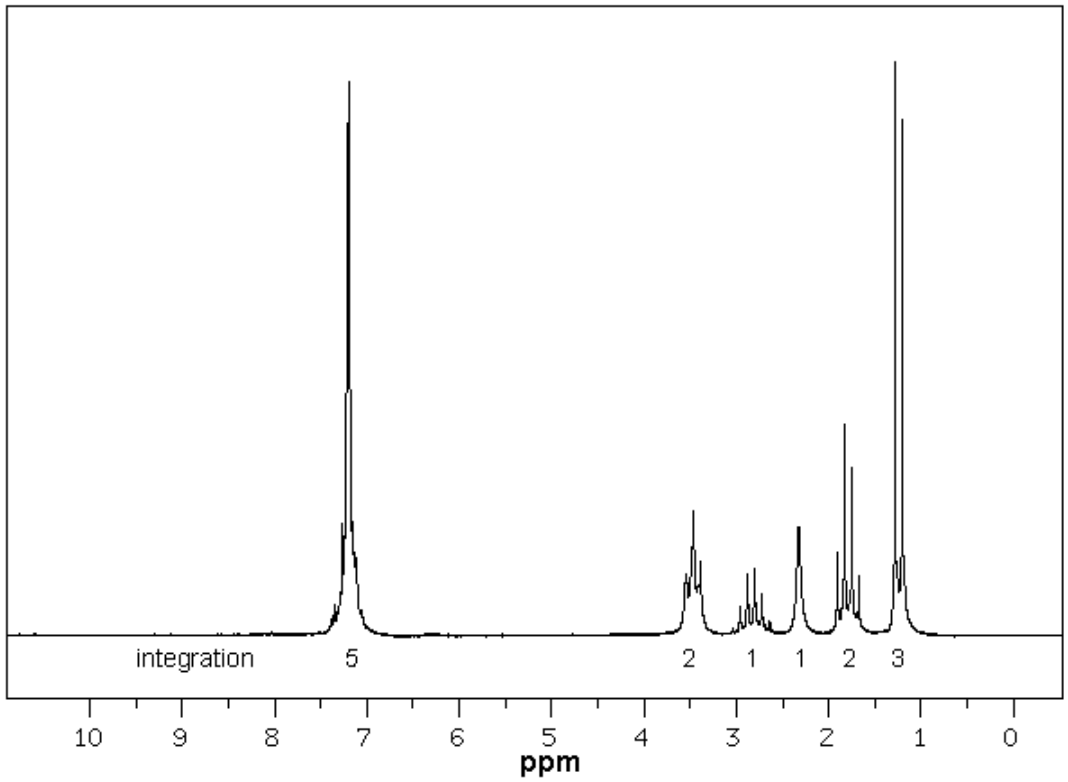
From the data provided below, identify the structure of the "unknown" molecule.





Cont'd -->


200
180
160
140
120
100
80
60
40
20
0
ppm


integration
5
2
1
1
2
3
10
9
8
7
6
5
4
3
2
1
0
ppm

Cont'd -->

12% PART 9: STRUCTURE DETERMINATION

WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED

A hydrocarbon **A**, C_6H_{14}, was heated with bromine to give **B** $C_6H_{13}Br$ as the major product. **B** was observed to react at a moderate rate with either aqueous ethanolic silver nitrate or with sodium iodide in acetone. When **B** was reacted with either KOH / EtOH/ heat or KOtBu / DMSO / heat it gave the product **C**, C_6H_{12} (IR : 1650cm^{-1}). Reduction of **C** via catalytic hydrogenation (H_2 / Pd) gave the original hydrocarbon **A** as the sole product.

When **B** was reacted with cold aq. NaOH solution the major product was **D**, $C_6H_{14}O$ (IR : 3500cm^{-1}, broad).

When **D** was reacted with PBr_3 / Et_3N, **B** was obtained but when **D** was treated with HBr the reaction gave **E** as the major product. **E** was observed to react rapidly with aqueous ethanolic silver nitrate but very slowly (if at all) with sodium iodide in acetone. **E** was found to be a constitutional isomer of **B**. **E** could also be obtained on reaction of 2,3-dimethylbutane with bromine / uv light.

When **D** was heated with conc. H_2SO_4, the major product was **F**, a constitutional isomer of **C**. **F** was also formed as the major product of the reaction of **E** with hot ethanolic KOH. Reduction of **F** via catalytic hydrogenation (H_2 / Pd) gave a constitutional isomer of the original hydrocarbon **A** as the sole product.

In a normal ^{13}C nmr spectroscopic analysis of the compounds, **A** - **E** each had 4 peaks, while **F** had only 2 peaks.

Of the compunds **A - F**, only **B** and **D** have chirality centers.

- **Identify A-F (only structures are needed)**
- **Draw a structure showing the stereochemistry and give the complete name of one enantiomer of B.**

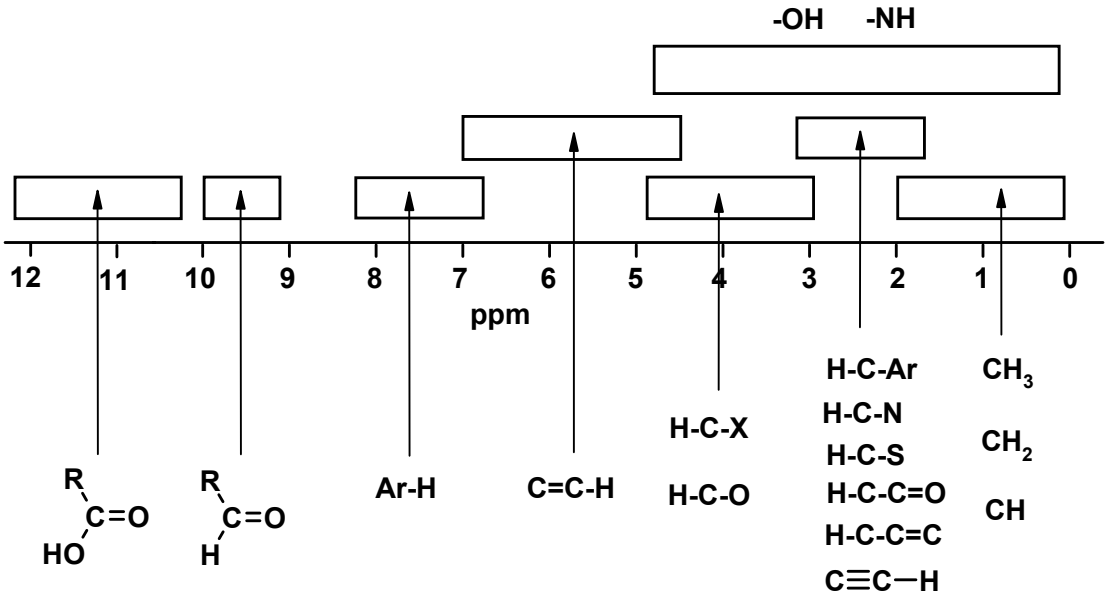
**** THE END ****

IRH/AC : F2006

Cont'd -->

SPECTROSCOPIC TABLES

^{1}H NMR



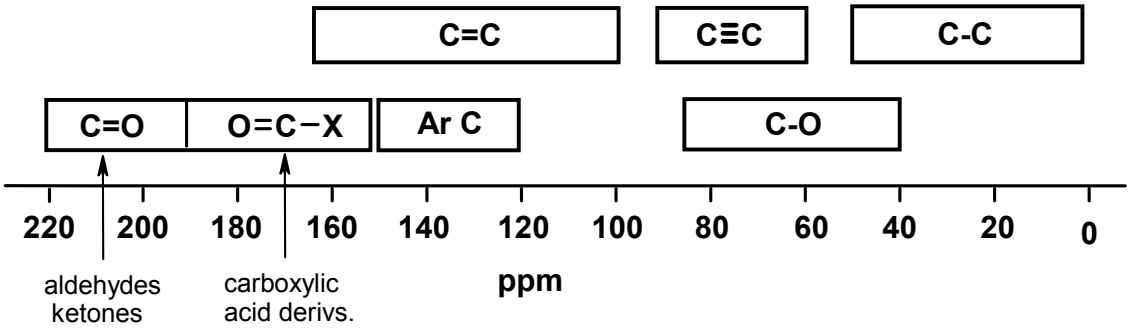
^{1}H NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm

	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

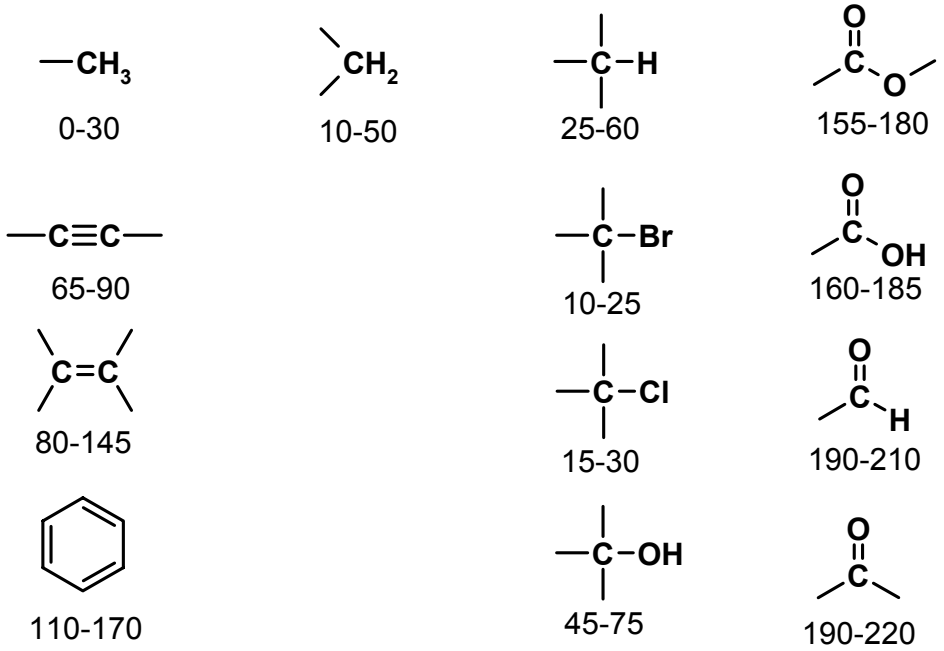
other	
-OH	1-5
-NH	1-3
C≡CH	2.5
C=C H	5.5
Ar-H	7.3
O C R H	10
O C R OH	9-12

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
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)