UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

FINAL EXAMINATION

CHEMISTRY 353

April 23rd, 2013 **Time: 3 Hours**

PLEASE WRITE YOUR **NAME, STUDENT I.D. NUMBER** ON THE **COMPUTER ANSWER SHEET** AND THE **BOOKLET** FOR THE WRITTEN ANSWER QUESTIONS.

READ THE INSTRUCTIONS CAREFULLY

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 examination booklet. Parts 1 - 6 consist of a series of multiple choice questions numbered 1 - 55 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***.

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 are permitted during the exam; calculators are also permitted, ***but NOT programmable calculators***.

Absolutely no other electronic devices are allowed.

Value

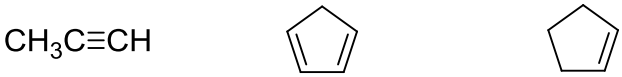
12% **PART 1: RELATIVE PROPERTIES**

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:

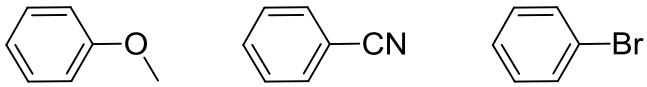
A	**i > ii > iii**	**D**	**ii > iii > i**
B	**i > iii > ii**	**E**	**iii > i > ii**
C	**ii > i > iii**	**AB**	**iii > ii > i**

1. The relative pKa of the most acidic hydrogen in each of the following:



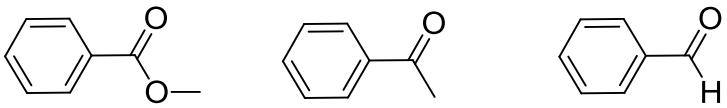
i **ii** **iii**

2. The relative rate of reaction of CH_3CH_2Cl / $AlCl_3$ with each of the following:



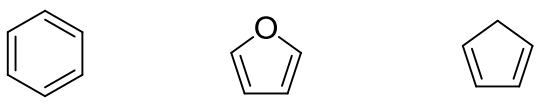
i **ii** **iii**

3. The relative reactivity towards $NaBH_4$ / EtOH of each of the following:



i **ii** **iii**

4. The resonance energies of each of the following:



i **ii** **iii**

5. The number of enolisable (or α-protons) in each of the following:

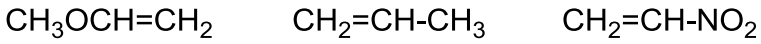
i 2-pentanone **ii** ethanal **iii** cyclobutanone

CONTINUED -->

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

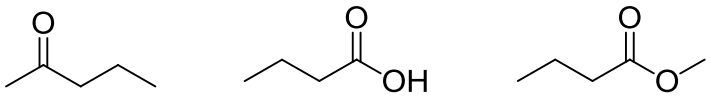
A	**i > ii > iii**	**D**	**ii > iii > i**
B	**i > iii > ii**	**E**	**iii > i > ii**
C	**ii > i > iii**	**AB**	**iii > ii > i**

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



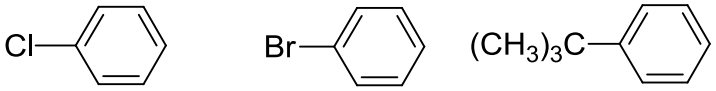
i **ii** **iii**

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



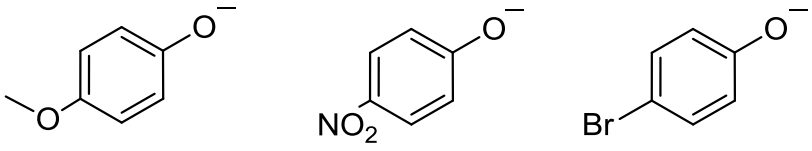
i **ii** **iii**

8. The % yield of the ***ortho*** product produced by the reaction of Br_2 / $FeBr_3$ with each of the following:



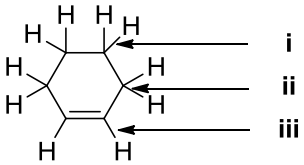
i **ii** **iii**

9. The relative basicity of the following:



i **ii** **iii**

10. The relative strength of the indicated C-H bonds:



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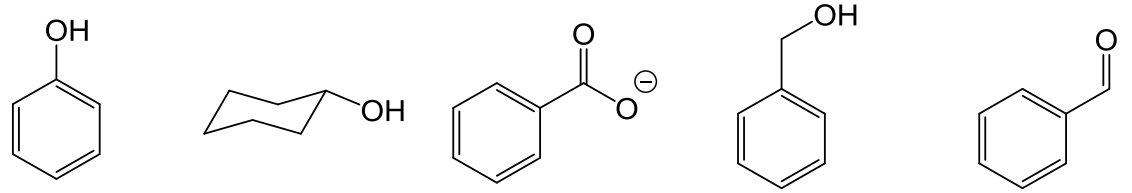
Value

8 % **PART 2: STRUCTURE AND PROPERTIES**

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

IN SOME CASES more than one answer may be correct and ALL compounds that apply MUST be selected for full credit.

SET 1:



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

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

11. Select the structure that is the most acidic.

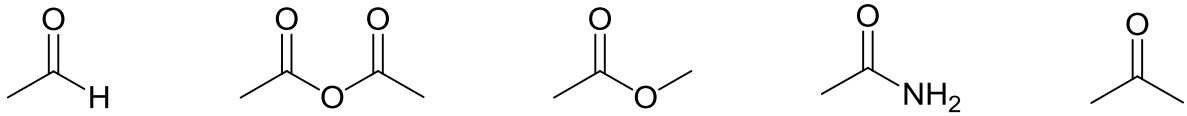
12. Select **ALL** structures that would give a hydrate when reacted with water

13. Select **ALL** structures that could be synthesized by reducing a ketone.

14. Select the structure with the **shortest** carbon oxygen bond.

15. Select the structure that would be a product following the hydrolysis of phenyl ethanoate

SET 2



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

Answer questions 16-19 by selecting the compounds from SET 2 above.

16. Select the compound that has the **most** types of hydrogen atom.

17. Select **ALL** the compounds that would give a primary alcohol when reduced with excess $LiAlH_4$ followed by a normal aqueous acid work up?

18. Select the compound that has the hydrogen with the **lowest** pKa.

19. Select the compound that would be the **most** reactive towards hydrolysis using aqueous sodium hydroxide solution.

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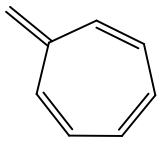
Value

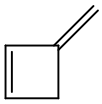
9% **PART 3: AROMATICITY AND RESONANCE**

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

SET 3:

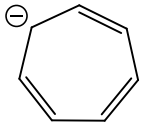


A

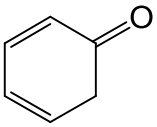


B

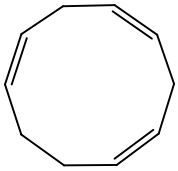
C



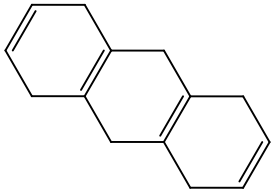
D



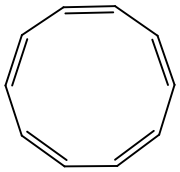
E



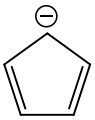
AB



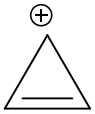
AC



AD



AE



BC

Answer questions 20-24 by selecting a <u>SINGLE compound</u> from SET 3 above.

20. An aromatic compound where n = 1 when applying the Hückel rule.

21. Non-aromatic as drawn, but has an aromatic resonance structure.

22. Non-aromatic as drawn, but can react with a proton to form an aromatic conjugate acid.

23. A conjugated tetraene.

24. Anti-aromatic as drawn.

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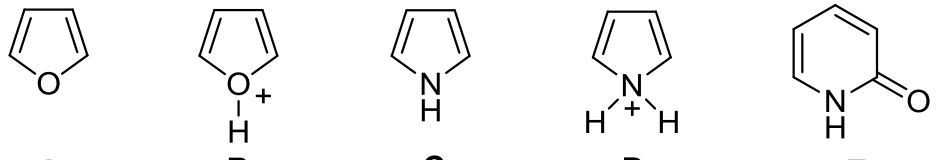
SET 4:



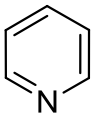
A

B

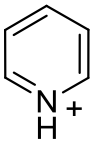
C

D

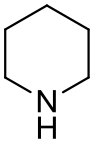
E



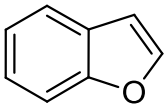
AB



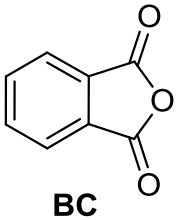
AC



AD



AE



BC

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

25. Select the structure that has the **most** acidic proton.

26. Select the structure that is the **most** basic.

27. Select a **single** compound that is aromatic as drawn, but also has a non-aromatic conjugate acid.

28. Select a **single** compound that has an sp^3 hybridised heteroatom.

29. Select a **single** compound that has an aromatic tautomer.

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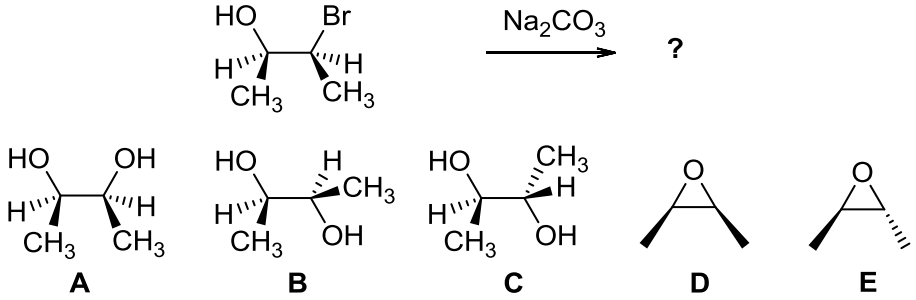
16% PART 4: STARTING MATERIALS AND PRODUCTS OF SYNTHESIS

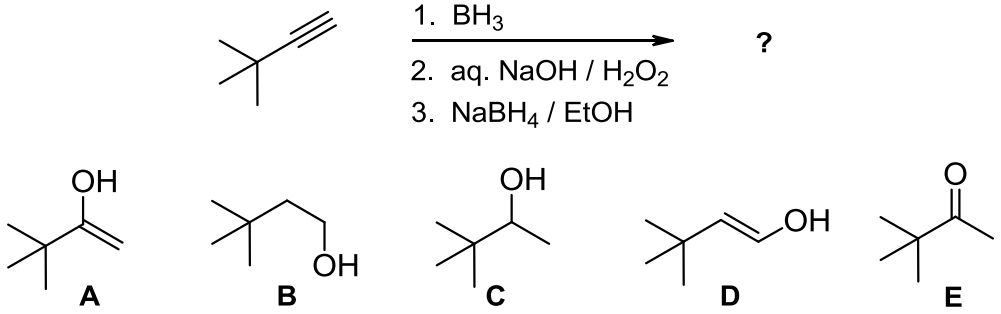
ANSWER ANY EIGHT (8) OF THE NINE (9) QUESTIONS 30-38.

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.

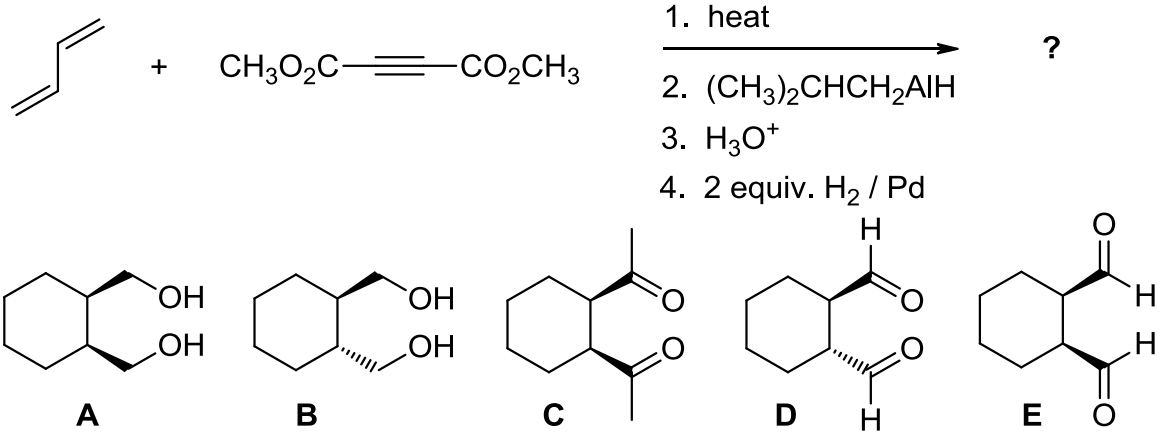
30.



31.



32.



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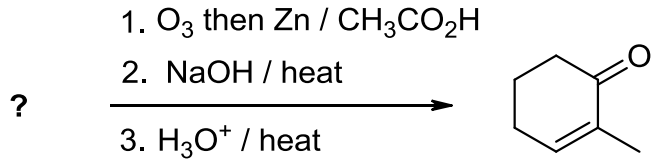
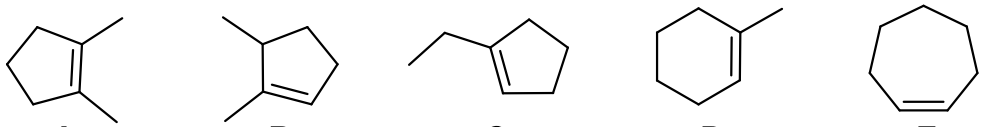
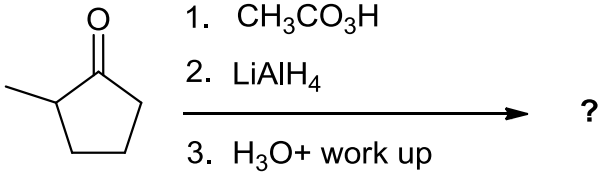
33.

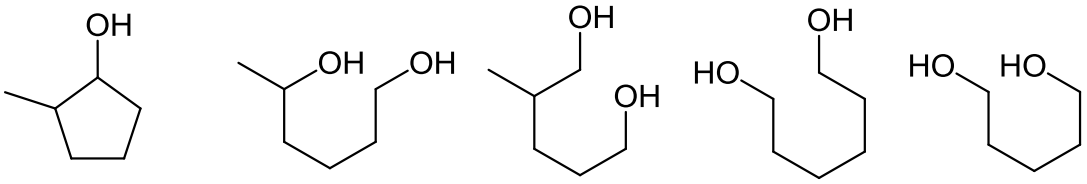




A **B** **C** **D** **E**

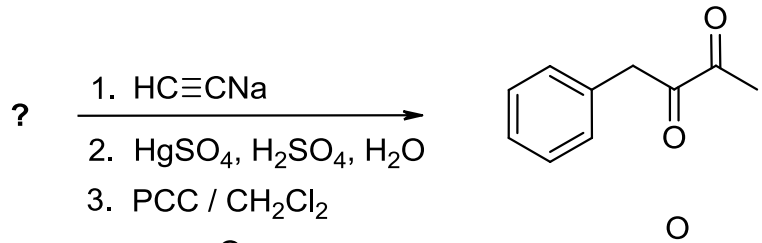
34.

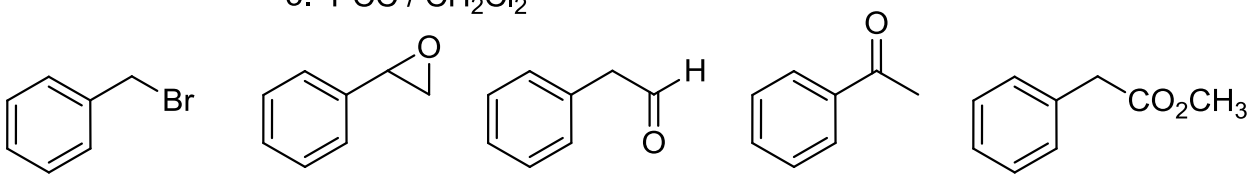




A **B** **C** **D** **E**

35.





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

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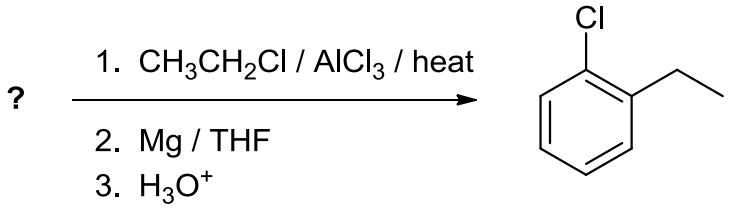
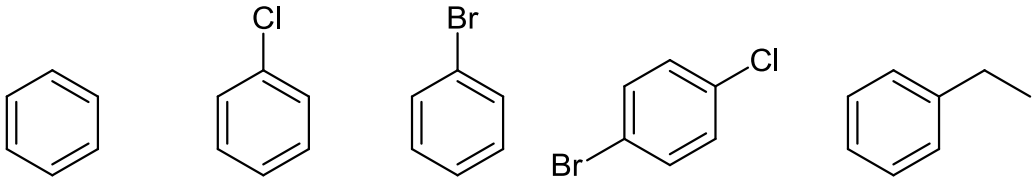
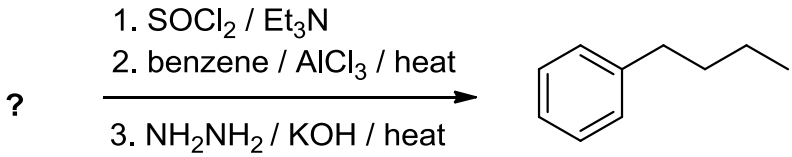
36.

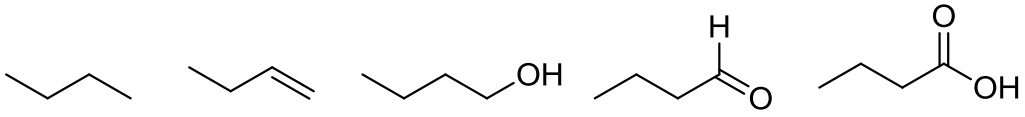




A **B** **C** **D** **E**

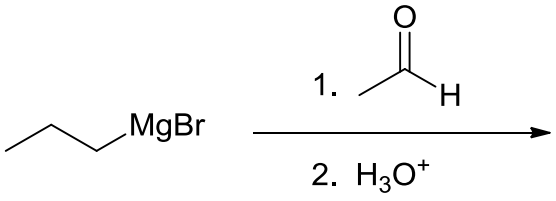
37.

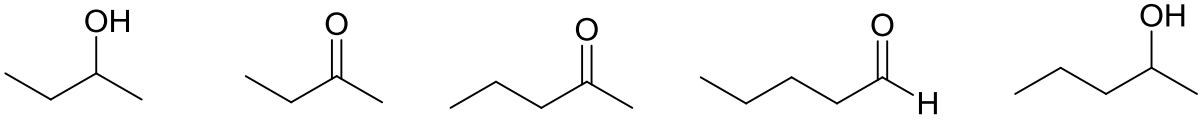




A **B** **C** **D** **E**

38.





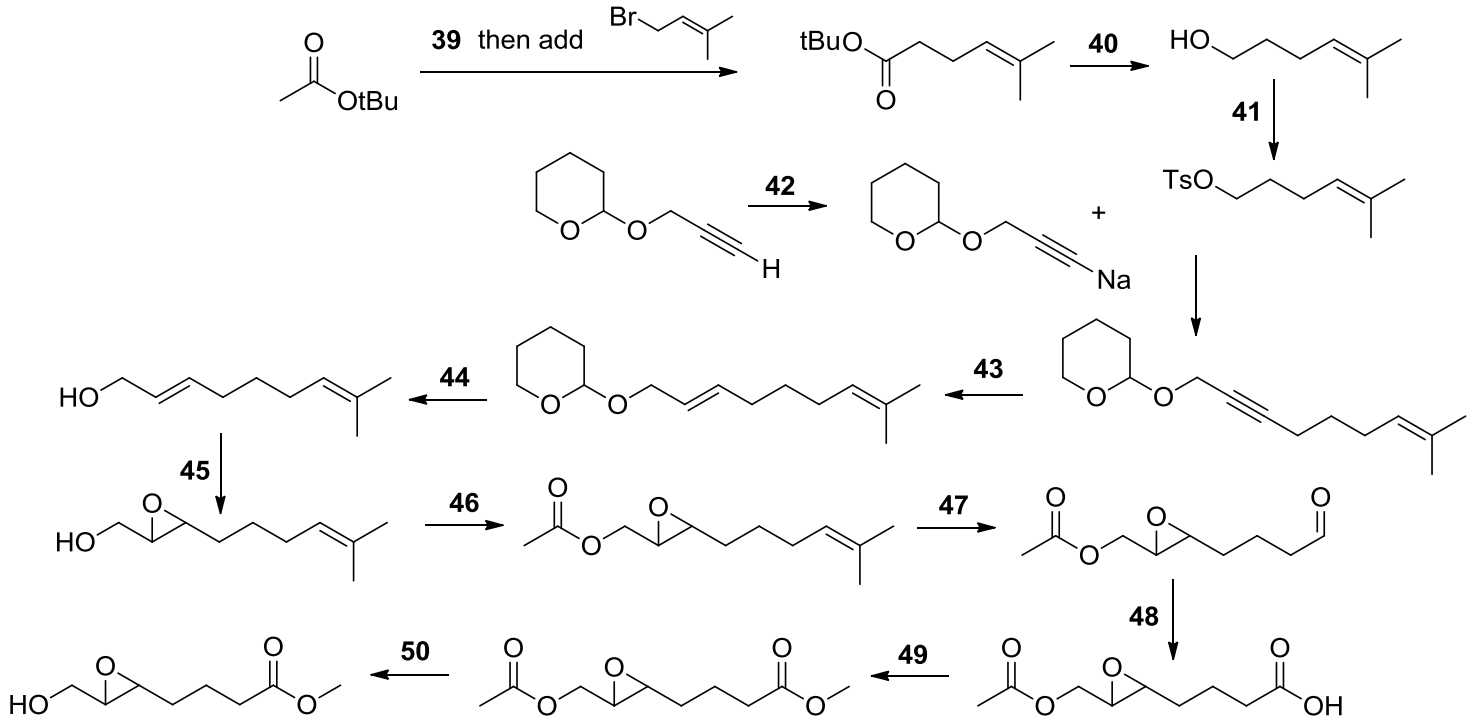
A **B** **C** **D** **E**

CONTINUED -->

10% **PART 5: REAGENTS FOR SYNTHESIS**

ANSWER ANY TEN (10) OF THE TWELVE (12) QUESTIONS 39 - 50

The following reaction scheme shows the synthesis of a component used in the Corey *et al*. synthesis of Leukotriene A_4 (LTA_4), part of a group of compounds with important roles in cell and tissue biology. From the list of reagents provided in the table below, select the ***BEST*** reagent combination to carry out each of the reactions required at each numbered step. Reagents can be used in more than one step if required.



A. TsOH / CH_3OH	BC. H_3O^+ / Δ
B. TsCl / pyridine	BD. K_2CO_3 / CH_3OH
C. $NaBH_4$ then H_3O^+	BE. K_2CO_3 / CH_3I
D. $LiAlH_4$ / Et_2O then H_3O^+	CD. NaOH / EtOH
E. $(CH_3CO)_2O$ / pyridine	CE. Lithium diisopropylamide
AB. PCC	DE. $NaNH_2$
AC. CrO_3 / aq. H_2SO_4 / acetone	ABC. Na / NH_3
AD. O_3 then $(CH_3)_2S$	ABD. H_2 / Lindlar's catalyst
AE. CH_3MgBr / THF then H_3O^+	ABE. CH_3CO_3H

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Value

10% **PART 6: EXPLANATION OF PHENOMENA**

ANSWER ALL FIVE (5) OF THE QUESTIONS 51 - 55.

CHOOSE THE SINGLE EXPLANATION THAT BEST RATIONALISES THE PHENOMENON INDICATED.

51. When propene is reacted with hydrogen bromide in the presence of peroxides the major product is:

A. 2-bromopropane because a secondary radical is formed in the rate determining step.
B. 1-bromopropane because a secondary radical is formed in the rate determining step.
C. 2-bromopropane because a primary radical is formed in the rate determining step.
D. 1-bromopropane because a primary radical is formed in the rate determining step.
E. 1,2-Dibromopropane because this is an electrophilic addition.

52. When hexafluoropropanone is added to water it more readily forms a hydrate than propanone because:

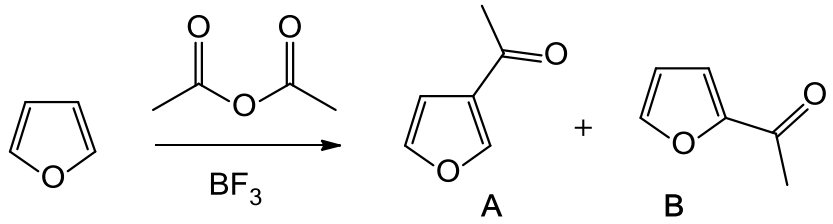
A. The hexafluoropropanone hydrate is more stable due to steric factors.
B. The hexafluoropropanone hydrate is less stable due to steric factors.
C. Propanone reacts with the nucleophilic water molecule at a faster rate.
D. Hexafluoropropanone reacts with the electrophilic water molecule at a faster rate.
E. Hexafluoropropanone is destabilized by induction.

53. The reaction of an ethoxide ion with a carboxylic acid does not result in the formation of an ethyl ester because:

A. OH^- is a poor leaving group.
B. The carboxylic acid is relatively stable.
C. The actual product of this reaction is an aldol condensation adduct.
D. The actual product of this reaction is a diethyl acetal.
E. The actual product of this reaction is a carboxylate ion.

CONTINUED -->

54. When furan undergoes electrophilic aromatic substitution, the substitution occurs preferentially to give **product B** rather than the **product A**. This is because:



A. **Product A** is more stable.

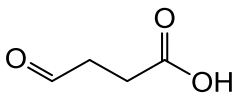
B. **Product B** is more stable.

C. The cationic intermediate leading to **product A** is more stable.

D. The cationic intermediate leading to **product B** is more stable.

E. The oxygen atom in furan is an *ortho-para* directing group.

55. A chemist attempted to synthesise 4-hydroxybutanoic acid by reducing the compound shown below with $NaBH_4$, but could not isolate the desired product. This is because:



A. $NaBH_4$ reduced both the carboxylic acid and the aldehyde.

B. $NaBH_4$ is not reactive enough to reduce the carboxylic acid or the aldehyde.

C. An intermediate was formed that reacted to give a cyclic acetal.

D. An intermediate was formed that reacted to give a cyclic ester.

E. An intermediate was formed that reacted to give an aldol reaction.

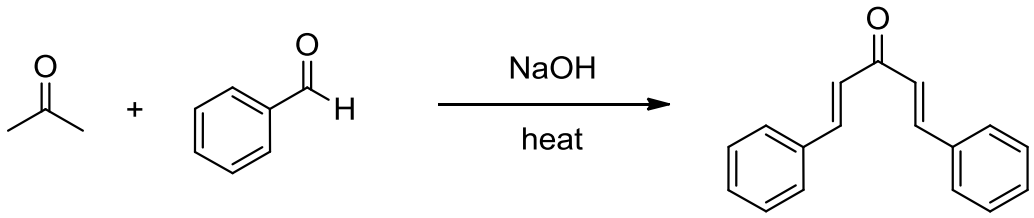
CONTINUED -->

Value

5% **PART 7: LABORATORY**

WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED.

Calculate the **% yield of dibenzalacetone** based on the following experimental data:



dibenzalacetone

Benzaldehyde (1.59 g) and propan-2-one (*i.e*. acetone) (0.58 g) were stirred at 50^{o}C in a solution of NaOH (1.75 g) in ethanol (50 mL). After 45 minutes, the reaction was cooled in an ice bath and the precipitate was collected by vacuum filtration, washed three times with cold water (50 mL) and then recrystallised from 70% aqueous ethanol to give dibenzalacetone (1.58 g).

CONTINUED -->

Value

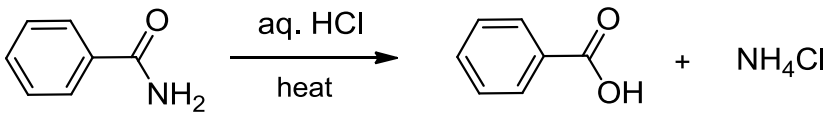
8% **PART 8: MECHANISM**

WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED.

NO REAGENTS OTHER THAN THOSE ALREADY SHOWN IN EACH QUESTION ARE REQUIRED.

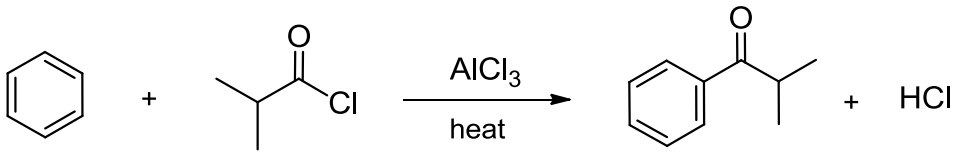
(4) PART A: Draw the curly arrow mechanism for ONE of the following transformations :

i.



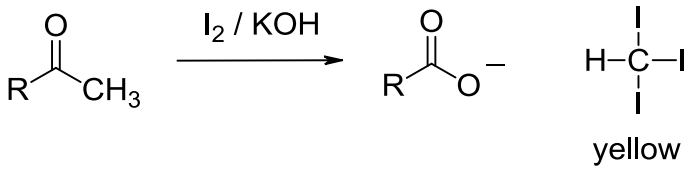
OR

ii.



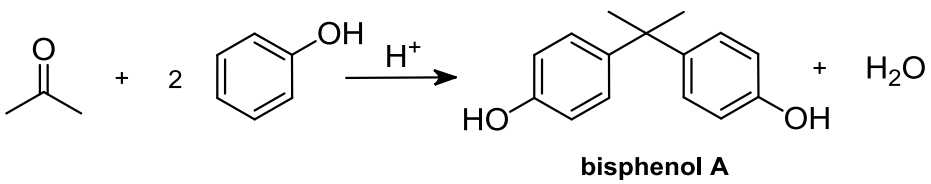
(4) PART B : Draw the curly arrow mechanism for ONE of the following transformations:

i. Methyl ketones react with iodine in basic solution to give a yellow precipitate due to the formation of iodoform (shown below). This reaction is an example of the haloform reaction.



OR

ii.



bisphenol A

CONTINUED -->

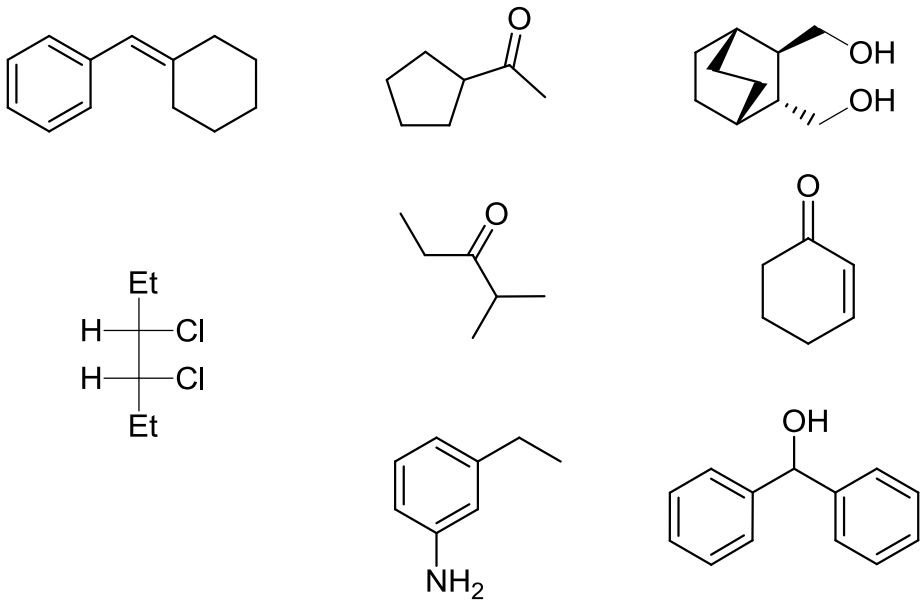
12% **PART 9: TOTAL SYNTHESIS**

WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED.

Design an efficient synthesis for any THREE (3) of the following target molecules using any of the starting materials and reagents given in the accompanying list.

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.



Permitted Materials and Reagents

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

- Any organic compounds with no more than **FOUR** carbons
- benzene
- cyclohexanol

You can use any solvents or other reagents for the reactions provided that they do not contribute carbon atoms to the target.

CONTINUED -->

Value

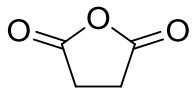
10% **PART 10: STRUCTURE DETERMINATION**

WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED

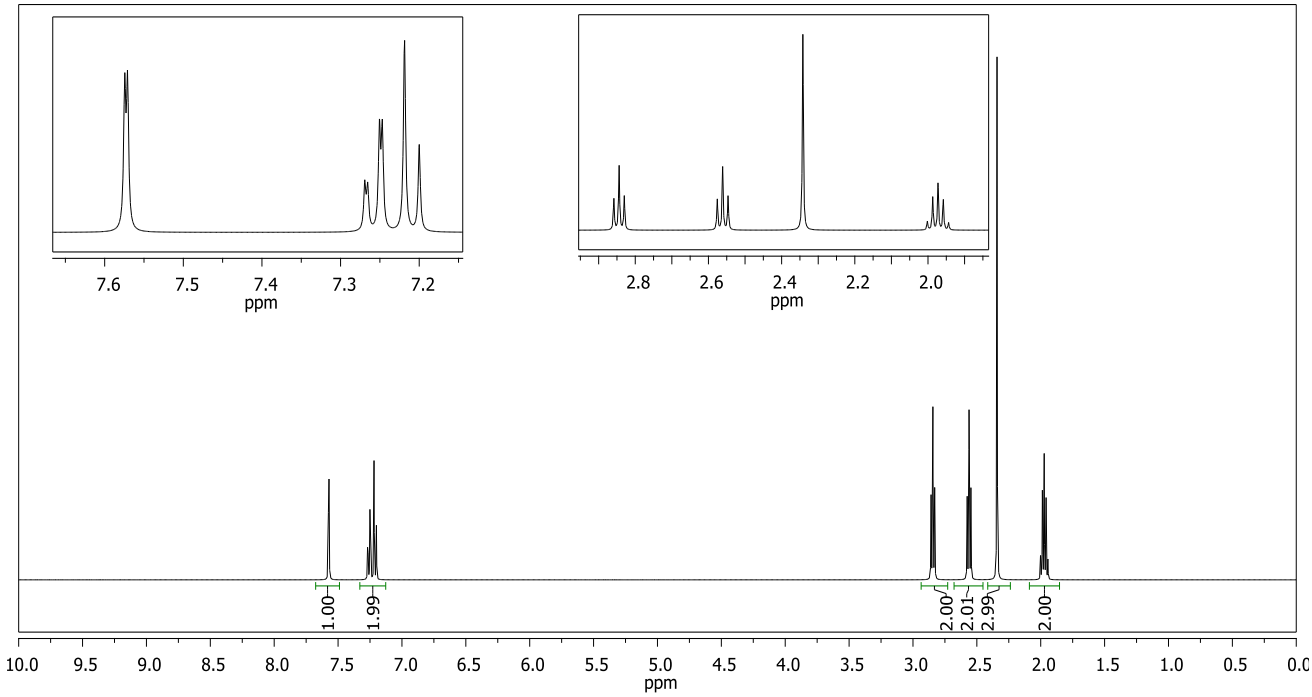
Compound **A** was found to be a hydrocarbon where the mass spectra showed the M+ at 92. When **A** was heated with butandioic anhydride (shown below) and $AlCl_3$, followed by an aqueous acid work-up, the major product was **B**, $C_{11}H_{12}O_3$. **B** was then treated with Zn / Hg in conc. HCl to give **C** $C_{11}H_{14}O_2$. **C** was then reacted with thionyl chloride / Et_3N to give **D** which was then heated with $AlCl_3$ to give **E** $C_{11}H_{12}O$ as the major product. The H-NMR spectra of **E** is shown below. **E** gave a negative ferric chloride test and an orange precipitate with 2,4-dinitrophenylhydrazone (2,4-DNP)

When **E** was reacted with CH_3CO_3H it gave **F** $C_{11}H_{12}O_2$. When **F** was heated with aqueous acid, **G** $C_{11}H_{14}O_3$ was formed. **G** gave a positive ferric chloride test and did not react with 2,4-DNP. The IR of **G** showed absorptions from 3000-3500 cm^{-1} (strong and broad) and near 1710 cm^{-1} (strong)

What are **A - G** ?

butandioic anhydride = 

H-NMR of **E**



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

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)

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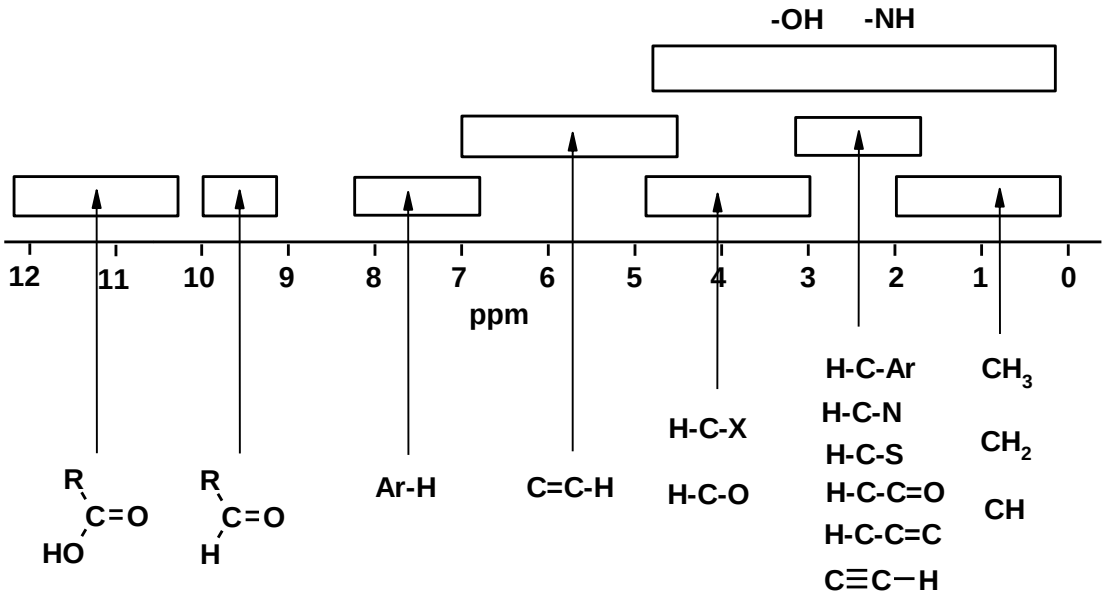
Schematic diagrams of NMR chemical shift data for H and ^{13}C NMR

^{1}H NMR



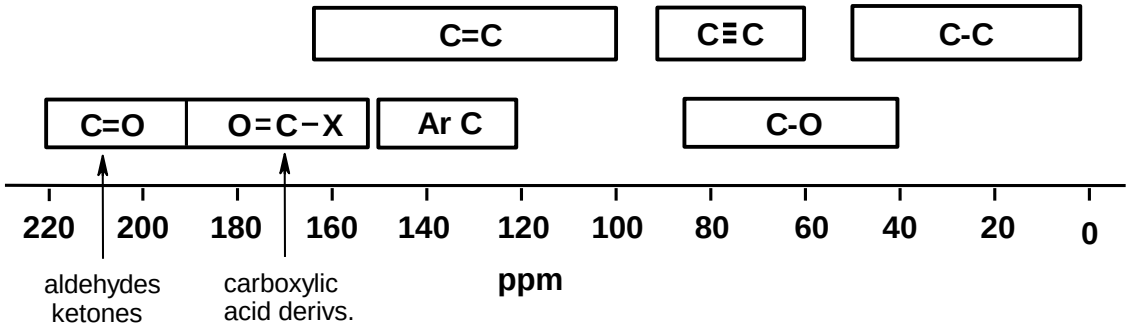
^{1}H NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm

	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

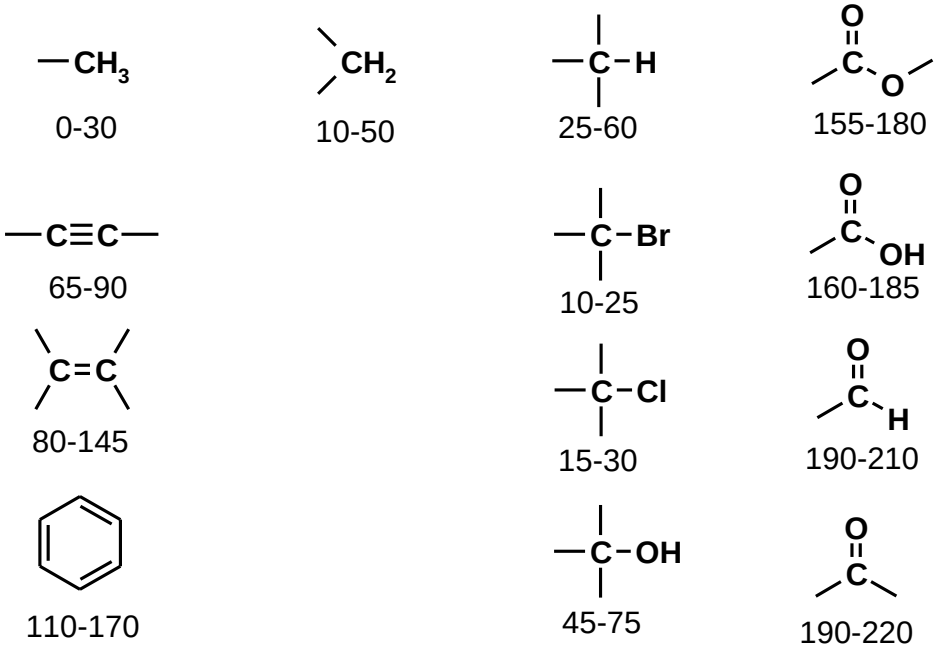
other	
-OH	1-5
-NH	1-3
C≡CH	2.5
C=C, H	5.5
Ar-H	7.3
O, C, R, H	10
O, C, R, OH	9-12

CONTINUED -->

^{13}C NMR



^{13}C NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm



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INFRA-RED GROUP ABSORPTION FREQUENCIES

		TYPE OF VIBRATION	FREQUENCY (cm^{-1})	WAVELENGTH (μ)	INTENSITY (1)
C–H	Alkanes	(stretch)	3000-2850	3.33-3.51	s
	$-CH_3$	(bend)	1450 and 1375	6.90 and 7.27	m
	$-CH_2-$	(bend)	1465	6.83	m
	Alkenes	(stretch)	3100-3000	3.23-3.33	m
		(bend)	1700-1000	5.88-10.0	s
	Aromatics	(stretch)	3150-3050	3.17-3.28	s
		(out-of-plane bend)	1000-700	10.0-14.3	s
	Alkyne	(stretch)	ca. 3300	ca.3.03	s
	Aldehyde		2900-2800	3.45-3.57	w
			2800-2700	3.57-3.70	w
C–C	Alkane	not usually useful			
C=C	Alkene		1680-1600	5.95-6.25	m-w
	Aromatic		1600-1400	6.25-7.14	m-w
C≡C	Alkyne		2250-2100	4.44-4.76	m-w
C=O	Aldehyde		1740-1720	5.75-5.81	s
	Ketone		1725-1705	5.80-5.87	s
	Carboxylic acid		1725-1700	5.80-5.88	s
	Ester		1750-1730	5.71-5.78	s
	Amide		1700-1640	5.88-6.10	s
	Anhydride		ca. 1810	ca. 5.52	s
			ca. 1760	ca. 5.68	s
	Acyl chloride		1800	5.55	s
C–O	Alcohols, Ethers, Esters,				
	Carboxylic acids		1300-1000	7.69-10.0	s
O–H	Alcohols, Phenols				
	Free		3650-3600	2.74-2.78	m
	H-Bonded		3400-3200	2.94-3.12	m
	Carboxylic acids (2)		3300-2500	3.03-4.00	m
N–H	Primary and secondary amines		ca. 3500	ca. 2.86	m
C≡N	Nitriles		2260-2240	4.42-4.46	m
N=O	Nitro ($R-NO_2$)		1600-1500	6.25-6.67	s
			1400-1300	7.14-7.69	s
C–X	Fluoride		1400-1000	7.14-10.0	s
	Chloride		800-600	12.5-16.7	s
	Bromide, Iodide		<600	>16.7	s

(1) s = strong, m = medium and w = weak

(2) note that the -OH absorption of solid carboxylic acids which run as a nujol mull can be difficult to see as they maybe very broad.

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1 1A																	18 8A
1 **H** 1.008	**2** 2A											**13** 3A	**14** 4A	**15** 5A	**16** 6A	**17** 7A	2 **He** 4.003
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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)							

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