UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

FINAL EXAMINATION

CHEMISTRY 353

Version 1

April 24th, 2015 **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 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 and calculators are permitted, ***but NOT programmable calculators***.

Absolutely no other electronic devices are allowed.

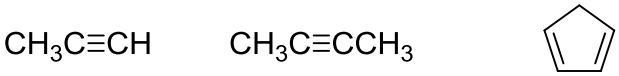
12% PART 1: RELATIVE PROPERTIES

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:

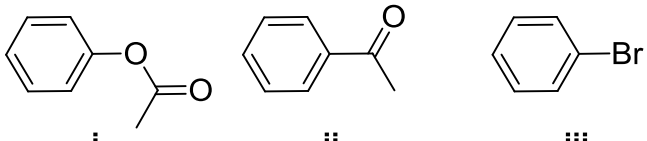
A	**i > ii > iii**	**D**	**ii > iii > i**
B	**i > iii > ii**	**E**	**iii > i > ii**
C	**ii > i > iii**	**AB**	**iii > ii > i**

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



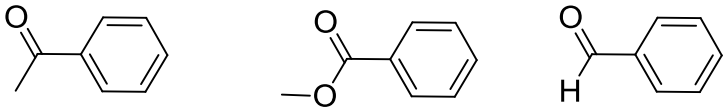
i **ii** **iii**

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



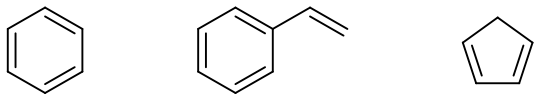
i **ii** **iii**

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



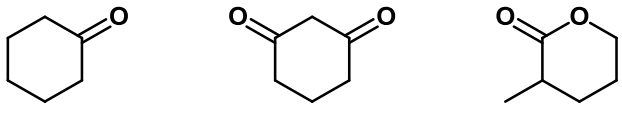
i **ii** **iii**

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:



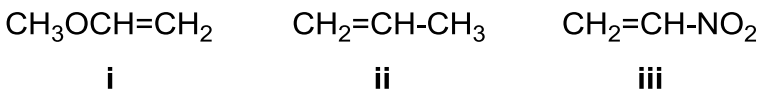
i **ii** **iii**

CONTINUED -->

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

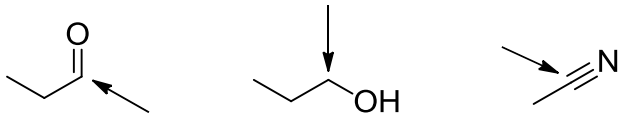
A	**i > ii > iii**	**D**	**ii > iii > i**
B	**i > iii > ii**	**E**	**iii > i > ii**
C	**ii > i > iii**	**AB**	**iii > ii > i**

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



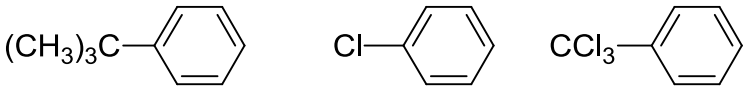
i **ii** **iii**

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



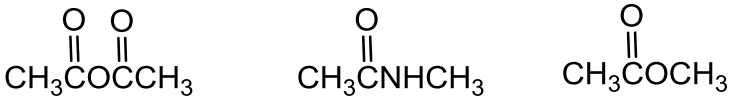
i **ii** **iii**

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



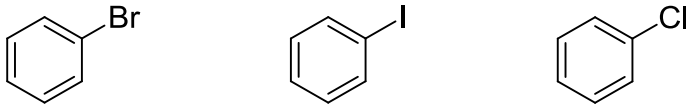
i **ii** **iii**

9. The relative reactivity towards hydrolysis using aqueous NaOH of the following:



i **ii** **iii**

10. The relative reactivity towards Mg of each of the following:



i **ii** **iii**

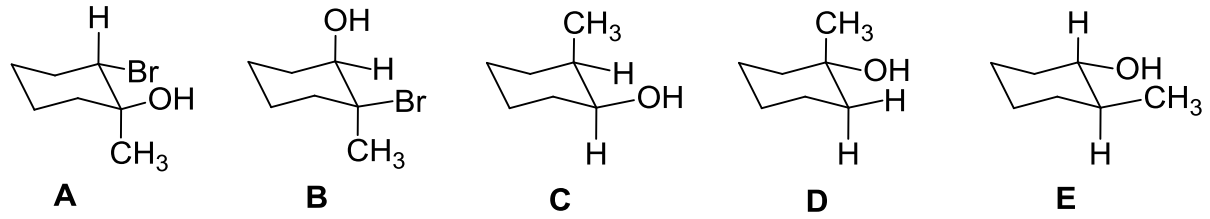
CONTINUED -->

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



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

11. Which compound is the **major product** formed from the reaction of 1-methylcyclohexene with HOBr ?

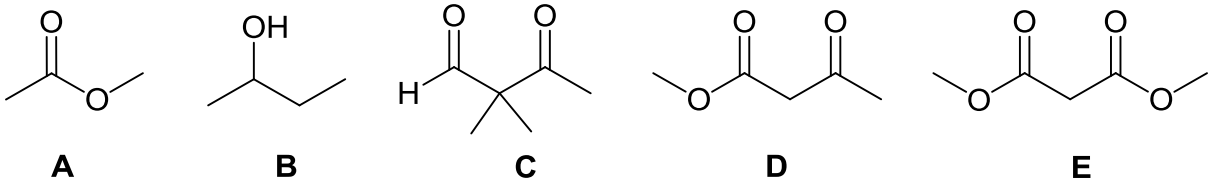
12. Which compound(s) can be treated with NaH / THF to form an epoxide ?

13. Which compound is the **major product** formed from the reaction of 1-methylcyclohexene with aqueous H_2SO_4 ?

14. Which compound is the **major product** from the hydroboration / oxidation of 1-methylcyclohexene ?

15. Which compound(s) has (have) a hydroxyl group that is **cis** to a methyl group ?

SET 2



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

16. Which compound has the **most** acidic hydrogen

17. Which compound(s) has (have) an active methylene group ?

18. Select **ALL** the compounds that would be reduced with excess $LiAlH_4$ followed by a normal aqueous acid work up to give butane-1,3-diol ?

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

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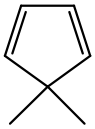
9% PART 3: AROMATICITY AND RESONANCE

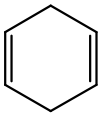
ANSWER ANY NINE (9) OF THE TEN (10) QUESTIONS 20 - 29.

SET 3:

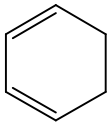
A



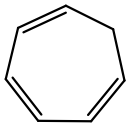
B



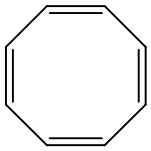
C



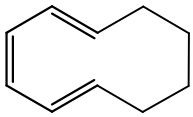
D



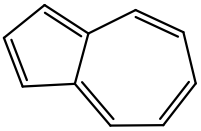
E



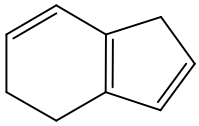
AB



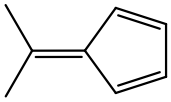
AC



AD



AE



BC

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

20. An aromatic compound where n $\neq$ 1 when applying the Hückel rule.

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

22. Non-aromatic as drawn, but has an aromatic conjugate base.

23. A polyene with the most resonance energy stabilization.

24. A polyene with no resonance energy stabilization.

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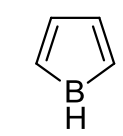
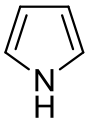
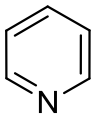
SET 4:



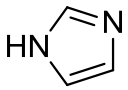
A



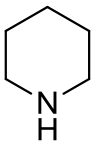
B



C

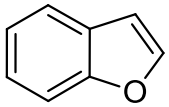


D

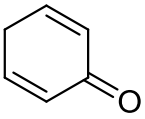


E

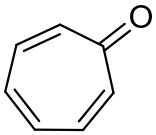
AB



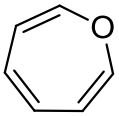
AC



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** basic N atom.

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

27. Select a **single** compound that is non-aromatic as drawn, but has an aromatic resonance structure.

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

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

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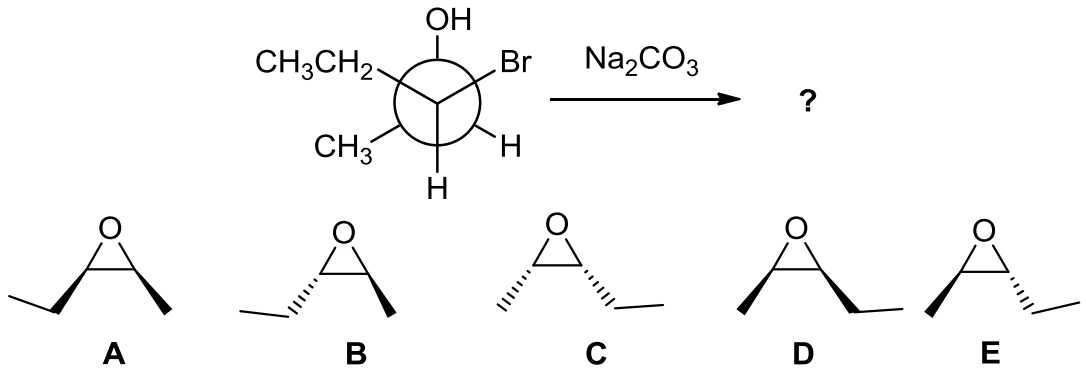
16% PART 4: STARTING MATERIALS AND PRODUCTS OF SYNTHESIS

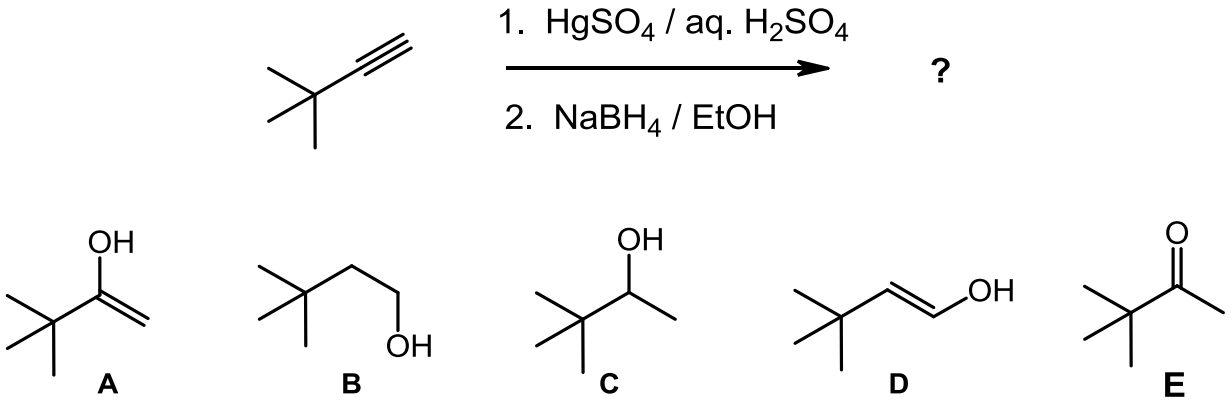
ANSWER ANY EIGHT (8) OF THE NINE (9) QUESTIONS 30-38.

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.



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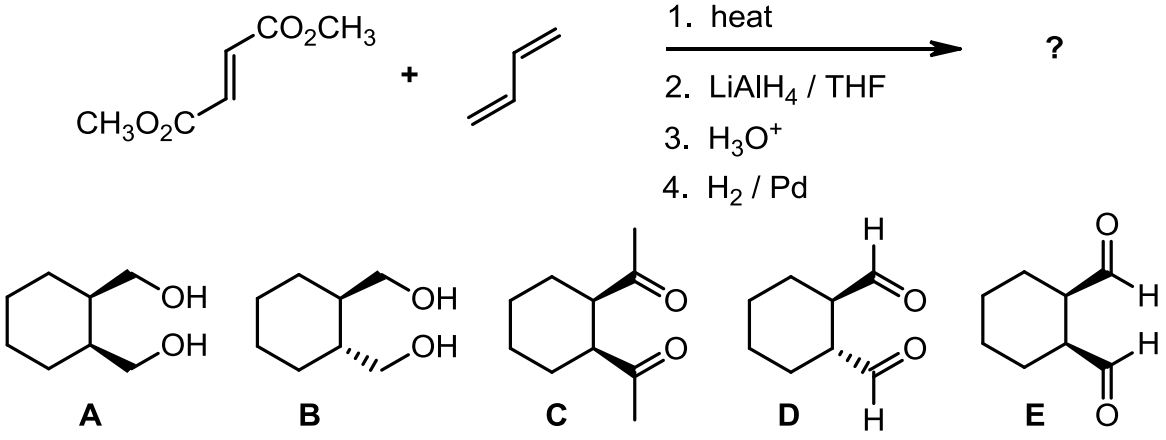

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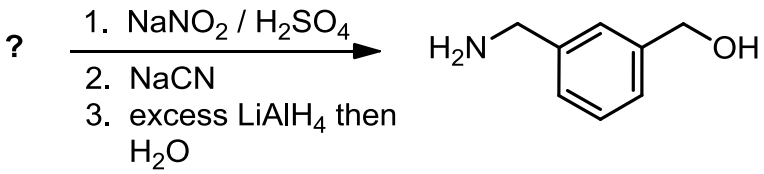
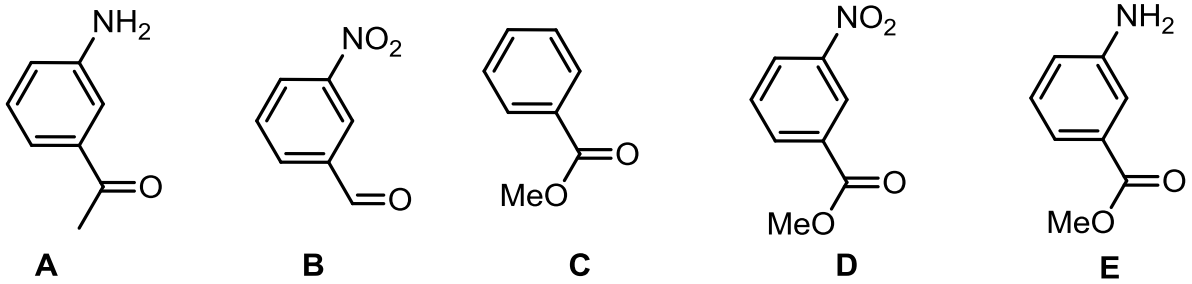
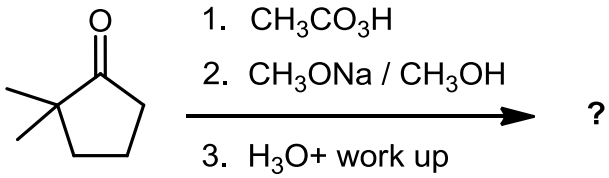
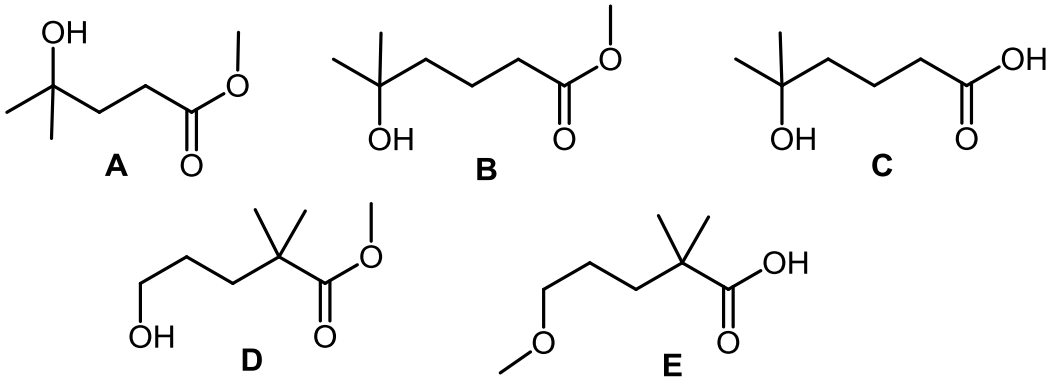
33.





34.





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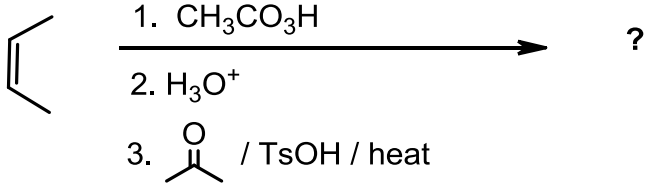

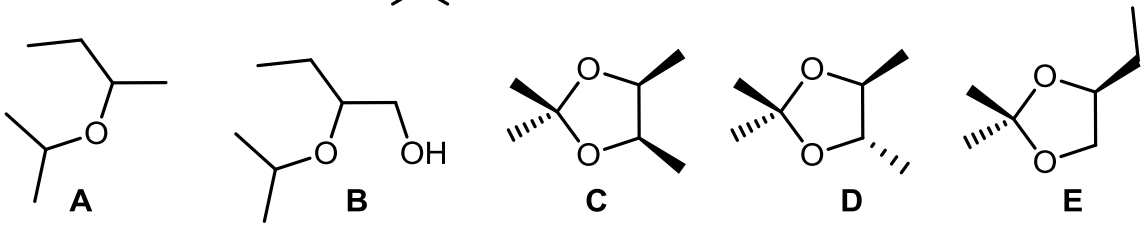

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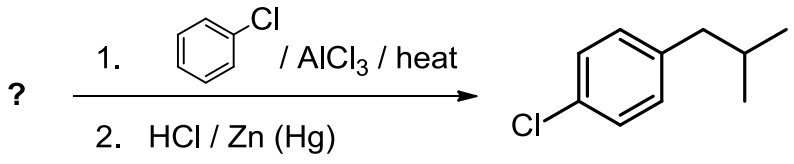
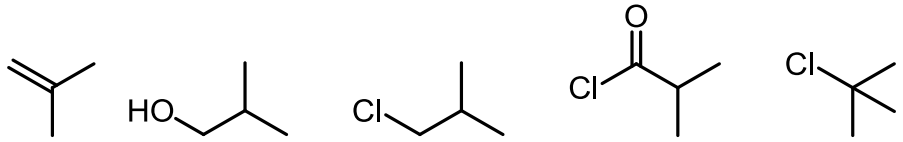
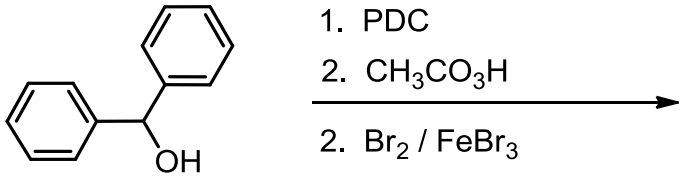
36.

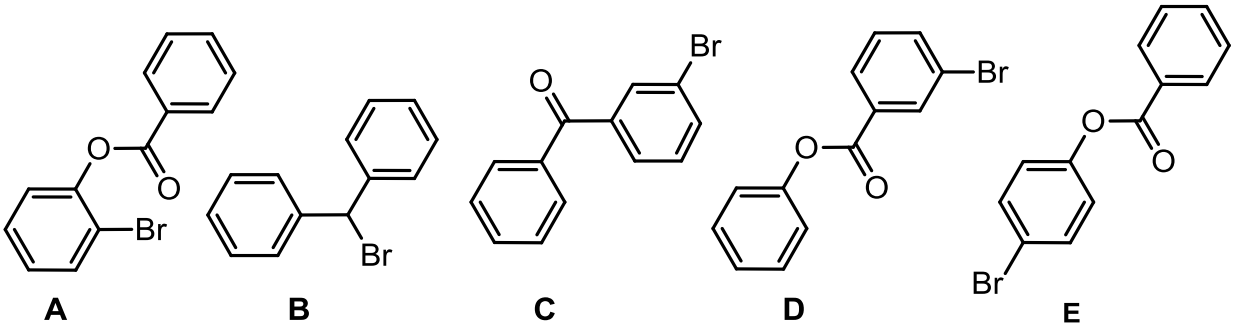




A **B** **C** **D** **E**

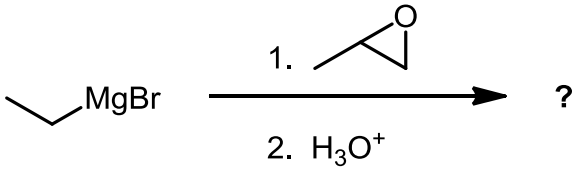
37.

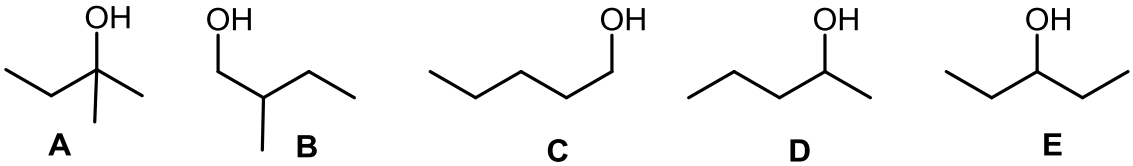




A **B** **C** **D** **E**

38.





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

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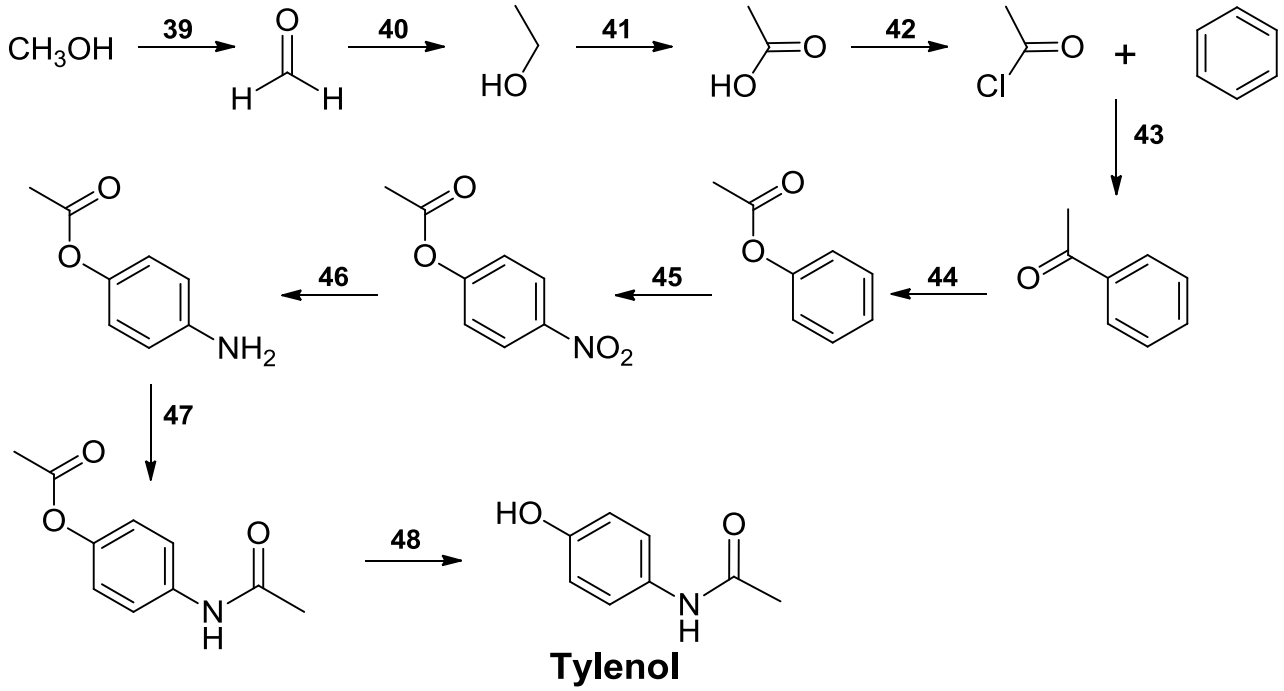
10% PART 5: REAGENTS FOR SYNTHESIS

ANSWER ALL TEN (10) OF THE QUESTIONS 39 - 48

The following reaction scheme shows a possible synthesis of Tylenol, a cold medicine, commonly found in commercial products. From the list of reagents provided in the table below, select **the best reagent combination** (meaning in some steps, you might need more than one reagent) to carry out each of the reactions required at each numbered step.



A.	$NaNO_2$ / H_2SO_4	**BD.**	$SOCl_2$
B.	PDC / CH_2Cl_2	**BE.**	$AlCl_3$
C.	$NaBH_4$	**CD.**	CH_3CO_2H / pyridine
D.	CH_3MgBr, then HBr heat	**CE.**	CH_3CH_2Li, then H_3O^+
E.	$K_2Cr_2O_7$ / aq. H_2SO_4	**DE.**	Sn / HCl then NaOH
AB.	Mg/Et_2O then CO_2, then H+	**ABC.**	NaOH / H_2O / heat then H_3O^+
AC.	$(CH_3CO)_2O$ / pyridine	**ABD.**	O_3 then H_2O
AD.	HNO_3 / H_2SO_4	**ABE.**	CH_3I
AE.	Aq. HCl	**BCD.**	CH_3MgBr then H_3O^+
BC.	Concentrated HCl	**BCE.**	CH_3CO_3H

CONTINUED -->

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 benzoic acid is heacted with HNO_3 / H_2SO_4, the major product is 3-nitrobenzoic acid. This is because:

A. The $–NO_2$ group is deactivating and an o,p-director.

B. The $–NO_2$ group is deactivating and a m-director.

C. The $–CO_2H$ group is deactivating and an o,p-director.

D. The $–CO_2H$ group is deactivating and a m-director.

E. The $–SO_3H$ group is deactivating and acts as a blocking group.

AB. The $–SO_3H$ group is activating and acts as a blocking group.

52. When 2,2,2-trichloroethanal is added to water forms more hydrate than ethanal because:

A. The 2,2,2-trichloroethanal hydrate is more stable due to steric factors.

B. The 2,2,2-trichloroethanal is less stable due to steric factors.

C. Ethanal reacts with the nucleophilic water molecule at a faster rate.

D. 2,2,2-Trichloroethanal reacts with the nucleophilic water molecule at a faster rate.

E. The carbonyl C in 2,2,2-trichloroethanal is more electrophilic due to inductive effects.

AB. The carbonyl C in ethanal is more electrophilic due to inductive effects.

53. The conversion of 2,2-diethoxypropane to propan-2-one and ethanol does not work in aq. NaOH. This is because:

A. The reaction would lack a good nucleophile.

B. The reaction would lack a good electrophile.

C. The starting material would be deprotonated by the hydroxide ion.

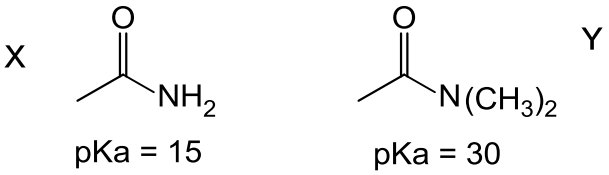
D. Due to Le Chatilier's principle, the presence of H_2O would favour the ketal form.

E. Due to Le Chatilier's principle, the presence of H_2O would favour the ketone form.

AB. The reaction would lack a good leaving group.

CONTINUED -->

54. Two amides and their pKas for the most acidic hydrogens are shown below. Amide **X** is more acidic because:



A. The conjugate base of **X** is better stabilized by resonance.

B. The conjugate base of **X** is better stabilized by inductive effects

C. The conjugate base of **Y** is better stabilized by resonance

D. The conjugate base of **Y** is better stabilized by inductive effects

E. The N atom in **X** is sp^2 hybridised.

AB. The N atom in **Y** is sp^3 hybridised.

55. Propanal reacts with MeMgBr faster than propan-2-one. This is because:

A. The α-protons of propanal are more acidic than the α-protons of propan-2-one.

B. The α-protons of propan-2-one are more acidic than the α-protons of propanal

C. The methyl group in propan-2-one makes the carbonyl C less electrophilic.

D. The methyl group in propanal makes the carbonyl C less electrophilic.

E. The aldehyde proton, -CHO, is more acidic than the protons in propan-2-one.

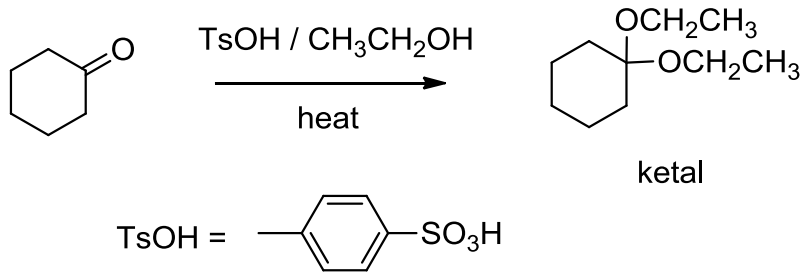
AB. The alcohol proton, -COH, is more acidic than the protons in propan-2-one

CONTINUED -->

5% PART 7: LABORATORY

WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED.

Calculate the % yield of the ketal product based on the following experimental data:



TsOH =

Densities:

Cyclohexanone = 0.9478 g/mL

Ethanol = 0.789 g/mL

Ketal = 0.908 g/mL

Cyclohexanone (9.815 g), tosic acid (0.1722 g) and ethanol (10 mL) were heated at reflux for an hour. The reaction was cooled in an ice bath and the ketal product was collected by distillation, to provide the product (10.00 g).

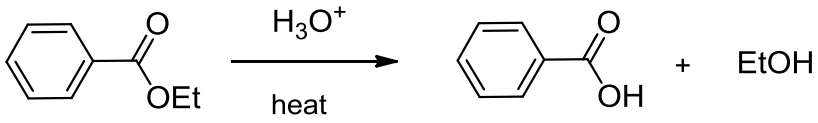
CONTINUED -->

8% PART 8: MECHANISM

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

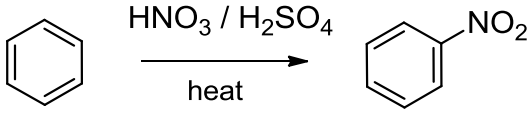
(4) PART A: Draw the curly arrow mechanism for ONE of the following transformations :

i.



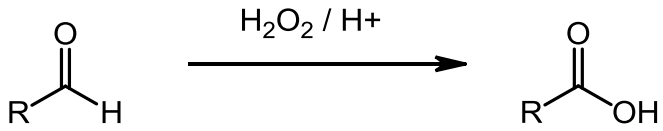
OR

ii.



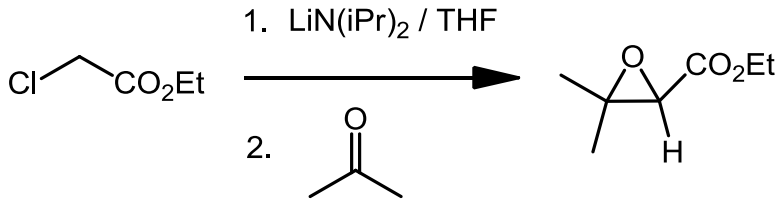
(4) PART B : Draw the curly arrow mechanism for ONE of the following transformations:

i. Aldehydes react with hydrogen peroxide to give carboxylic acids:



OR

ii. When an α-halo ester is reacted with a strong base, then an aldehyde or ketone is added, an α,β-epoxy ester is obtained, see below.
Propose a mechanism for this reaction.



CONTINUED -->

12% PART 9: TOTAL SYNTHESIS

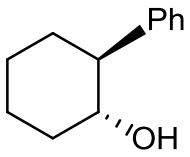
WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED.

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.

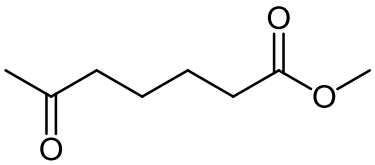
DO NOT SHOW MECHANISMS (*i.e.* curly arrows are NOT required)

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

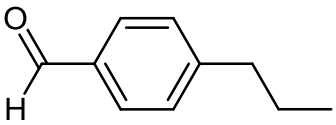
A



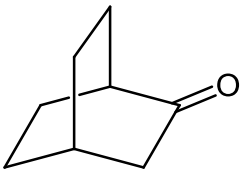
or



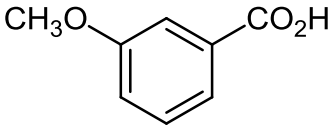
B



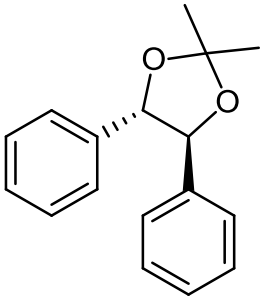
or



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 **FIVE** carbons
2. Benzene
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 -->

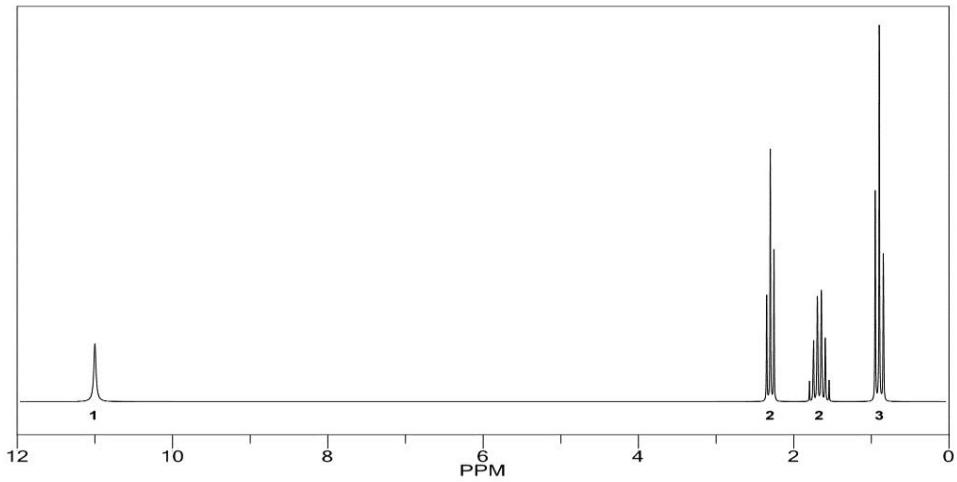
10% PART 10: STRUCTURE DETERMINATION

WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED

A (**$C_6H_{12}O_2$**, IR: 1720 cm^{-1}) does not react with $NaBH_4$ but readily reacts with $LiAlH_4$ to produce compounds **B** and **C** after acid work-up. The treatment of **A** with LDA (Lithium N,N'-diisopropylamide) in THF followed by iodoethane provides compound **D**. When **D** is reacted with aqueous NaOH followed by an acidic workup, two compounds **E** (IR:1720 cm^{-1}; 2700-3600 cm^{-1}) and **C** (IR:3200-3600 cm^{-1}) are obtained. The ^1H NMR spectrum of compound **E** is shown below. The treatment of **E** with $LiAlH_4$ in ether followed by acid work up gives compound **F** (IR: 3200-3600 cm^{-1}). **F** is a constitutional isomer of **C**.

When **C** is reacted with pyridinium dichromate (PDC) in CH_2Cl_2, compound **G** is obtained. **G** gives an orange precipitate when reacted with DNP (2,4-dinitrophenylhydrazine) test and a clear solution in Tollen's test.

G readily reacts with $Ph_3P{=}CHCH_3$ to provide compound **H** as a mixture of the E/Z isomers. Hydroboration of **H** with 9-BBN followed by a treatment with H_2O_2/NaOH provides compound **I** as the major product. When **I** is reacted with PDC in CH_2Cl_2, compound **J** is obtained. The reaction of **J** with peroxyethanoic acid gives compound **A** as the major product, and a minor compound which can be treated aqueous H_2SO_4 to give 2-methylbutanoic acid and methanol.



^1H NMR spectra of compound **E**

Identify the compounds A – J (Only structures are required).

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

IRH/CCL W2015

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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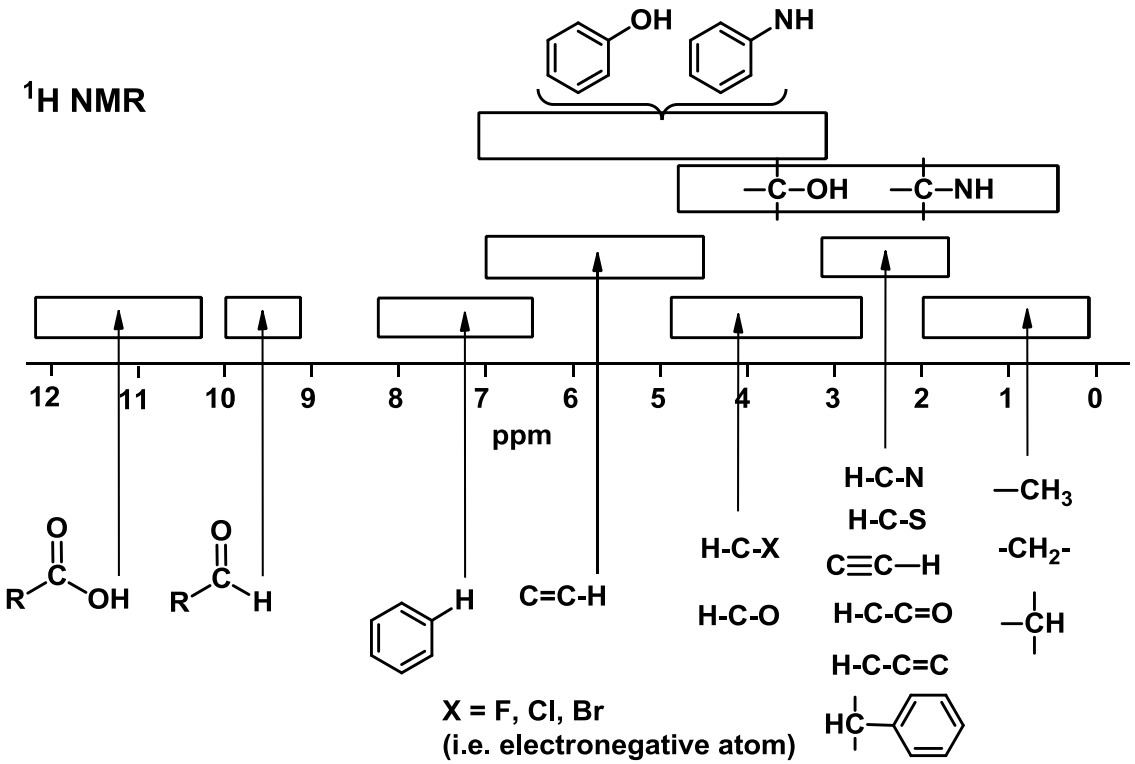
SPECTROSCOPIC TABLES



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

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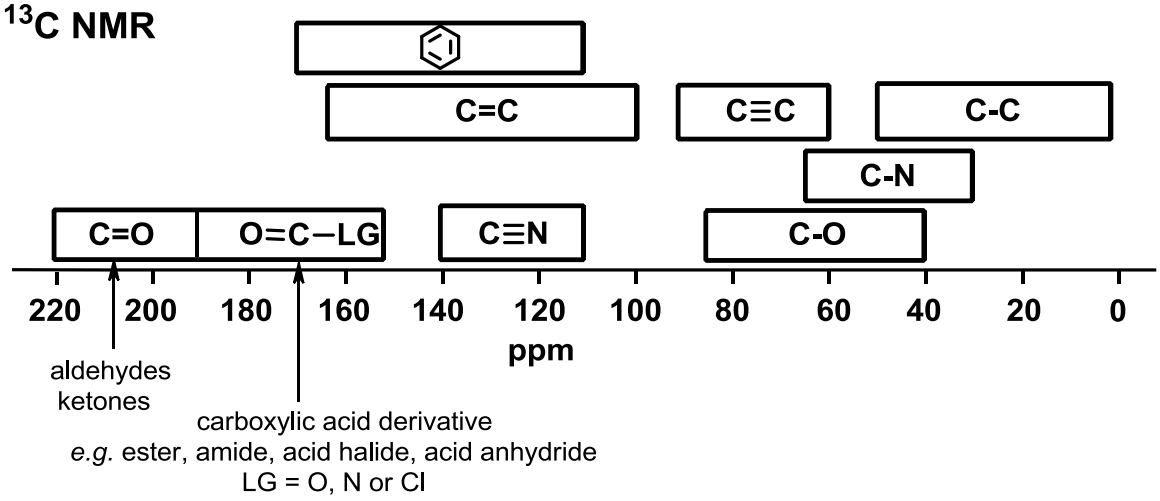
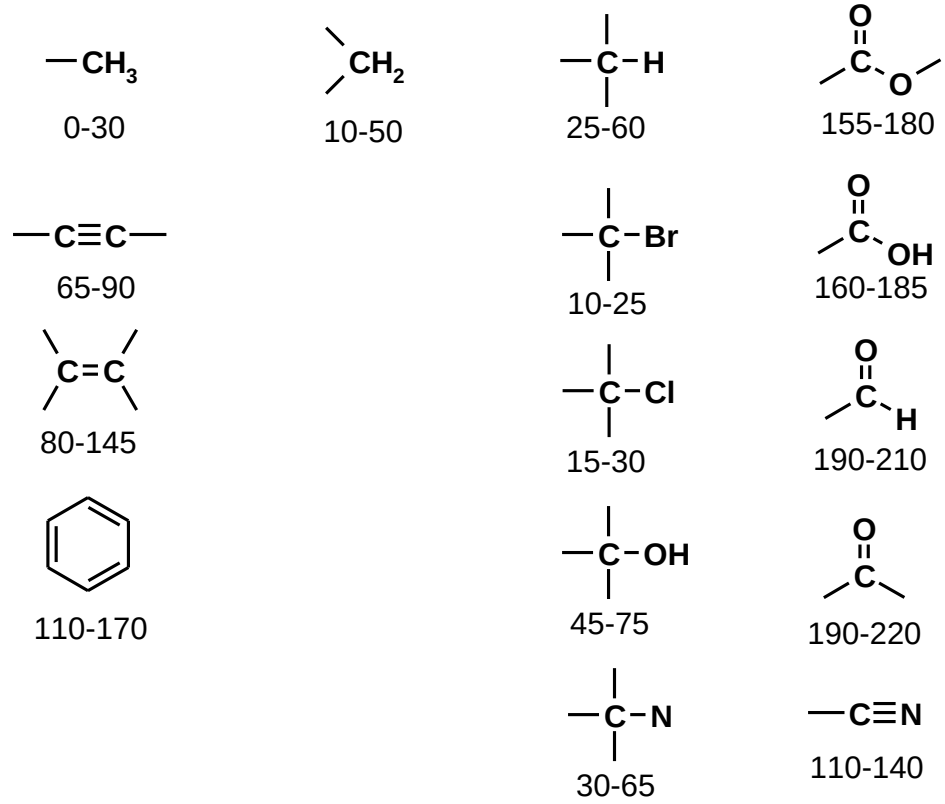


^{13}C NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm



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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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