UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

FINAL EXAMINATION

CHEMISTRY 353

Version 1

April 15th, 2017 **Time: 3 Hours**

READ THE INSTRUCTIONS CAREFULLY

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

The examination consists of Parts **1 - 10**, each of which should be attempted. Note that some Parts provide you with a choice of questions, *e.g*. answer 5 out of 6. These will be graded in order the answers appear until the required number have been completed, ***regardless*** of whether they are right or wrong.

Parts **1 - 6** will be computer graded, and Parts **7 - 10** are to be answered in the blue answer booklet. Parts **1 - 6** consist of a series of multiple choice questions numbered **1 - 49** which are to be answered on your optical score 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***.

A periodic table with atomic numbers and atomic weights and tables of spectroscopic data are provided at the end of the examination paper. **No other resources are allowed**.

Molecular models and calculators are permitted, ***but NOT programmable calculators***.

Absolutely no other electronic devices are allowed.

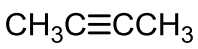
12% PART 1: RELATIVE PROPERTIES

ANSWER ANY EIGHT (8) OF THE TEN (10) QUESTIONS 1-10.

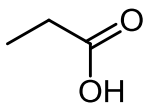
Arrange the items in questions 1-10 in DECREASING ORDER (*i.e.* greatest, most *etc*. first) with respect to the indicated property. Use the following code to indicate your answers in the box provided:

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 most acidic hydrogen in each of the following:



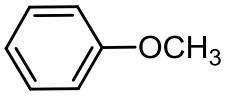
i



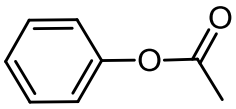
ii

iii

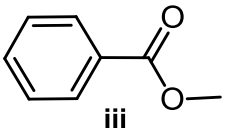
2. The relative rate of reaction of H_2SO_4 / HNO_3 with each of the following:



i

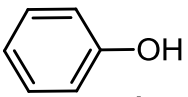


ii

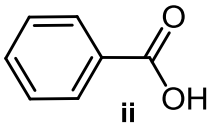


iii

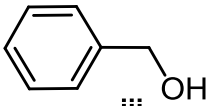
3. The relative solubility in 5% aqueous sodium bicarbonate of each of the following:



i



ii

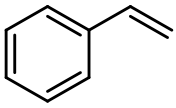


iii

4. The relative reactivity of each of the following towards H_2SO_4:

i

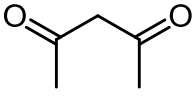
ii



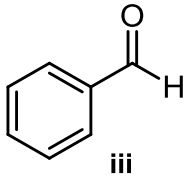
iii

5. The relative acidity of the most acidic hydrogen in each of the following:

i



ii



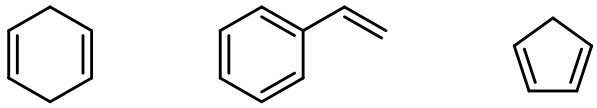
iii

CONTINUED -->

Use the following code to indicate your answers in the box provided:

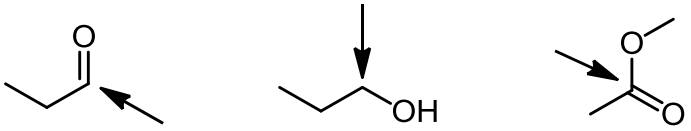
A	**i > ii > iii**	**D**	**ii > iii > i**
B	**i > iii > ii**	**E**	**iii > i > ii**
C	**ii > i > iii**	**AB**	**iii > ii > i**

6. The resonance energies of each of the following:



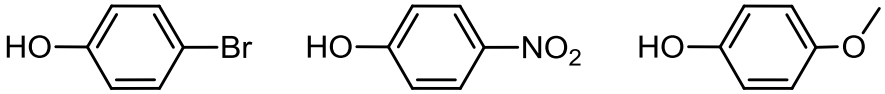
i **ii** **iii**

7. The relative oxidation state of the C atom indicated in each of the following:



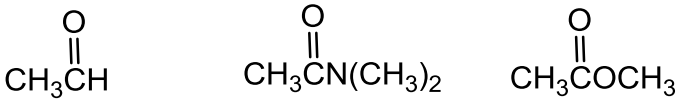
i **ii** **iii**

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



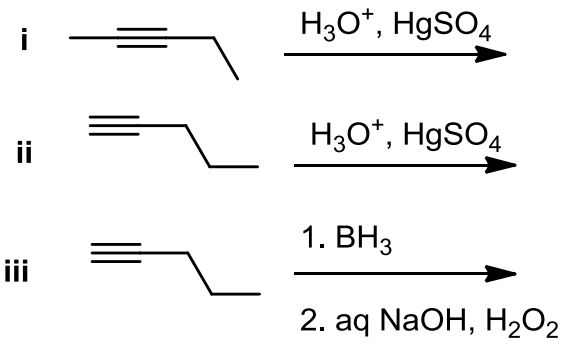
i **ii** **iii**

9. The relative reactivity towards CH_3MgBr of each of the following:



i **ii** **iii**

10. The relative yields of pentan-2-one from each of the following reactions:



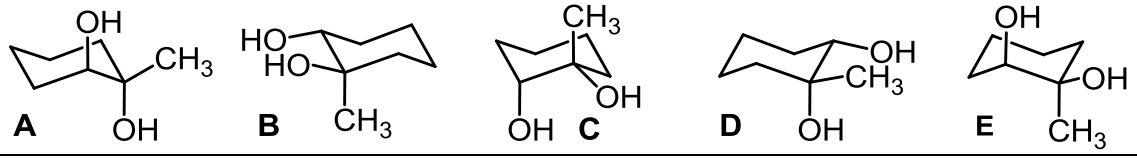
CONTINUED -->

8 % PART 2: STRUCTURE AND PROPERTIES

ANSWER ANY EIGHT (8) OF THE NINE (9) QUESTIONS 11-19.

IN SOME CASES multiple items need to be selected for full credit.

SET 1



Answer questions 11-15 by selecting the compounds from SET 1 above.

11. Select **TWO** structures that have an axial methyl group.

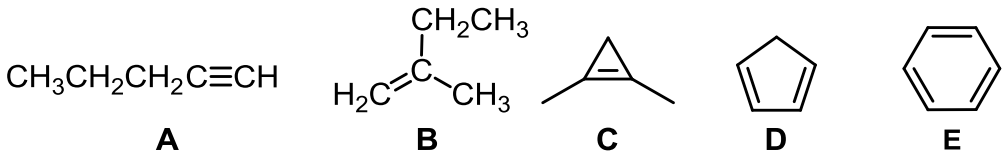
12. Select a **SINGLE** compound that has two –OH groups that are *trans* and gauche.

13. Select **TWO** structures that are the result of the reaction of 1-methylcyclohexene with cold alkaline potassium permanganate.

14. Select a **SINGLE** compound made via the reaction of 1-methylcyclohexene with CH_3CO_3H then H_3O+.

15. Select **TWO** structures represent different conformations of the same compound.

SET 2



Answer questions 16-19 by selecting a compound from SET 2 above.

16. Select the structure that has the **lowest** pKa.

17. Select the structure that gives the **most** stable carbocation when reacted with H+.

18. Select the structure has the **most** types of hydrogen.

19. Select a **SINGLE** structure that is an isomer of cyclopentane.

CONTINUED -->

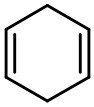
9% PART 3: AROMATICITY AND RESONANCE

ANSWER ANY NINE (9) OF THE TEN (10) QUESTIONS 20 - 29.

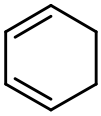
SET 3:

A

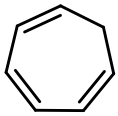
B



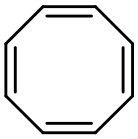
C



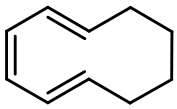
D



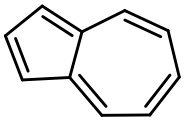
E



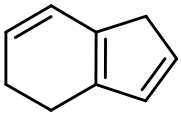
AB



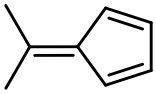
AC



AD



AE



BC

Answer questions 20-24 by selecting a SINGLE compound from SET 3 above.

20. Select a **SINGLE** compound that is a non-conjugated system.

21. Select a **SINGLE** compound that is non-aromatic as drawn, but has an important aromatic resonance contributor.

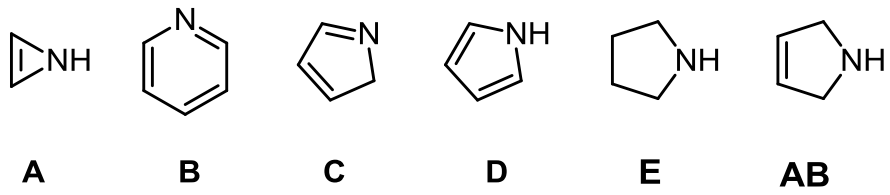
22. Select a **SINGLE** compound that is non-aromatic as drawn, but has an aromatic conjugate base.

23. Select a **SINGLE** compound that is aromatic as drawn.

24. Select a **SINGLE** compound that has no resonance energy stabilization.

CONTINUED -->

SET 4:



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

Answer questions 25-29 by selecting a <u>SINGLE compound</u> from SET 4 above.

25. Select a **SINGLE** compound that has an sp^2 N and is non-aromatic as drawn.

26. Select the **SINGLE** compound that when protonated on N has the lowest pKa.

27. Select a **SINGLE** compound that is anti-aromatic as drawn.

28. Select a **SINGLE** compound that is aromatic as drawn and has an aromatic conjugate acid.

29. Select a **SINGLE** compound that is non-aromatic as drawn but has an aromatic tautomer.

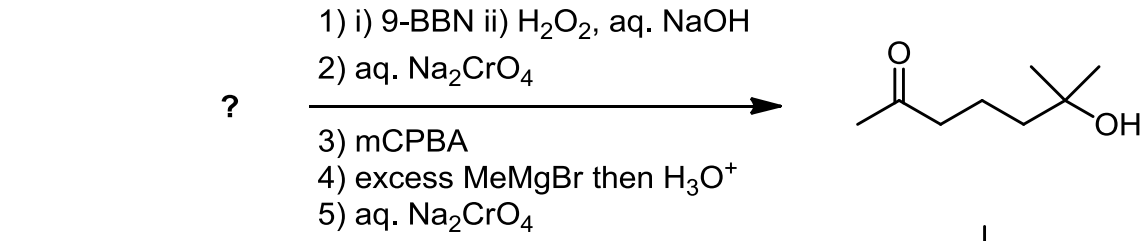
CONTINUED -->

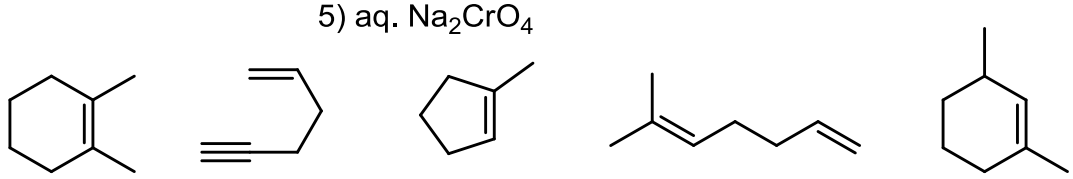
16% PART 4: STARTING MATERIALS AND PRODUCTS OF SYNTHESIS

ANSWER ANY EIGHT (8) OF THE NINE (9) QUESTIONS 30-38.

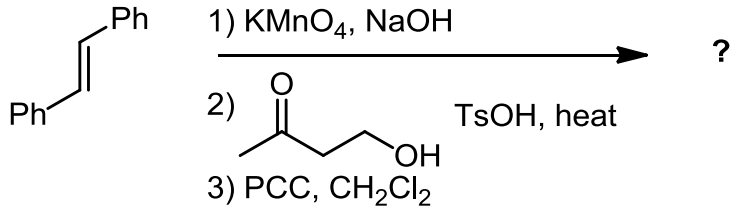
For each of the questions 30 - 38 identify the product(s) obtained or starting material(s) required in order to best complete each of the reaction sequences shown by selecting from the list provided.

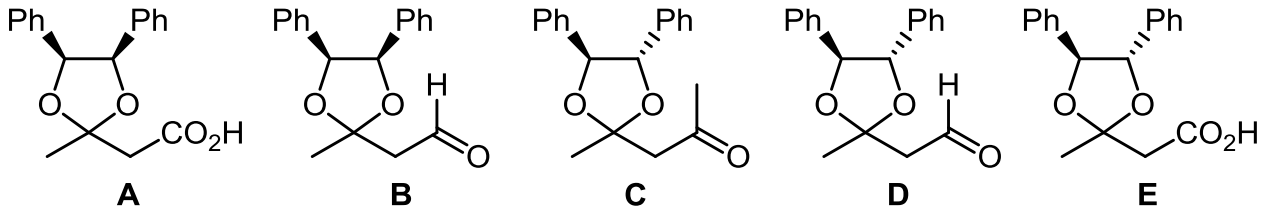
30.



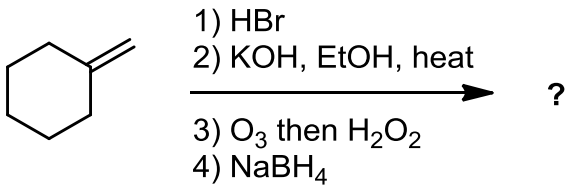


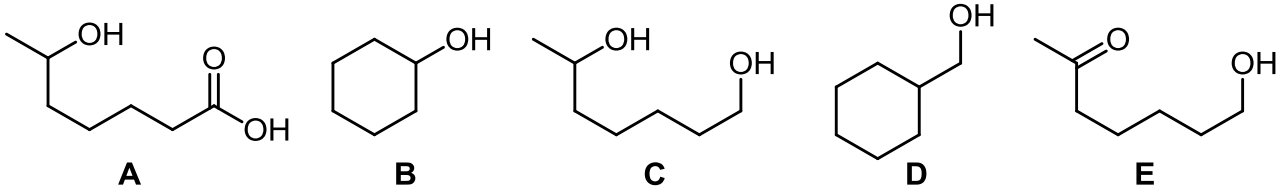
31.





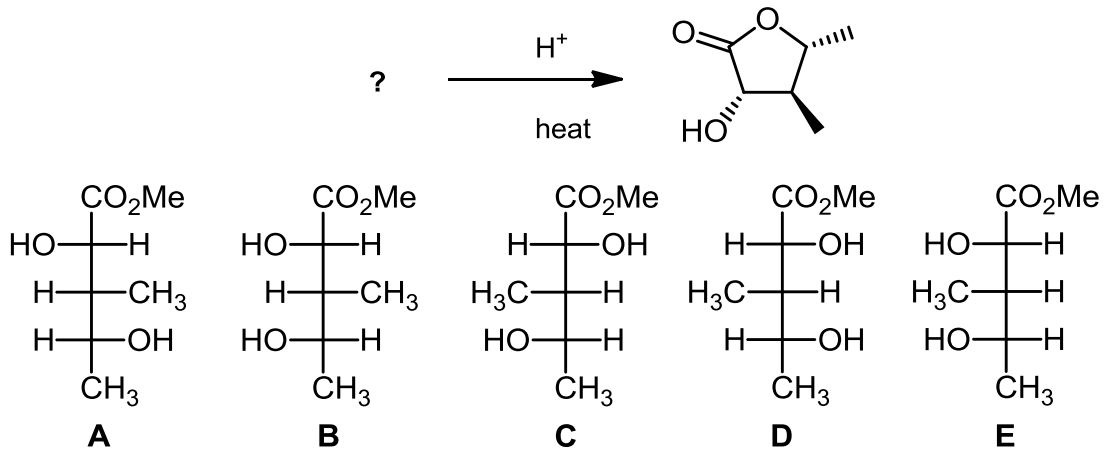
32.



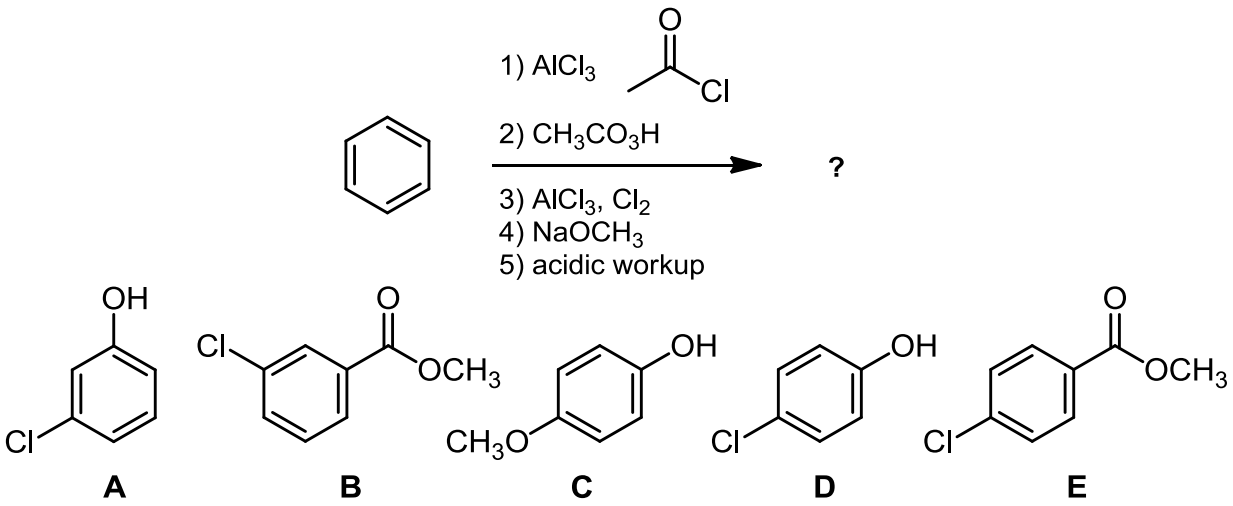


CONTINUED -->

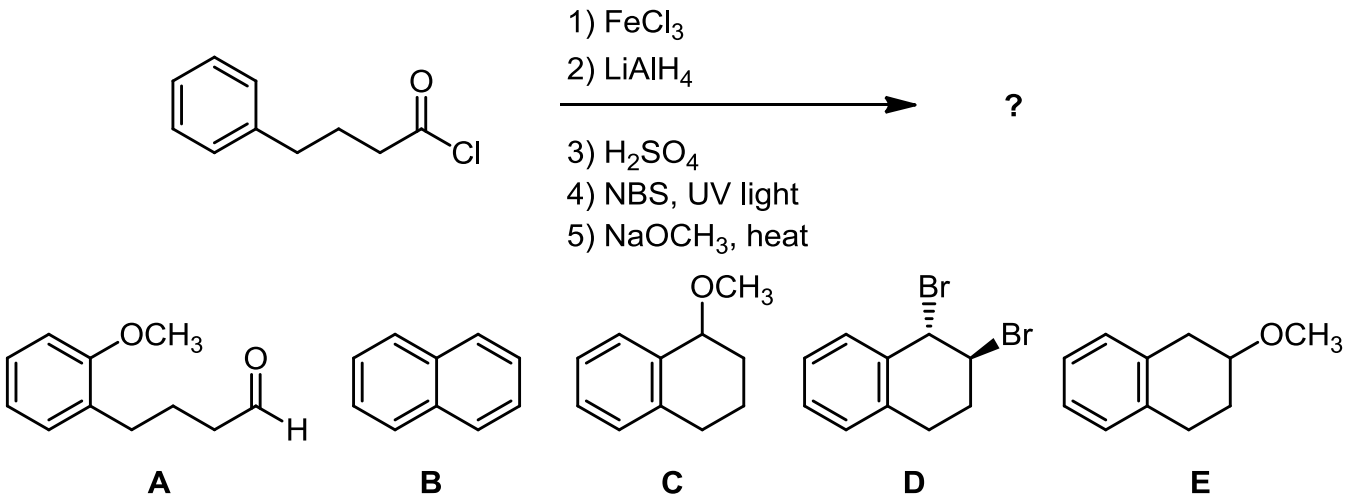
33.



34.

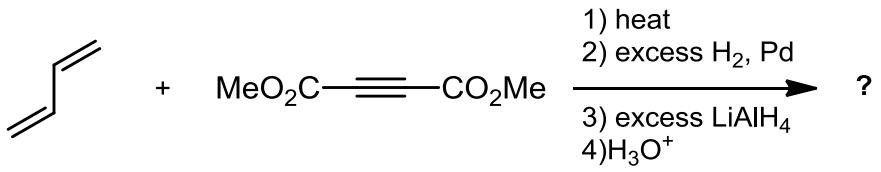


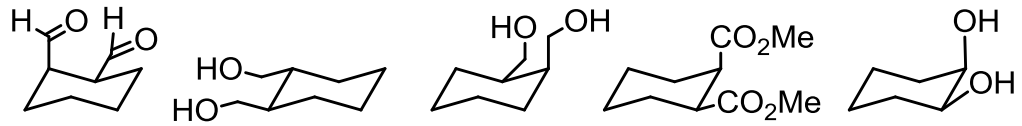
35.



CONTINUED -->

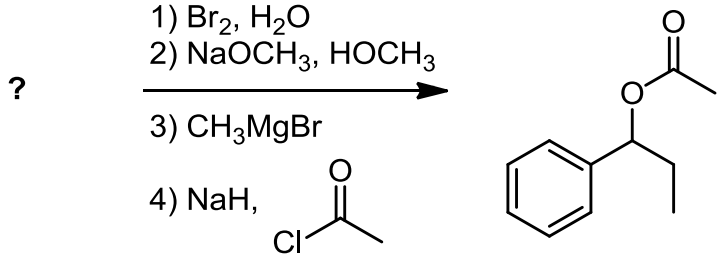
36.

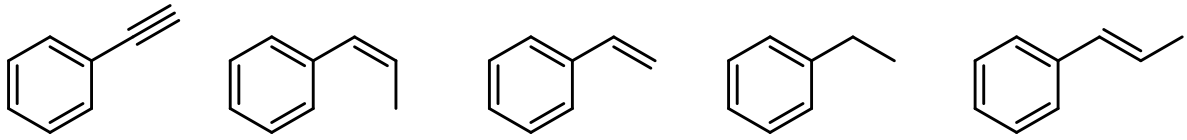




A **B** **C** **D** **E**

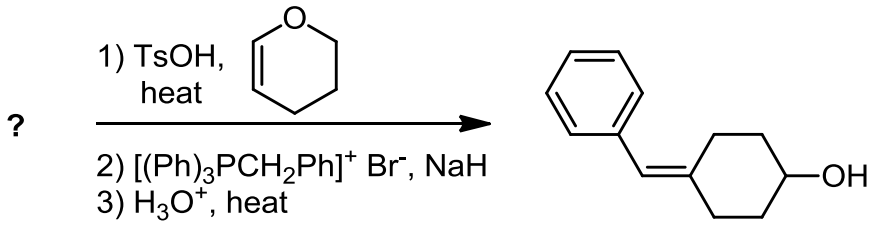
37.

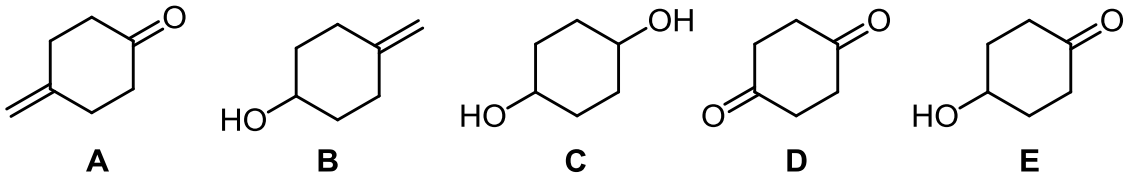




A **B** **C** **D** **E**

38.





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

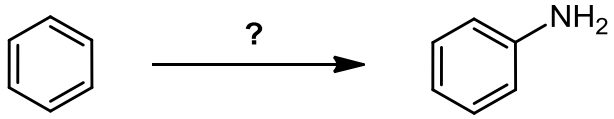
CONTINUED -->

10% PART 5: REAGENTS FOR SYNTHESIS

ANSWER ANY FIVE (5) OF THE SIX (6) QUESTIONS 39-44

For each of the questions 39-44 identify the reagent(s) required in order to BEST complete each of the reaction sequences shown by selecting from the list provided.

39.



A. i. $NaNO_2$ / HCl ii. Sn / HCl iii. NaOH

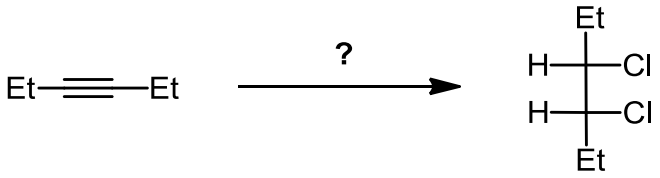
B. i. HNO_3 / H_2SO_4 ii. Sn / HCl iii. NaOH

C. i. $NaNO_2$ / HCl ii. H_2 / Pd

D. i. Br_2 / Fe ii. NH_3

E. H_2NNH_2 / NaOH / heat

40.



A. i. Na / NH_3, ii. Cl_2

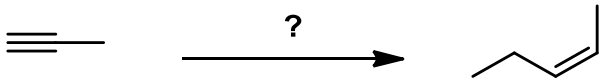
B. i. Na / NH_3, ii. CH_3CO_3H iii. $SOCl_2$ / Et_3N

C. i. H_2 / Pd, ii. Cl_2

D. i. H_2 / Lindlar's catalyst ii. Cl_2

E. i. H_2 / Lindlar's catalyst ii. CH_3CO_3H iii. $SOCl_2$ / Et_3N

41.



A. $NaNH_2$ ii. CH_3Br

B. $NaNH_2$ ii. CH_3CH_2Br

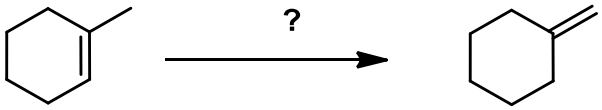
C. $NaNH_2$ ii. CH_3Br iii. H_2 / Lindlar's catalyst

D. $NaNH_2$ ii. CH_3CH_2Br iii. H_2 / Lindlar's catalyst

E. $NaNH_2$ ii. CH_3Br iii. Na / NH_3

CONTINUED -->

42.



A. H_2SO_4

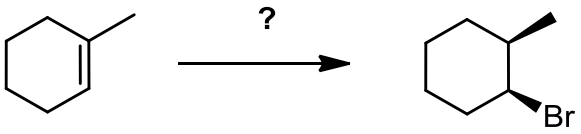
B. i. HBr ii. $KOC(CH_3)_3$ / $(CH_3)_3COH$ / heat

C. i. HBr / peroxides, ii. KOH / EtOH / heat

D. i. Br_2 ii. $KOC(CH_3)_3$ / $(CH_3)_3COH$ / heat

E. i. Br_2 ii. KOH / EtOH / heat

43.



A. HBr / peroxides / uv light

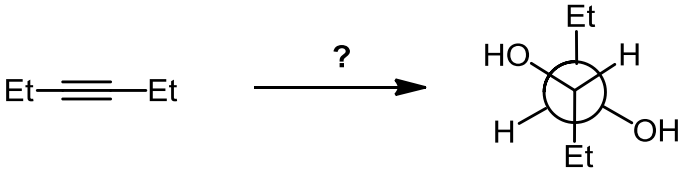
B. HBr / dark / N_2

C. i. BH_3 ii. aq. NaOH / H_2O_2 iii. HBr

D. i. aq. H_2SO_4 ii. HBr / peroxides / uv light

E. i. BH_3 ii. aq. NaOH / H_2O_2 iii. PBr_3 / Et_3N

44.



A. i. Na / NH_3, ii. O_3 iii. Zn / H^+

B. i. Na / NH_3 ii. $KMnO_4$ / aq. NaOH / 0^oC

C. i. H_2 / Pd ii. CH_3CO_3H iii. H_3O^+

D. i. H_2 / Lindlar's catalyst ii. $KMnO_4$ / aq. NaOH / 0^oC

E. i. H_2 / Lindlar's catalyst ii. CH_3CO_3H iii. H_3O^+

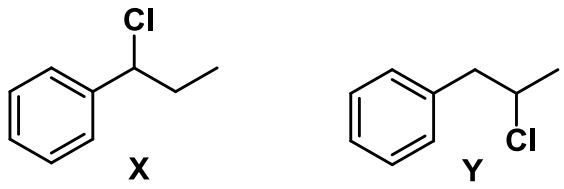
CONTINUED -->

10% PART 6: EXPLANATION OF PHENOMENA

ANSWER ALL FIVE (5) OF THE QUESTIONS 45 - 49.

Choose the single explanation that best rationalises the phenomenon indicated.

45. 1-Phenylprop-1-ene reacts with HCl to give **X** or **Y**. Which is the major product and why ?



A. **X** because the H adds end of the alkene with the most H already attached.

B. **X** because H+ adds first to give a benzylic carbocation.

C. **X** because Cl radical adds first to give a benzylic radical

D. **Y** because the H adds end of the alkene with the most H already attached..

E. **Y** because the Cl+ adds first to give a benzylic carbocation.

AB. **Y** because the H radical adds first to give a benzylic radical.

46. Consider the reaction of methoxybenzene (also known as anisole) with HNO_3 / H_2SO_4. Which isomer of nitroanisole is the major product and why ?

A. ortho because the $–NO_2$ group is activating and o,p-directing.

B. meta because the $–NO_2$ group is deactivating and m-directing.

C. para due to steric effects and because the $–NO_2$ is activating and o,p-directing.

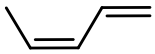
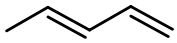
D. ortho because the $–OCH_3$ group is activating and o,p-directing.

E. meta because the $–OCH_3$ group is dectivating and m-directing.

AB. para due to steric effects and because the $–OCH_3$ is activating and o,p-directing.

CONTINUED -->

47. The two pentadienes shown below are geometric (E/Z) isomers. One of them undergoes Diels-Alder reactions significantly faster than the other. Which isomer is more reactive and why ?

A   **B**

A. **A** because it is the less stable isomer.

B. **A** because steric effects destabilise the s-cis conformation.

C. **A** because it has a more stable s-cis conformation.

D. **B** because it is the less stable isomer.

E. **B** because steric effects destabilise the s-cis conformation.

AB. **B** because it has a more stable s-cis conformation

48. Terminal alkynes react with 9-borabicyclononane (9-BBN) then aq. alkaline hydrogen peroxide to give aldehydes because:

A. Acid catalysed electrophilic addition of water follows Markovnikov's rule.

B. Acid catalysed electrophilic addition of water is anti-Markovnikov.

C. This radical addition is anti-Markovnikov.

D. Boron attacks the more substituted end of the system due to the cationic character.

E. The H atom adds end of the alkyne with the most H and then it tautomerises.

AB. Steric and electronic effects cause the boron to add at the terminal carbon.

49. Alkenes and alkynes often react in similar ways. But while alkenes react with peracids, RCO_3H to give epoxides in good yield, the analogous reaction of alkynes with peracids is far less successful. This is because:

A. Alkenes are more nucleophilic than alkynes.

B. The pi bonds in alkynes are stronger than those on alkenes.

C. The product of the alkyne reaction is anti-aromatic.

D. The product of the alkene reaction is aromatic.

E. Alkynes undergo an acid / base reaction that competes with the addition reaction.

AB. Steric effects interfere in the reaction of the alkyne with the peracid.

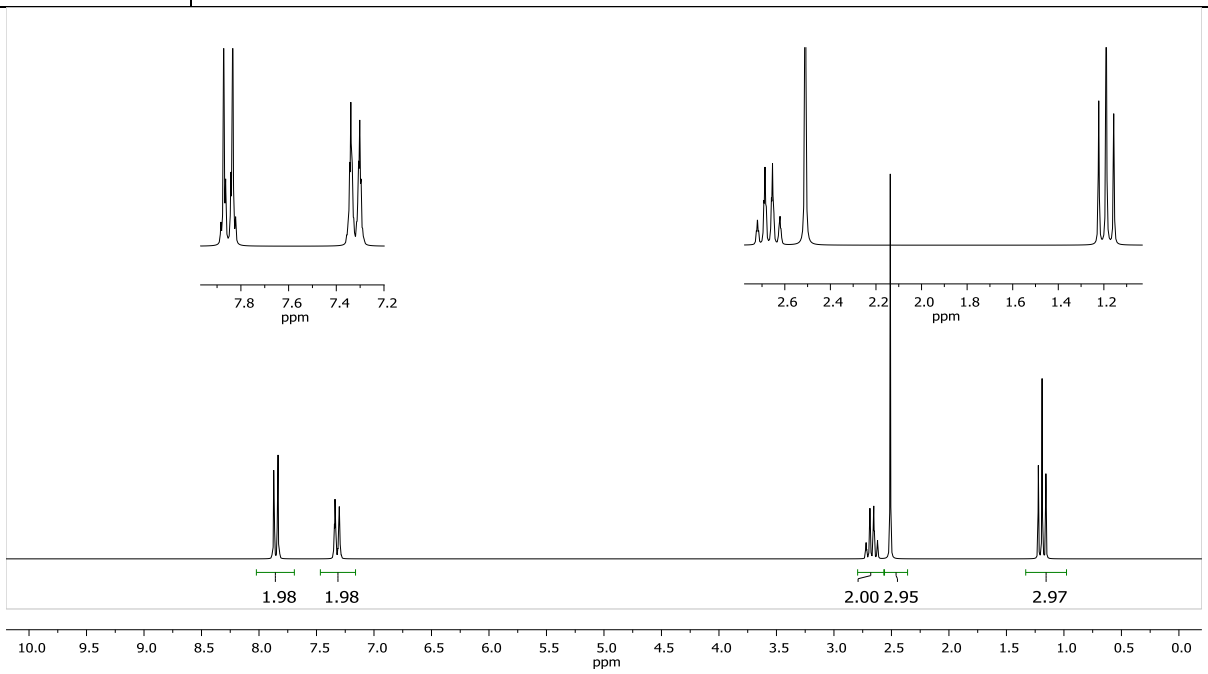
CONTINUED -->

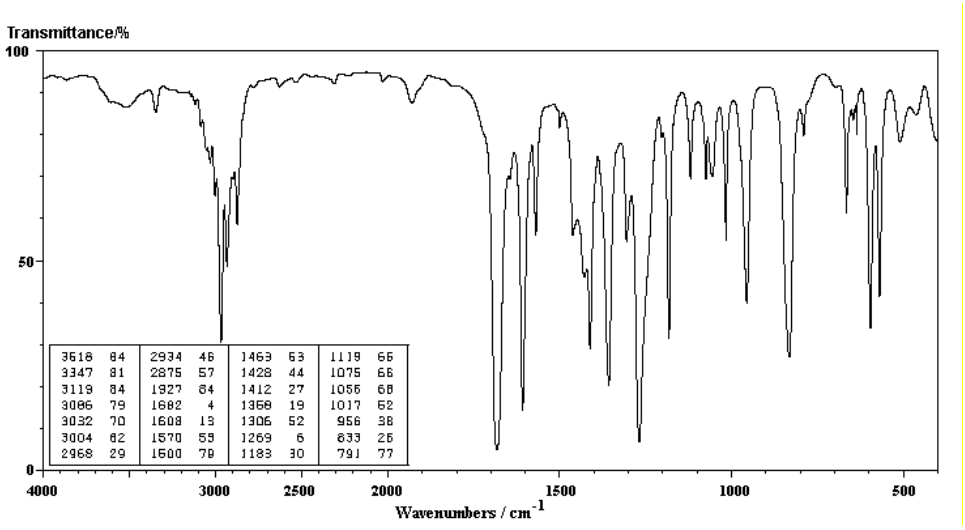
5% PART 7: LABORATORY

WRITE YOUR ANSWERS IN THE BLUE BOOKLET PROVIDED.

What is the structure of the following **unknown** based on the experimental data provided below ? Briefly rationalize your answer.

Unknown X:	Insoluble in water, 5% HCl, 5% aq. NaOH. Forms an orange precipitate when reacted with 2,4-dinitrophenylhydrazine. Forms a yellow precipitate in the iodoform test. Gave a clear solution in the Tollen's test. Gave a clear solution with ferric chloride.





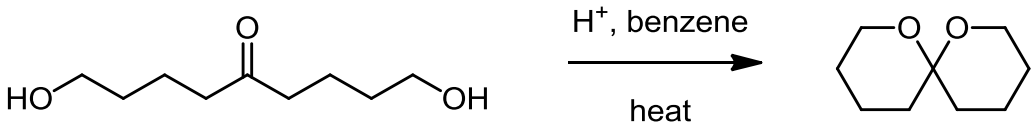
CONTINUED -->

8% **PART 8: MECHANISM**

ANSWER TWO (2) QUESTIONS, ONE FROM PART A AND ONE FROM PART B.
WRITE YOUR ANSWERS IN THE ANSWER BOOKLET PROVIDED.
NO REAGENTS OTHER THAN THOSE ALREADY SHOWN IN EACH QUESTION ARE REQUIRED.

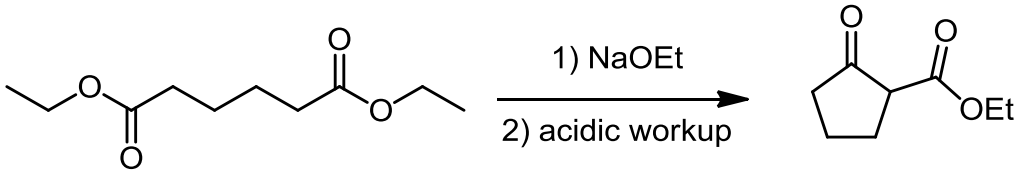
(4) PART A: Draw the curly arrow mechanism for ONE of the following transformations :

i.



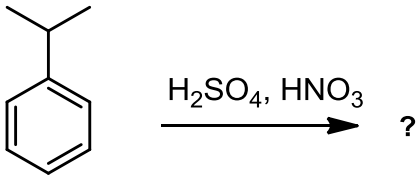
OR

ii.



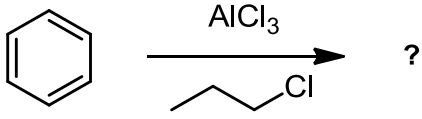
(4) PART B : Draw the curly arrow mechanism for ONE of the following transformations: (in each case assume only 1 equivelents of reagents)

i. :



OR

ii.



CONTINUED -->

12% PART 9: TOTAL SYNTHESIS

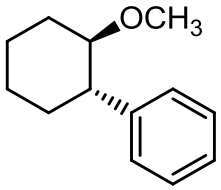
WRITE YOUR ANSWERS IN THE ANSWER BOOKLET PROVIDED.

Design an efficient synthesis from the starting materials in the list below for THREE (3) of the following target molecules. Choose one target from each of the three sections A, B and C.

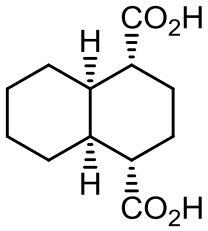
DO NOT SHOW MECHANISMS (*i.e.* curly arrows are NOT required)

SHOW YOUR ANSWER AS A STEPWISE REACTION SCHEME SHOWING THE REAGENT REQUIRED FOR EACH STEP AND THE SYNTHETIC INTERMEDIATE FORMED FROM EACH REACTION.

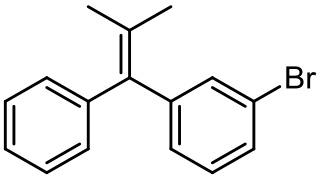
A



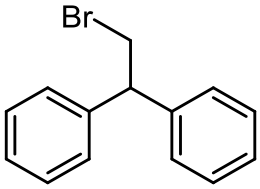
or



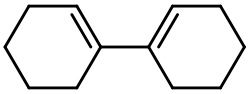
B



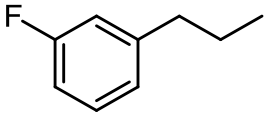
or



C



or



Permitted Materials and Reagents

NOTE: Any materials that contribute carbon atoms to the target molecule must come from this allowed list:

1. Any organic compounds with no more than **THREE** carbons
2. Benzene and / or cyclohexene
3. You can use any solvents or other reagents for the reactions as long as they do not contribute carbon atoms to the target.

CONTINUED -->

10% PART 10: STRUCTURE DETERMINATION

WRITE YOUR ANSWERS IN THE ANSWER BOOKLET PROVIDED

Compound **A**, C_4H_6O, had a strong IR absorption at about 1685cm^{-1} and ^{13}C NMR spectra peaks at 26, 129, 137 and 199 ppm.

Reagent **B** was prepared by the reaction of methyl bromide with triphenyl phosphine followed treatment with NaH.

A was then reacted with **B** to give hydrocarbon **C** as the major organic product with triphenylphospine oxide being formed at the by-product.

C was then heated with ethene at 200^{o}C it gave compound **D** which reacted rapidly with Br_2 / $CHCl_3$ to give a colourless solution.

When **D** was reacted with BH_3 and then H_2O_2 / aq. NaOH, compound **E** was formed, IR absorption near 3000cm^{-1} (broad). When **E** was reacted with acidic $K_2Cr_2O_7$ or PCC / CH_2Cl_2 compound **F**, $C_7H_{12}O$ was produced. The ^{13}C NMR spectra of **F** had 7 peaks, one at 213ppm and the rest were below 50ppm. The IR spectra of **F** had a strong absorption at 1712cm^{-1}. Reaction of **F** with CH_3CO_3H gave compound **G**, $C_7H_{12}O_2$ whose ^{13}C NMR spectra also had 7 peaks : 175, 70ppm and the rest below 50ppm. Reaction of **G** with excess methyl magnesium bromide / THF followed by a normal work-up gave 2-methyloctane-2,7-diol.

Compounds **E**, **F** and **G** were found to be chiral.

Identify the compounds **A**, **B**, **C**, **D**, **E**, **F** and **G** (structures are sufficient)

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

IRH/DJD W2017

CONTINUED -->

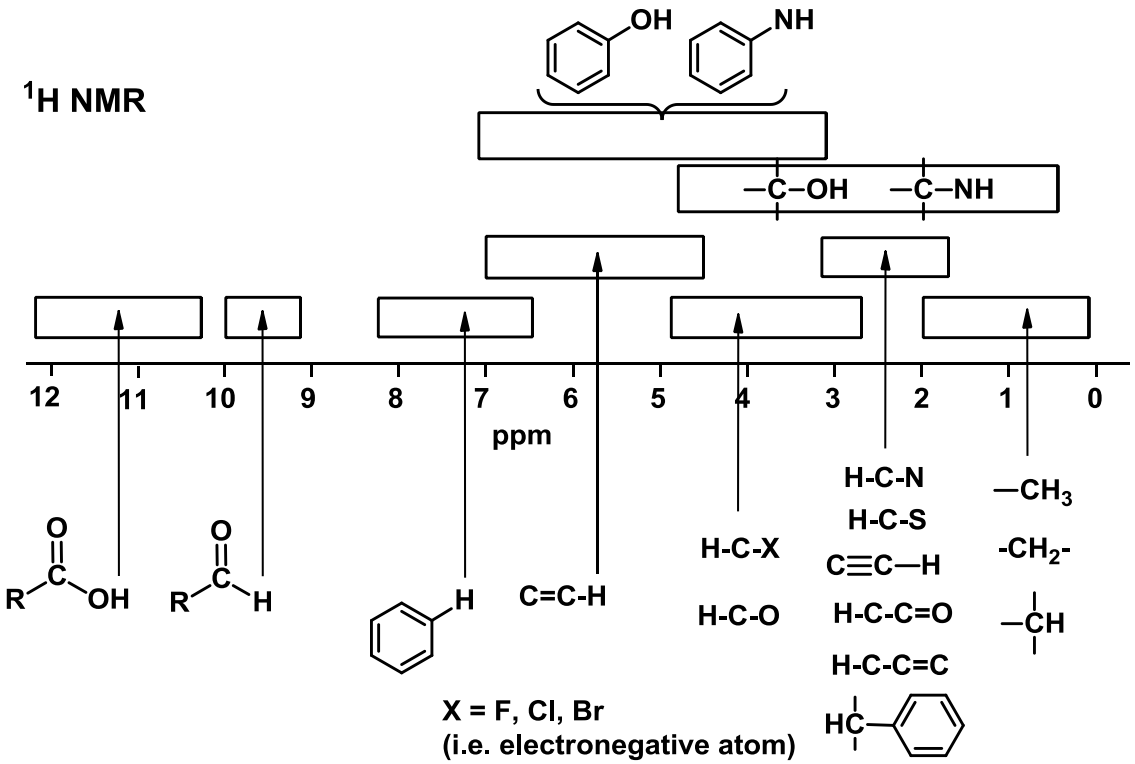
PERIODIC TABLE

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)

CONTINUED -->

SPECTROSCOPIC TABLES

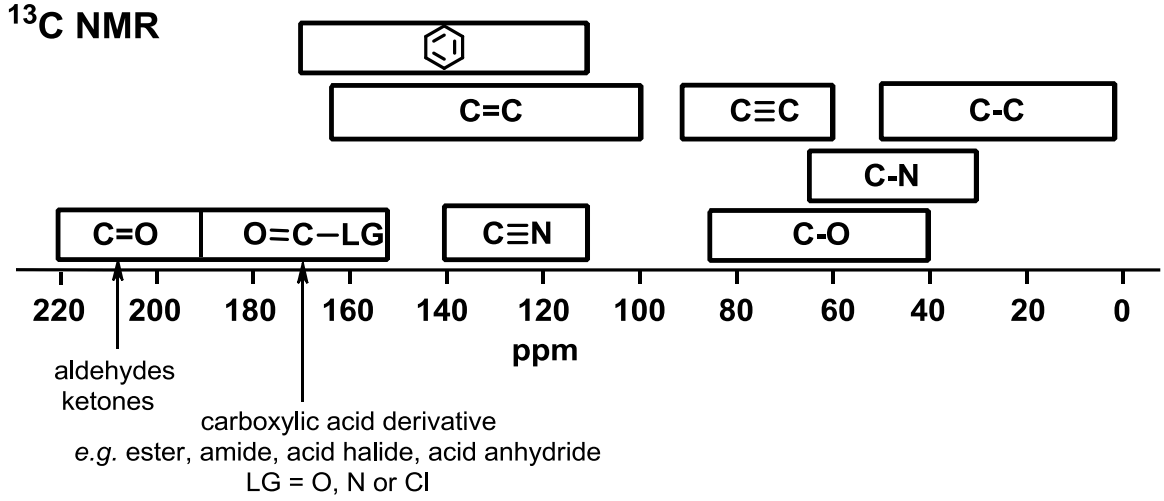


^{1}H NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm

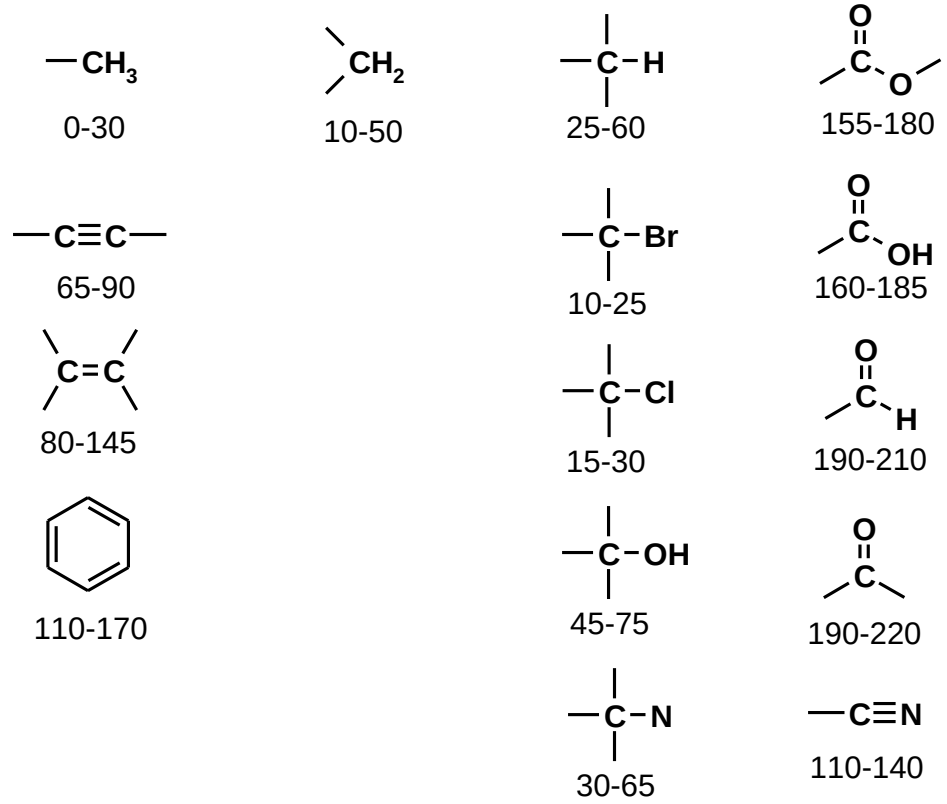
R =	methyl —CH$_3$	methylene -CH$_2$-	methyne —CH
R—C—	0.9	1.4	1.5
R, C=C	1.6	2.3	2.6
R—C(=O)—	2.1	2.4	2.5
R—N	2.2	2.5	2.9
R—(aryl)	2.3	2.7	3.0
R—Br	2.7	3.3	4.1
R—Cl	3.1	3.4	4.1
R—O—	3.3	3.4	3.7

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

CONTINUED -->



^{13}C NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm



CONTINUED -->

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.

CONTINUED -->