UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

FINAL EXAMINATION

CHEMISTRY 351

December 2009 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 - 8, 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 - 4 will be computer graded, and Parts 5 - 8 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 - 39, 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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20% PART 1 RELATIVE PROPERTIES

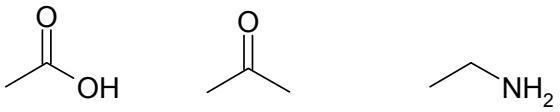
ANSWER ANY TEN (10) OF QUESTIONS 1 TO 12.

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 acidity of the following:

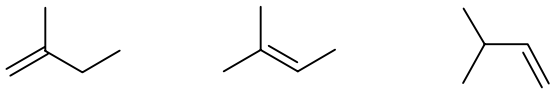


i **ii** **iii**

2. The number of constitutionally isomeric monochlorination products from the reaction of one molar equivalent of Cl_2 / uv light with each of the following

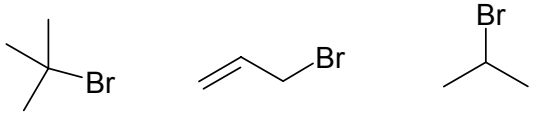
i 2-methylbutane
ii 2,2-dimethylpropane
iii *n*-pentane

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



i **ii** **iii**

4. The rate of reaction of each of the following with NaI/acetone:



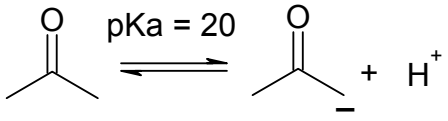
i **ii** **iii**

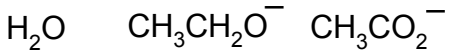
Cont'd -->

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**

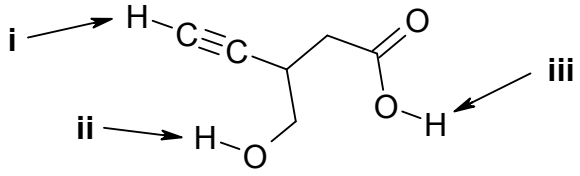
5. The relative amount of the conjugate base of 2-propanone formed by the reaction of 1 mole equivalent of each of the following:



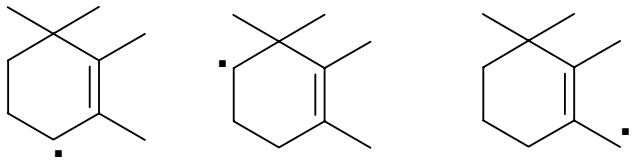


i **ii** **iii**

6. The relative acidity of the indicated atoms in the following structure:

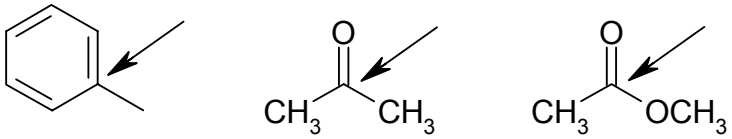


7. The relative stability of the following radicals:



i **ii** **iii**

8. The ^{13}C-NMR chemical shifts for the carbon atoms indicated in each of the following structures:



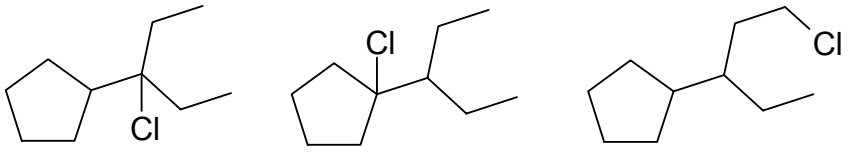
i **ii** **iii**

Cont'd -->

Use the following code to indicate your answers.

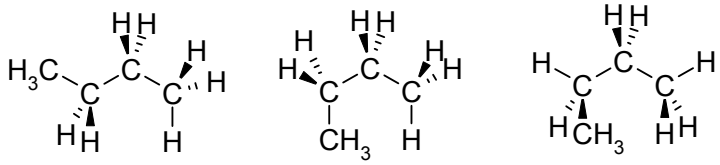
A.	**i > ii > iii**	**D**.	**ii > iii > i**
B.	**i > iii > ii**	**E**.	**iii > i > ii**
C.	**ii > i > iii**	**AB**.	**iii > ii > i**

9. The number of possible alkene isomers formed by reacting the following with KOH/EtOH and heat:



i **ii** **iii**

10. The relative energies of the conformations shown below:



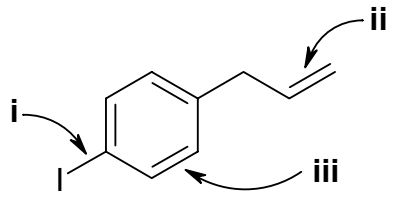
i **ii** **iii**

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

CH_3CH_2—**OTs** CH_3CH_2—**Cl** CH_3CH_2—**OH**

i **ii** **iii**

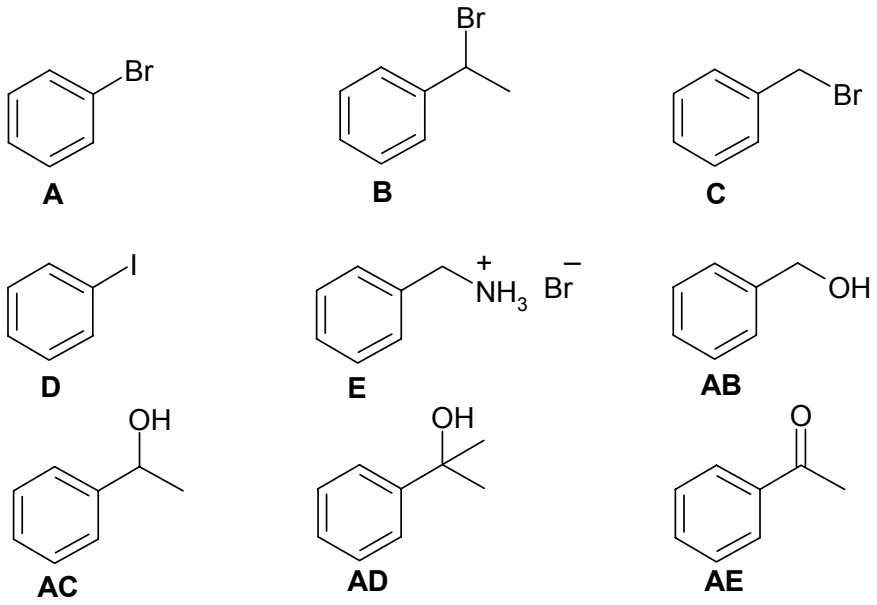
12. The relative bond lengths of the bonds indicated:



15% PART 2: MOLECULAR PROPERTIES

ANSWER ALL TEN (10) of the questions 13-22

Use the structures below to answer questions 13 – 17



13. Which structure has the most acidic hydrogen atom ?

14. When heated with H_2SO_4 which structure will eliminate the fastest ?

15. When reacted with NaI in acetone, which structure will substitute the fastest ?

16. When reacted with NaOEt, which structure will eliminate the fastest ?

17. When reacted under the $AgNO_3$/EtOH conditions, which structure will substitute the fastest ?

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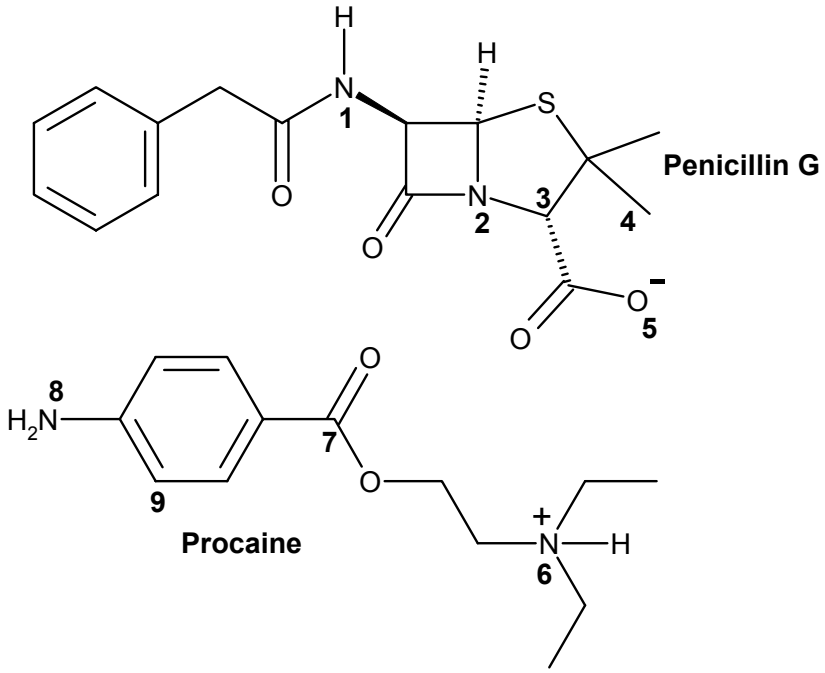
Questions 18 – 22 refer to the structure of commercial Penicilin G - Procaine salt:



18. What is the IHD of Penicillin G – Procaine salt ?

A. 11 **B.** 12 **C.** 13 **D.** 14 **E.** 15

19. For the **<u>Procaine portion</u>** of the salt, how many carbon signals do you expect in the ^{13}C NMR spectrum ?

A. 9 **B.** 10 **C.** 11 **D.** 12 **E.** 13

20. In Penicillin G – Procaine salt, which of the following protons has the lowest chemical shift (δ) in the ^{1}H NMR spectrum ?

A. H—N1 **B.** H—C4 **C.** H—C3 **D.** H—N6 **E.** H—C9

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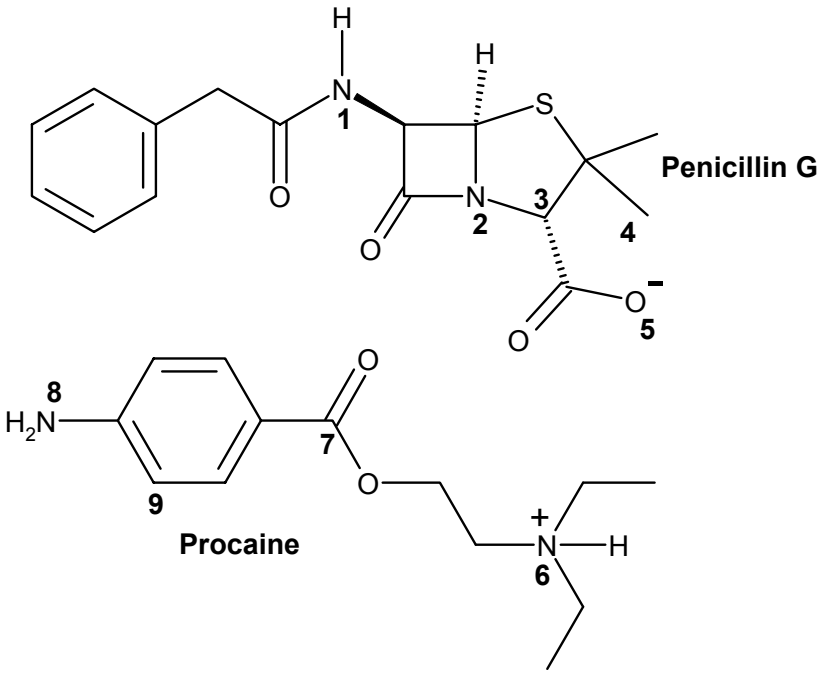

21. Which of the following best describes the orbitals of the three lone pairs on **O5** occupy ?

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

22. What is the absolute configuration of **C3** ?

A. R **B.** S **C.** E **D.** Z **E.** cis

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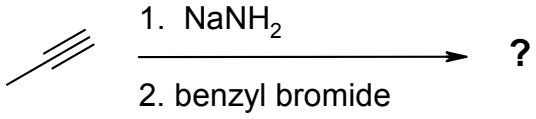
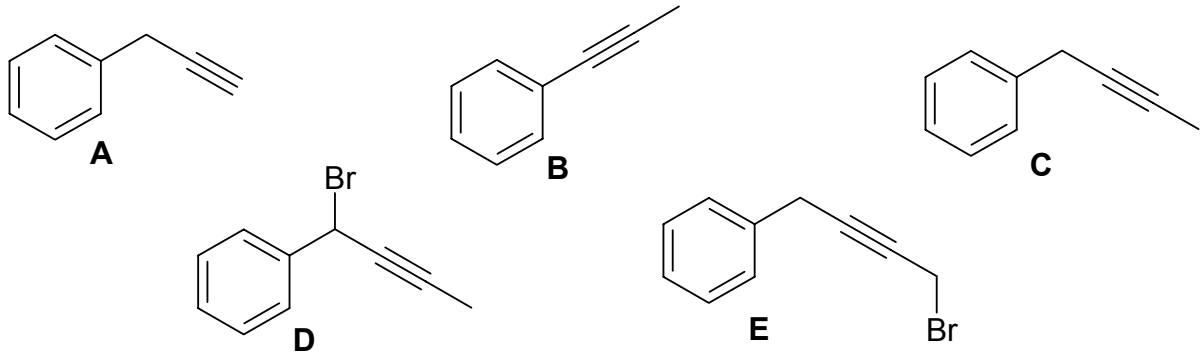
16% PART 3: REACTIONS

ANSWER ANY EIGHT (8) OF QUESTIONS 23-31.

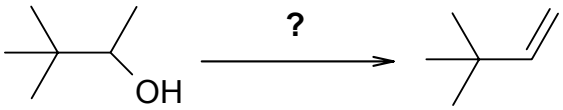
For each of questions 23-31 select the MISSING component (the best starting material, the major product or the best reagents) required in order to BEST complete each of the reaction schemes.

23.





24.



A H_2SO_4, heat

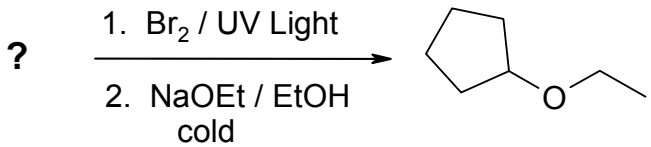
B KO^{t}Bu, DMSO, heat

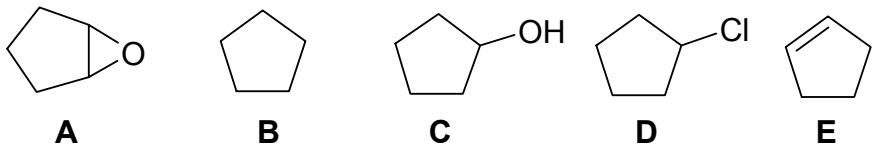
C Tosyl Chloride, NEt_3

D 1. PBr_3
2, ^{t}BuOK, DMSO, heat

E 1. $SOCl_2$, NEt_3
2. KOH, cold

25.





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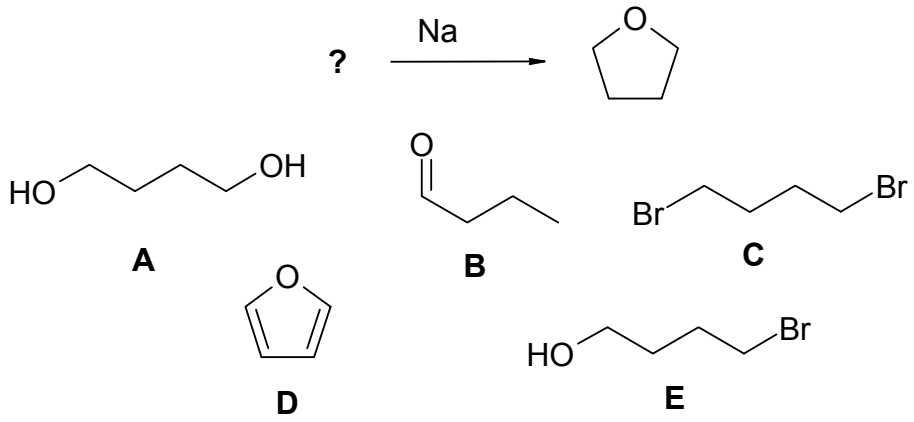
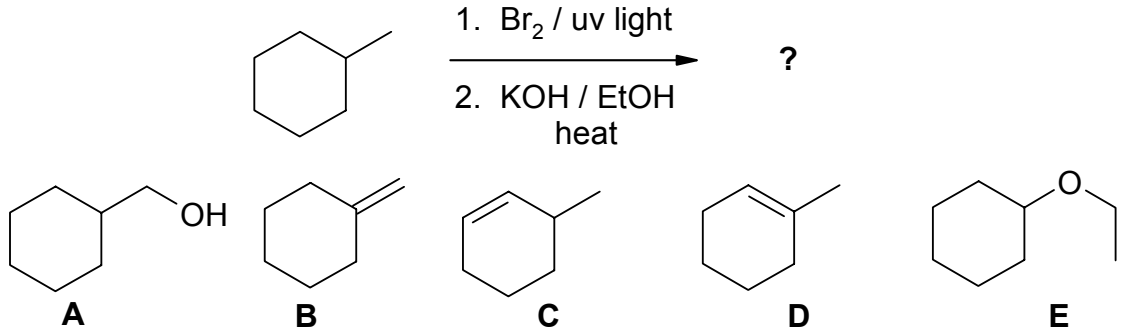
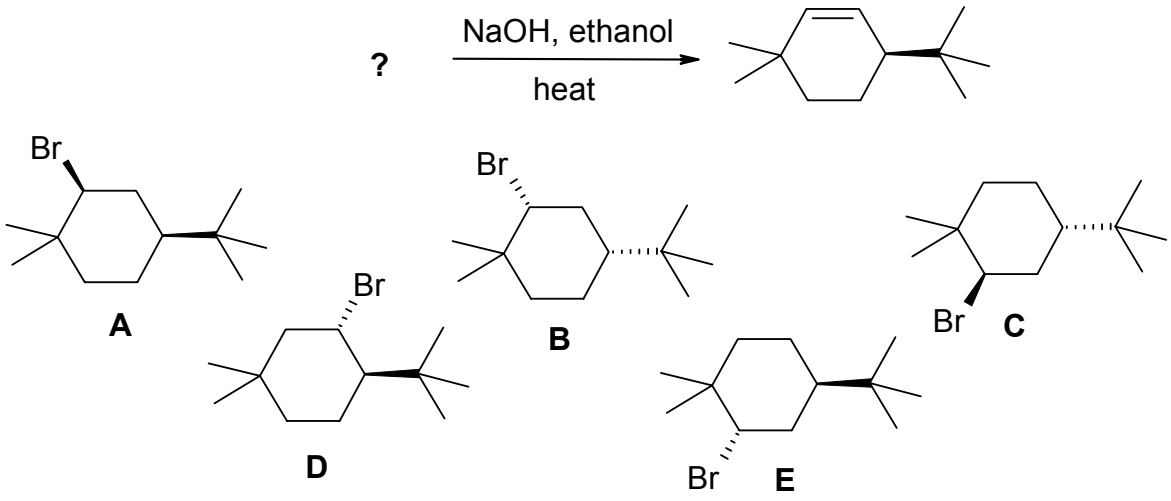
26.



27.



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



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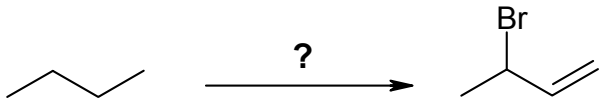
29.



A 1. Thionyl chloride / Et_3N
2. NaOEt / EtOH / heat
3. Br_2

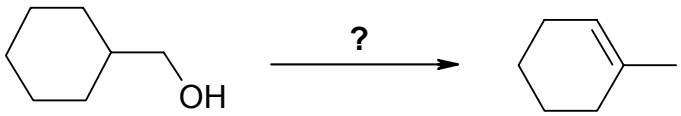
B 1. PBr_3
2. KOH / EtOH / heat

C 1. Br_2, uv light
2. H_2O, heat
3. PBr_3

D 1. conc. H_2SO_4 / heat
2. Br_2, uv light

E 1. Br_2, uv light
2. KOBu-t / t-BuOH / heat
3. NBS, uv light

30.



A 1. HBr
2. NaOEt / EtOH / heat

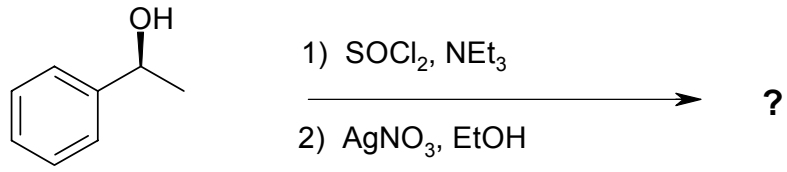
B 1. TsCl / Py
2. KOH / EtOH / heat

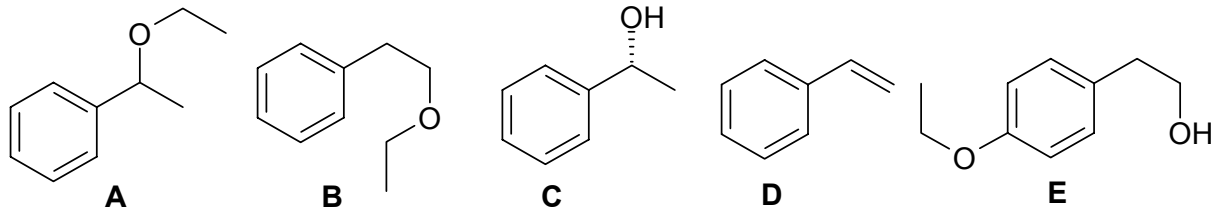
C 1. NBS, uv light
2. KOH / EtOH/ heat

D 1. $SOCl_2$ / NEt_3
2. KOH, cold

E 1. PBr_3
2. KOH / EtOH / heat

31.





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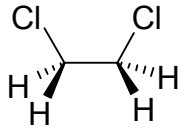
12% PART 4: CONFORMATIONAL ANALYSIS

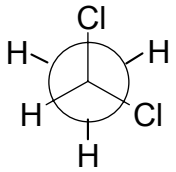
ANSWER ALL of the questions 32-39.

32. What is the **torsional** angle between the two bonds involving chlorine atoms in molecule shown below ?



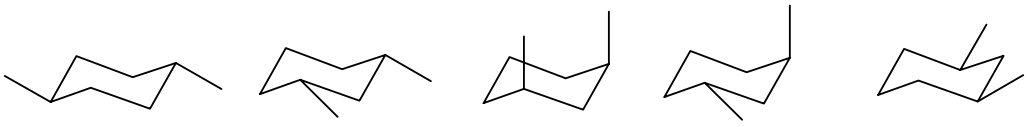
A 0° **B** 60° **C** 90° **D** 109.5° **E** 120° **AB** 180°

33. What is the **Cl-C-Cl** bond angle in the molecule that is represented by the Newman projection shown below ?



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

34. Which of the following diagrams represents the **most** stable conformation of trans-1,3-dimethylcyclohexane ?



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

35. Which of the following terms **best** describes the relative position of the two highlighted bonds in the conformation of methylcyclohexane shown below?

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

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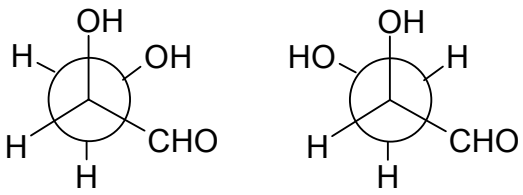
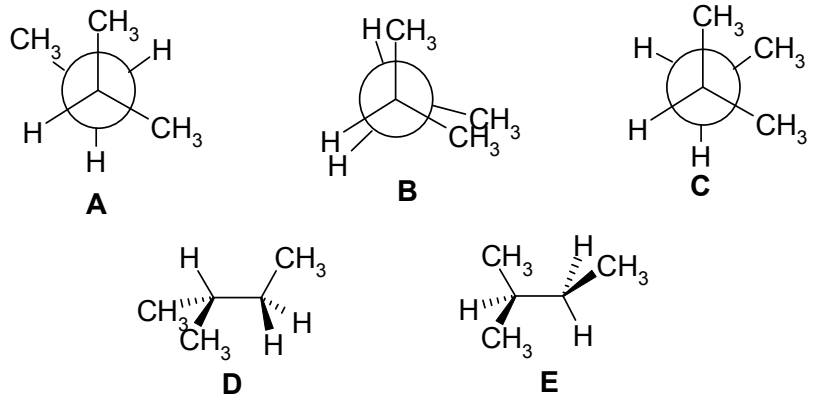
36. Which of the following terms **best** describes the relationship between the two molecules shown below ?

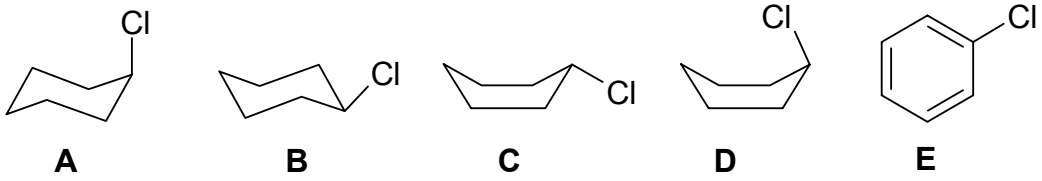


A constitutional isomers
B identical
C conformational isomers
D enantiomers
E geometric isomers

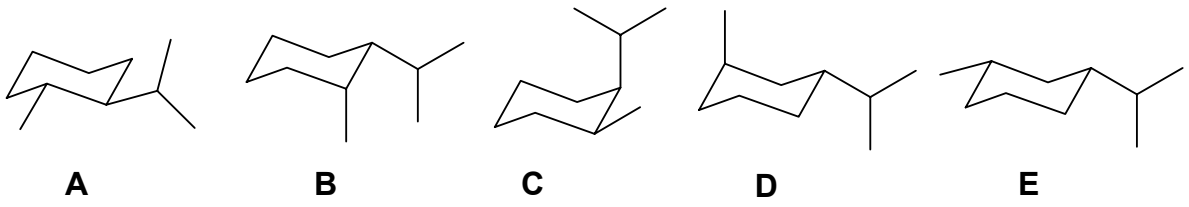
37. Which of the following conformations of 2-methylbutane is the **most** stable?



38. Which of the following is the **highest** energy conformation of chlorocyclohexane ?



39. Which of the following structures has the **lowest** energy ?



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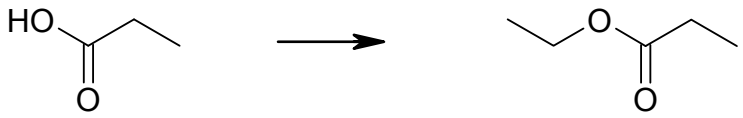
8% PART 5: SYNTHESIS

DESIGN EFFICIENT 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.

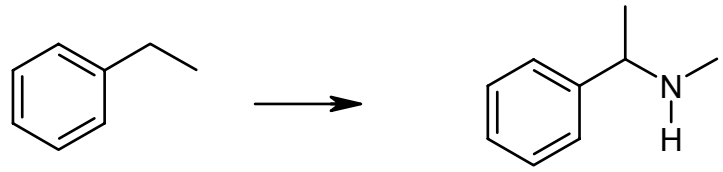
WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED.

DO NOT SHOW MECHANISMS.

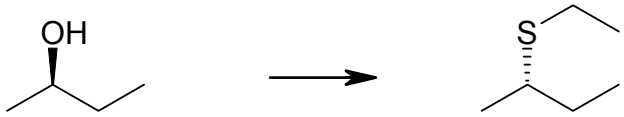
A



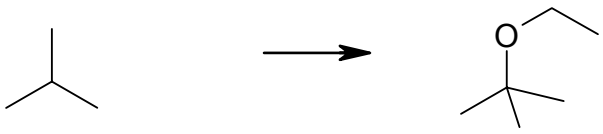
B



C



D



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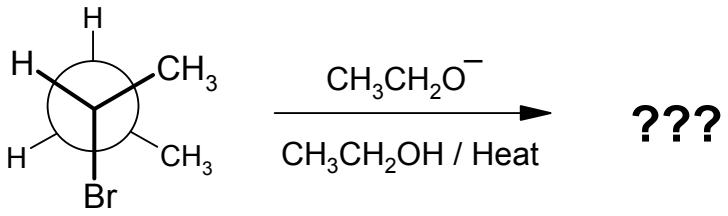
9% PART 6: MECHANISMS

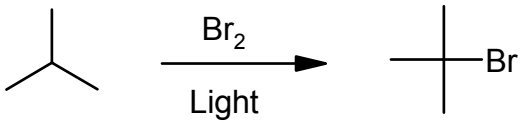
WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED

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

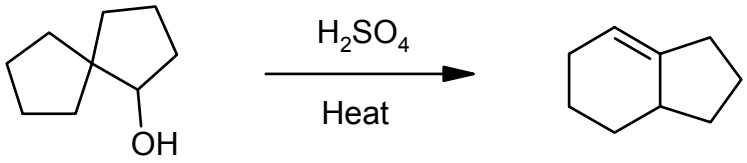
A Draw **ALL three** elimination products from the following reaction. Identify the major product and draw the reaction mechanism to explain your answer.



B Draw the reaction mechanism for the following reaction:



C Draw the reaction mechanism for the following reaction:



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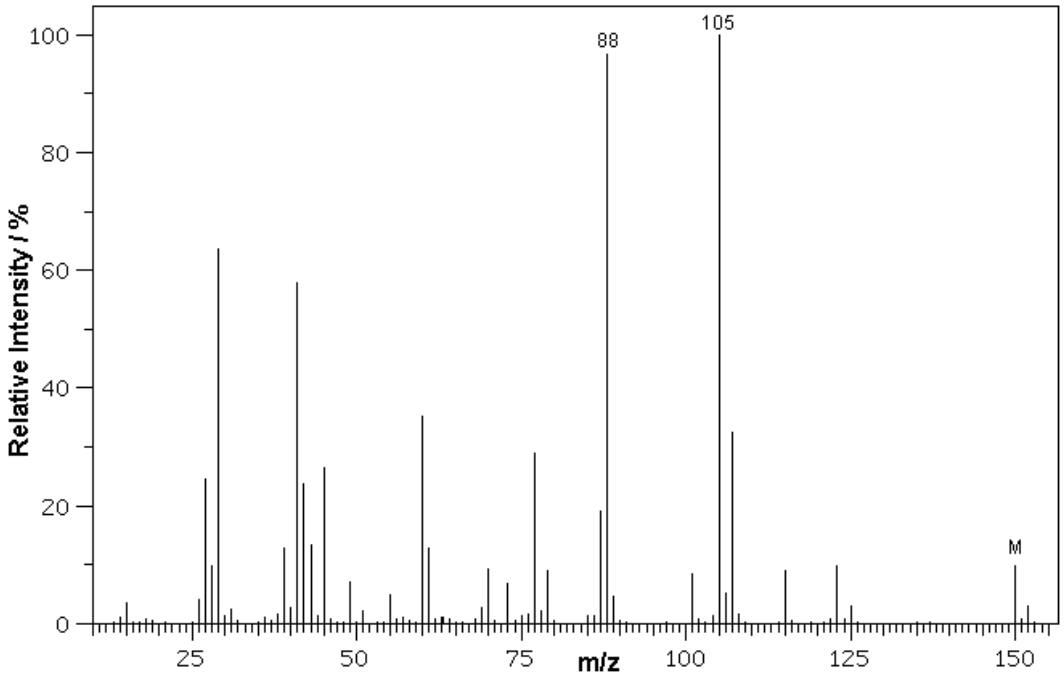
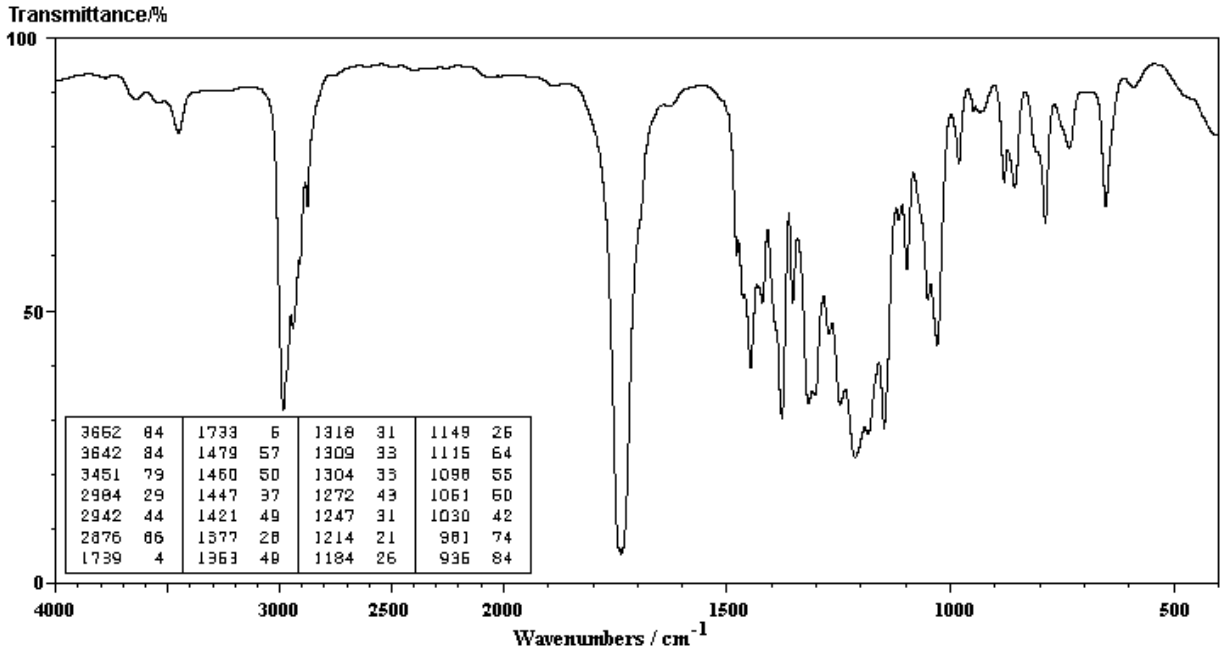
10% PART 7: SPECTROSCOPY

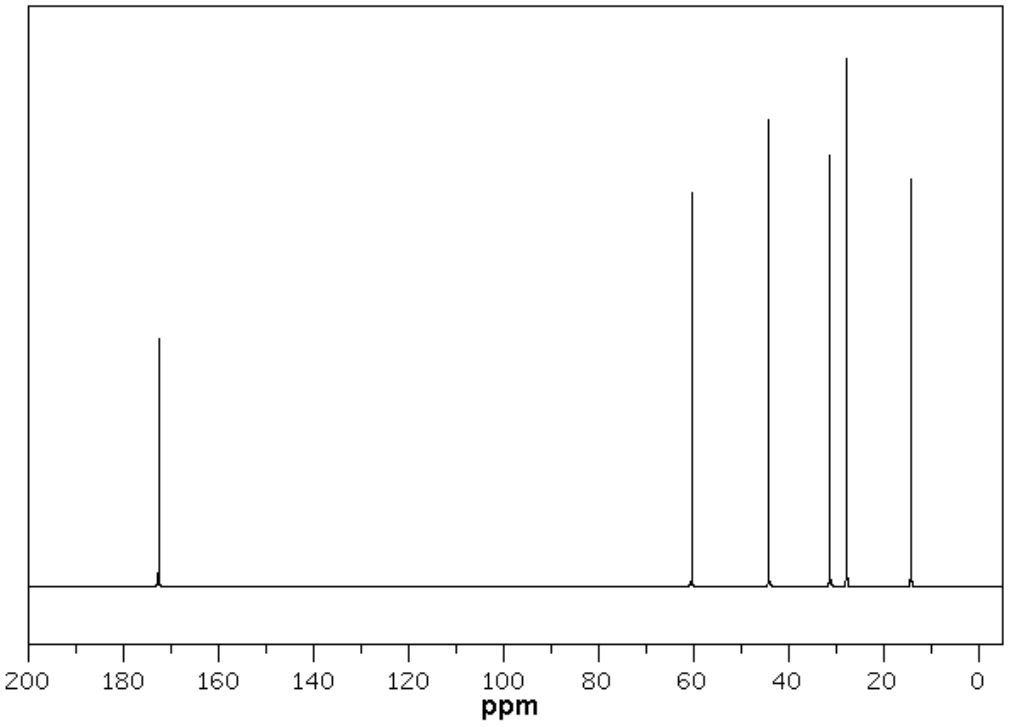
WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED. Show your workings as PARTIAL marks will be given.

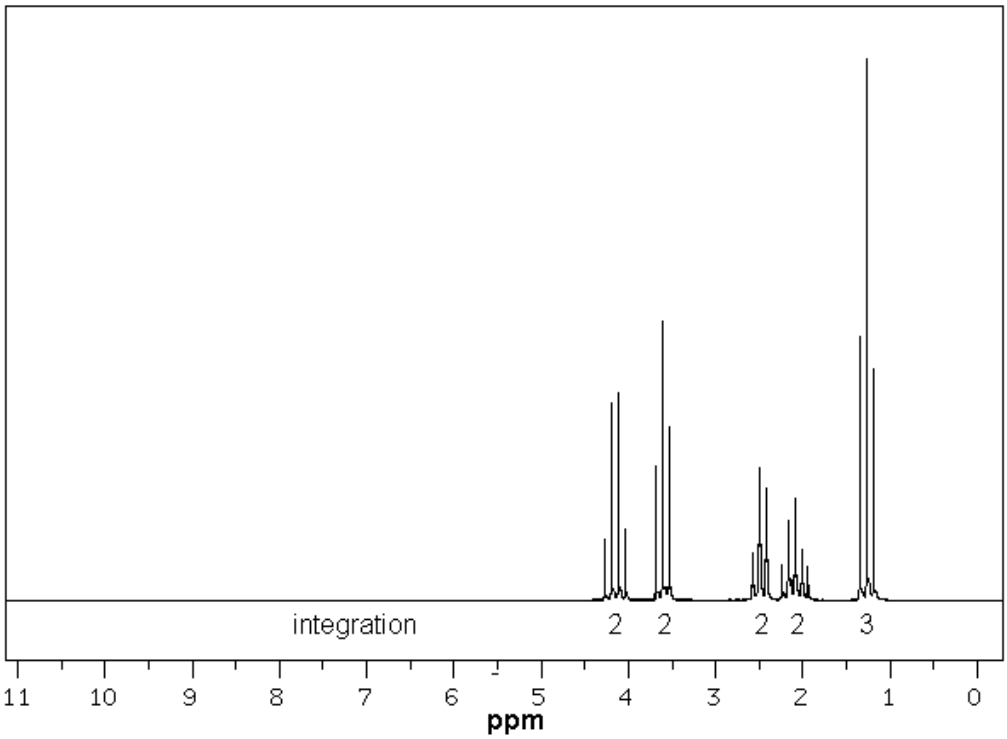
From the spectral data provided below, identify the structure of the "unknown" molecule.





Cont'd -->


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


integration
2
2
2
2
3
11
10
9
8
7
6
5
4
3
2
1
0
ppm

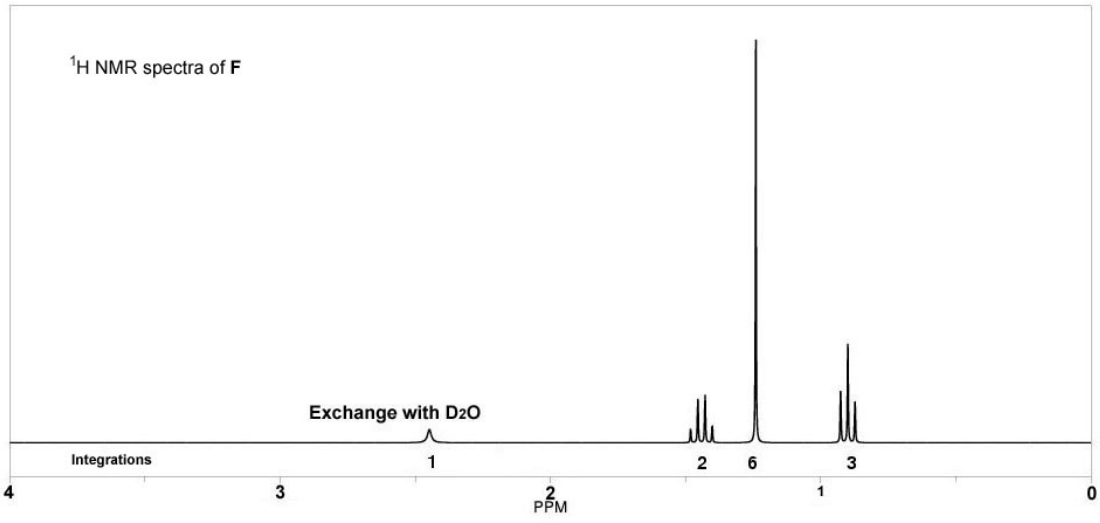
Cont'd -->

12% PART 8: STRUCTURE DETERMINATION

WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED

Molecule **A** is an acyclic, achiral monobromoalkane containing five carbons. When **A** is heated with NaOEt, **B** results as the minor product, and **C** as the major product. Molecule **D** is chiral and a constitutional isomer of **A**. When **D** is heated with potassium *tert*-butoxide, **E** formed as the major product and **C** is the minor product. Molecules **B**, **C**, and **E** are constitutional isomers of each other, and when hydrogenated in the presence of palladium on charcoal, they all gave the same alkane. Both **A** and **D** reacted with water to give compound **F** whose ^{1}H NMR spectra is given below. When **B** is reacted with N-bromosuccinimde under UV irradiation, **G** was obtained as the major product, but when **E** is treated with N-bromosuccinimide under the same conditions, **H** is obtained as the major product. **G** and **H** are constitutional isomer of each other with a molecular formula of C_5H_9Br.

1. Identify **A**-**H** (only structures are needed)
2. Draw a **pair** of enantiomers that correspond to the molecular formula C_5H_9Br and give an IUPAC names for each one of them.
3. Draw a **pair** of geometric isomers that correspond to the molecular formula C_5H_9Br and give an IUPAC names for each of them.



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

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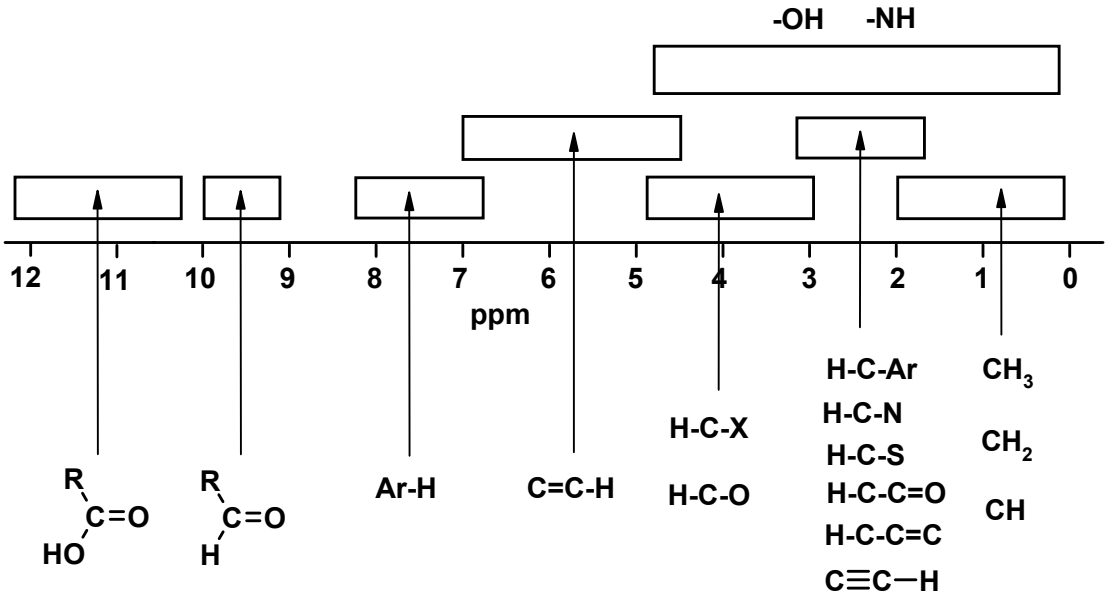
SPECTROSCOPIC TABLES

^{1}H NMR



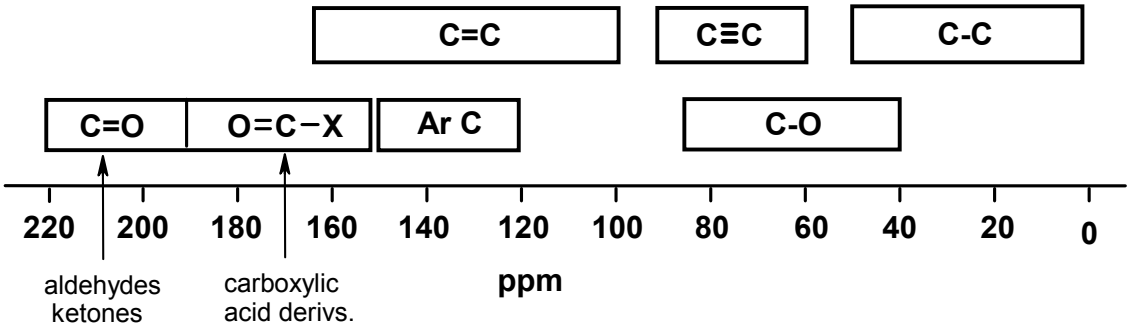
^{1}H NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm

	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

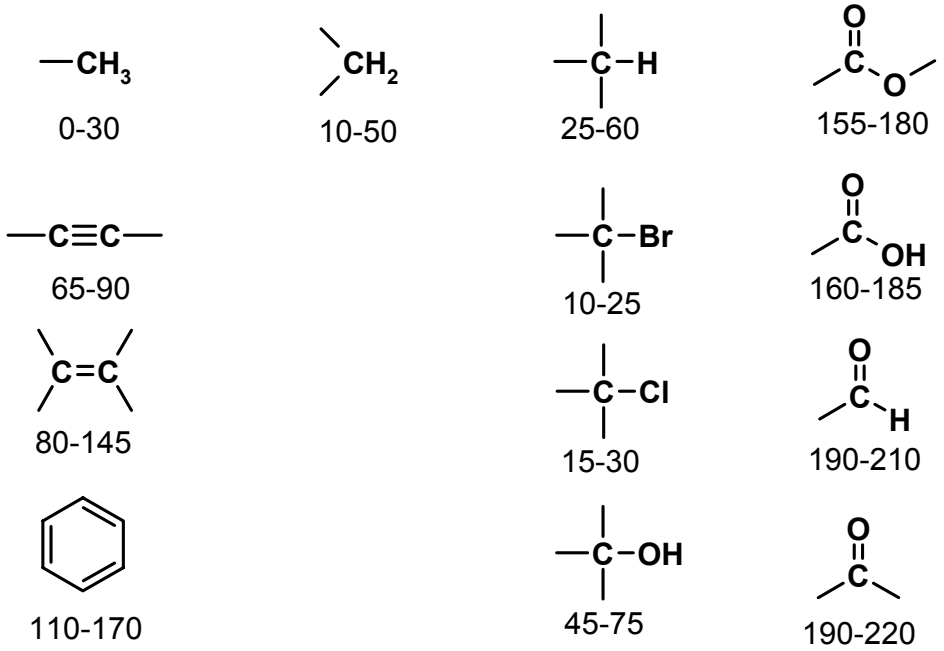
other	
-OH	1-5
-NH	1-3
C≡CH	2.5
C=C H	5.5
Ar-H	7.3
O C R H	10
O C R OH	9-12

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
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)