

UNIVERSITY OF CALGARY

Version

FACULTY OF SCIENCE

FINAL EXAMINATION

1

CHEMISTRY 353

April 26th, 2016

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 - 49 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.**

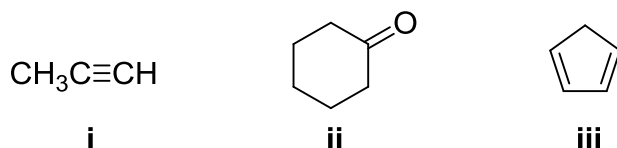
Molecular models and calculators are permitted, but NOT programmable calculators. **Absolutely no other electronic devices are allowed.**

12% PART 1: RELATIVE PROPERTIES**ANSWER ANY EIGHT (8) OF THE TEN (10) QUESTIONS 1-10.**

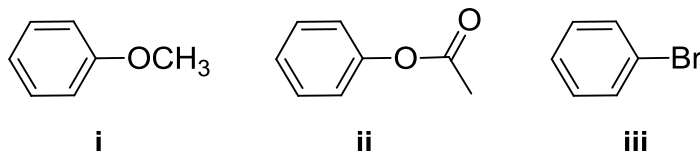
Arrange the items in questions 1-10 in **DECREASING ORDER** (*i.e.* greatest, most *etc.* first) with respect to the indicated property. Use the following code to indicate your answers in the box provided:

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

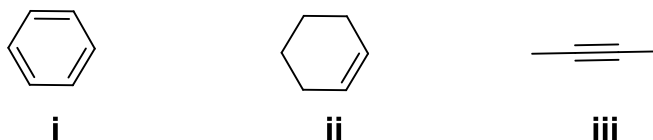
1. The relative acidity of the most acidic hydrogen in each of the following:



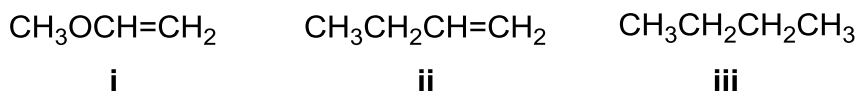
2. The relative rate of reaction of $\text{CH}_3\text{CH}_2\text{Cl} / \text{AlCl}_3$ with each of the following:



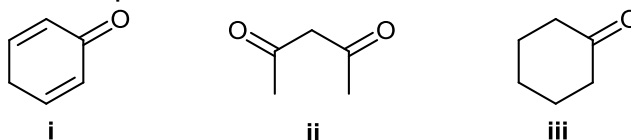
3. The relative reactivity towards H_2 / Pd of each of the following:



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



5. The % enol present in aqueous solutions of each of the following:



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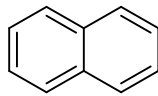
Use the following code to indicate your answers in the box provided:

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

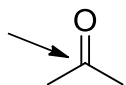


ii

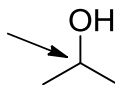


iii

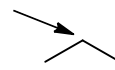
7. The relative oxidation state of the C atom indicated in each of the following:



i

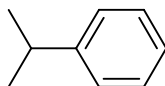


ii



iii

8. The % yield of the product indicated by the reaction of $\text{Br}_2 / \text{FeBr}_3$ with isopropylbenzene:



ortho

i

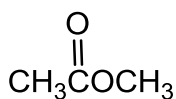
meta

ii

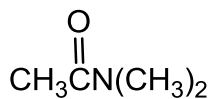
para

iii

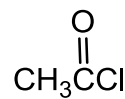
9. The relative reactivity towards hydrolysis using aqueous NaOH of the following:



i

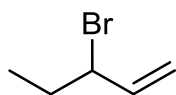


ii

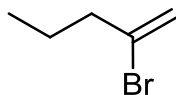


iii

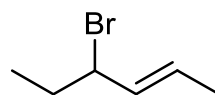
10. The number of configurational isomers of each of the following:



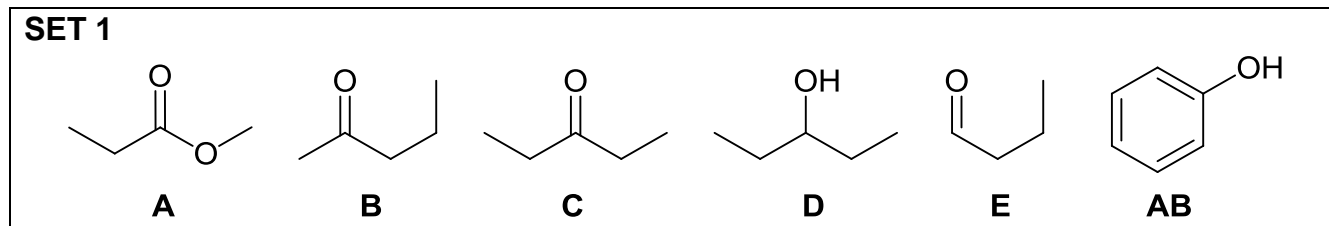
i



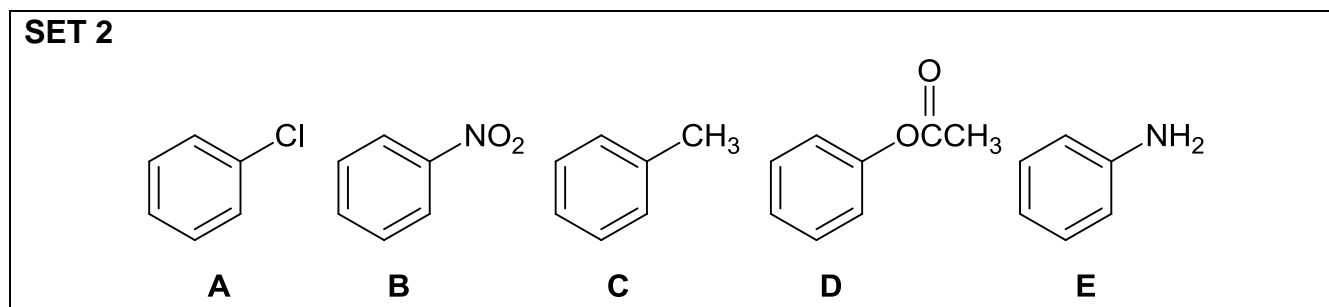
ii



iii

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

- Which compound has the **most** acidic hydrogen ?
- Which compound gives a yellow precipitate when tested with 2,4-dinitrophenylhydrazine and with iodoform ?
- Which compound gives a yellow precipitate when tested with 2,4-dinitrophenylhydrazine and a silver mirror with Tollen's test ?
- Which compound contains a carbonyl group and gives an orange solution with the 2,4-dinitrophenylhydrazine test ?
- Which compound forms a precipitate in the ferric chloride test ?

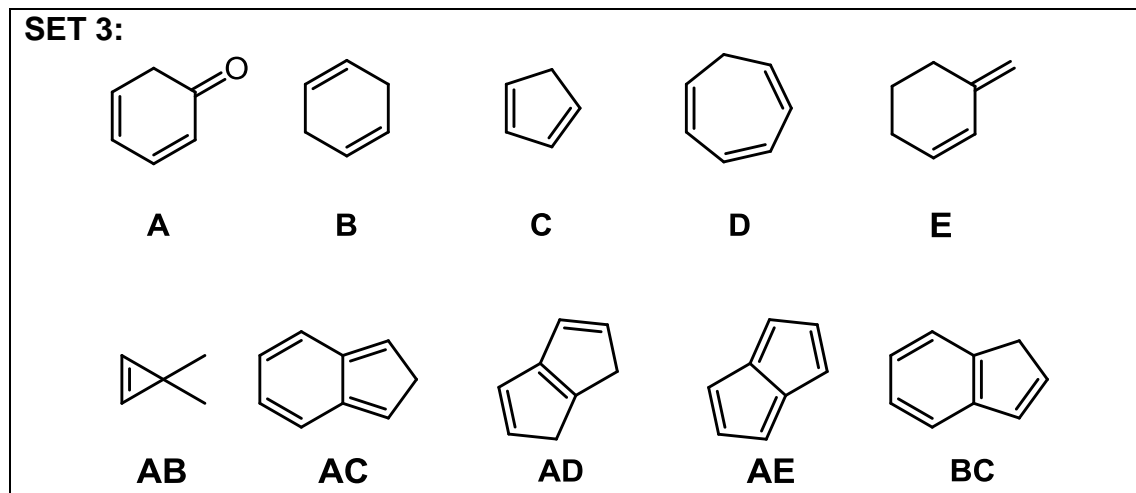
**Answer questions 16-19 by selecting a compound from SET 2 above.**

- Which compound is the **most** activated compared to benzene ?
- Which compound is the **most** deactivated compared to benzene ?
- Which **compound(s) is/are** deactivated and direct *ortho*- and *para*- ?
- Which **compound(s)** undergo successful Friedel-Crafts acylation with $\text{CH}_3\text{COCl} / \text{AlCl}_3$?

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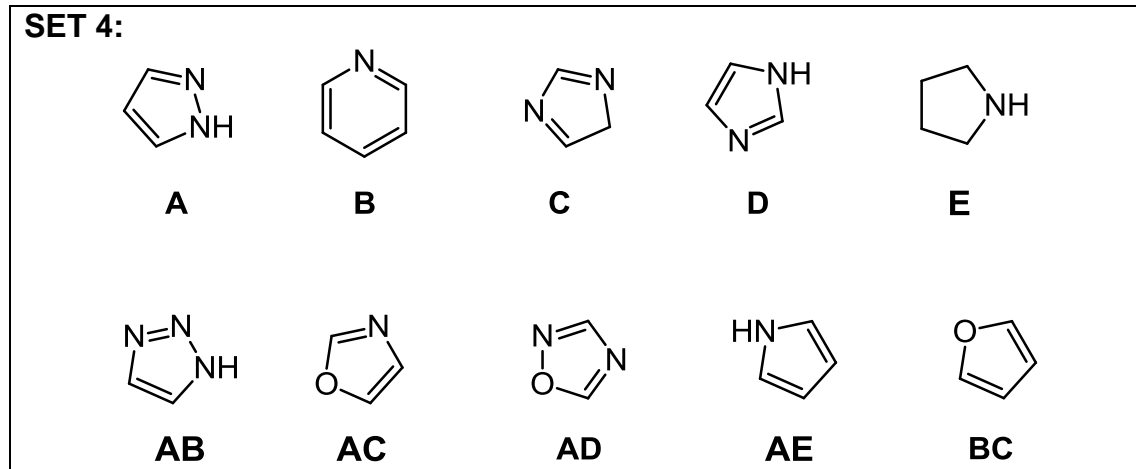
9% **PART 3: AROMATICITY AND RESONANCE**

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

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

20. Select the structure that contains the **least** stable diene.
21. Select the structure that is non-aromatic as drawn, but has an important aromatic tautomer.
22. Select a monocyclic hydrocarbon that is a non-aromatic as drawn, but has an aromatic conjugate base.
23. Select the bicyclic structure with an acidic benzylic hydrogen.
24. Select the bicyclic structure that would undergo the fastest Diel-Alder reaction with a dienophile.

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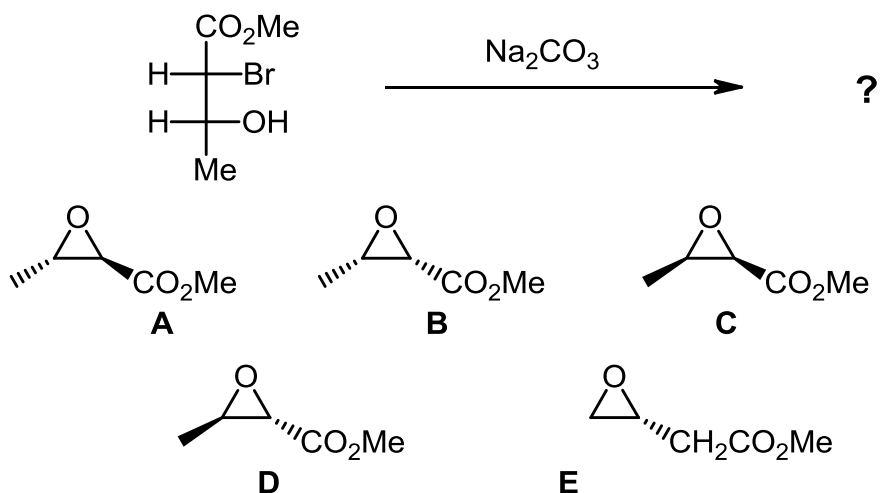
Answer questions 25-29 by selecting a **SINGLE compound** from SET 4 above.

25. Select the structure that is non-aromatic as drawn.
26. Select a **single** compound that has the **greatest** resonance stabilization.
27. Select a **single** compound that can be protonated the most number of times, yet retain its aromaticity.
28. Select a **single** aromatic compound that when monoprotated becomes non-aromatic.
29. Select a **single** compound that contains at least one sp^3 hybridised heteroatom.

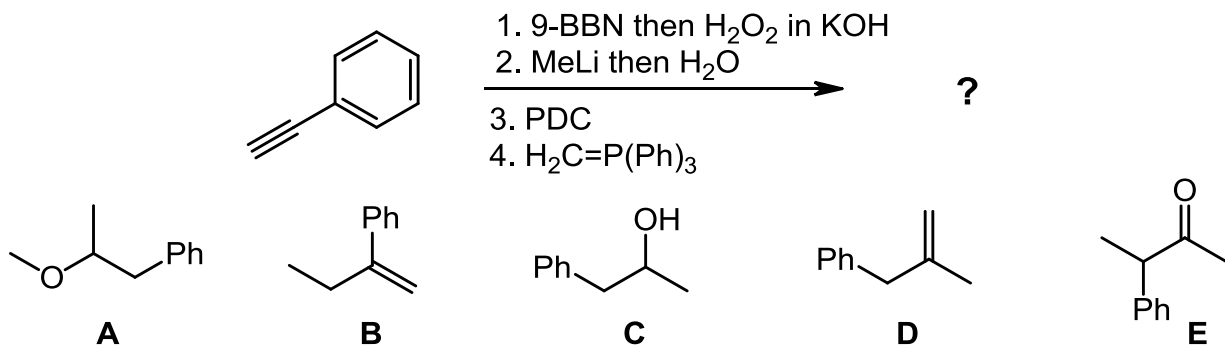
16% PART 4: STARTING MATERIALS AND PRODUCTS OF SYNTHESIS**ANSWER ANY EIGHT (8) OF THE NINE (9) QUESTIONS 30-38.**

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.

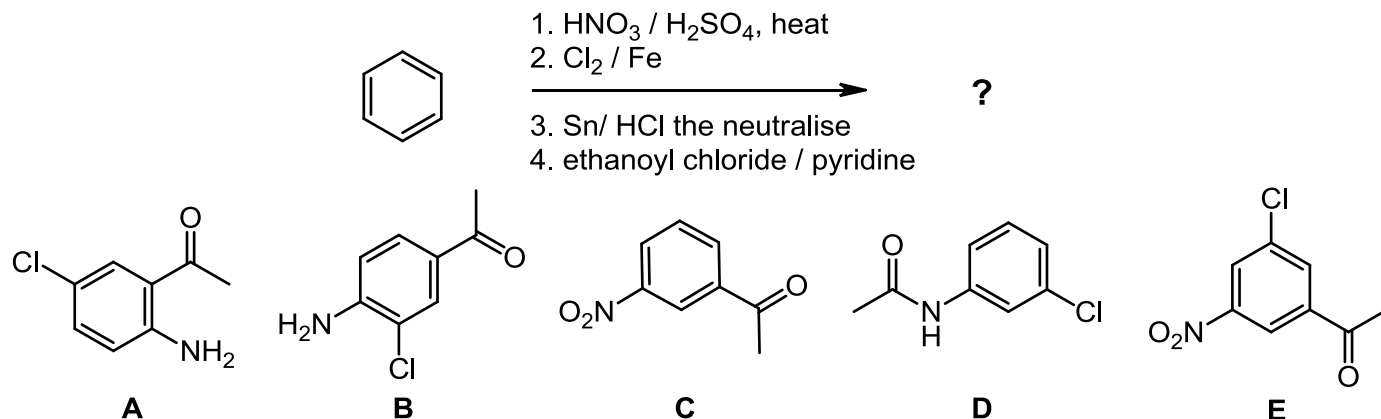
30.



31.

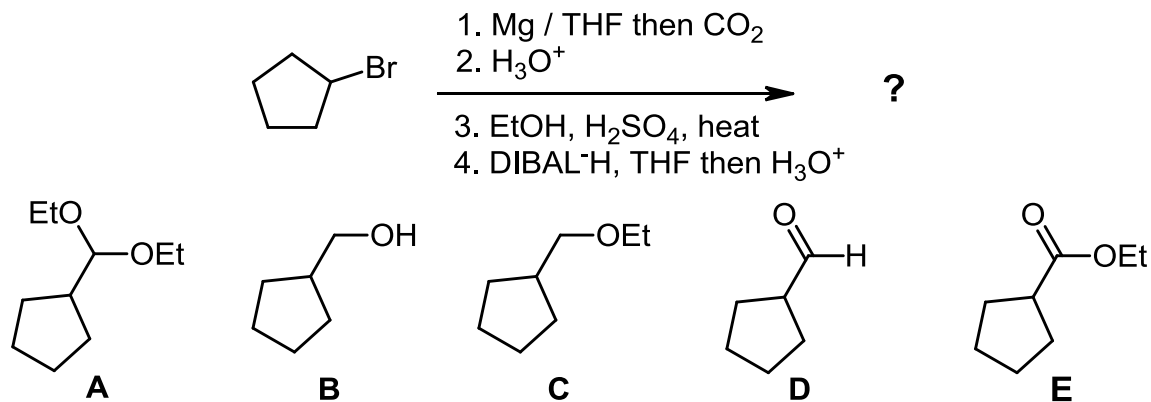


32.

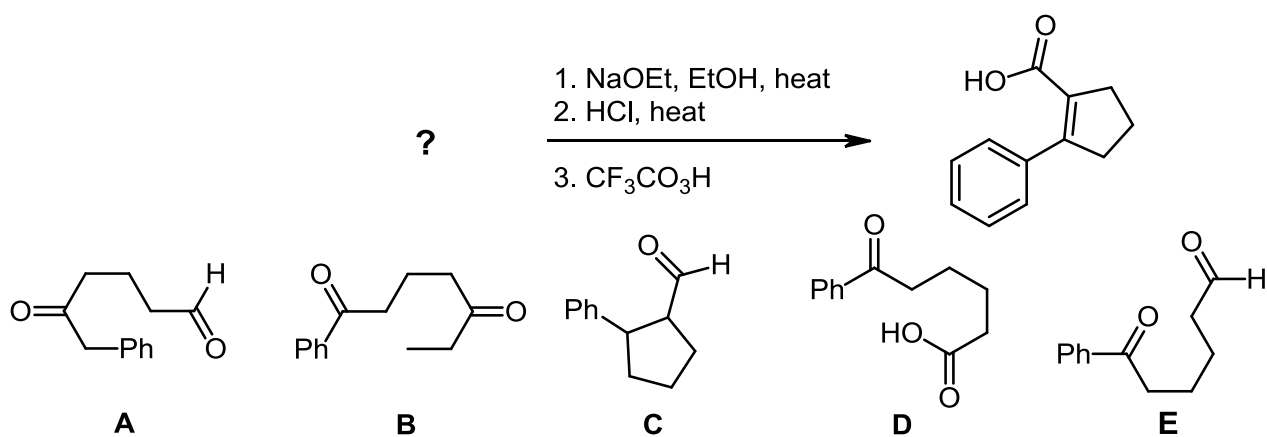


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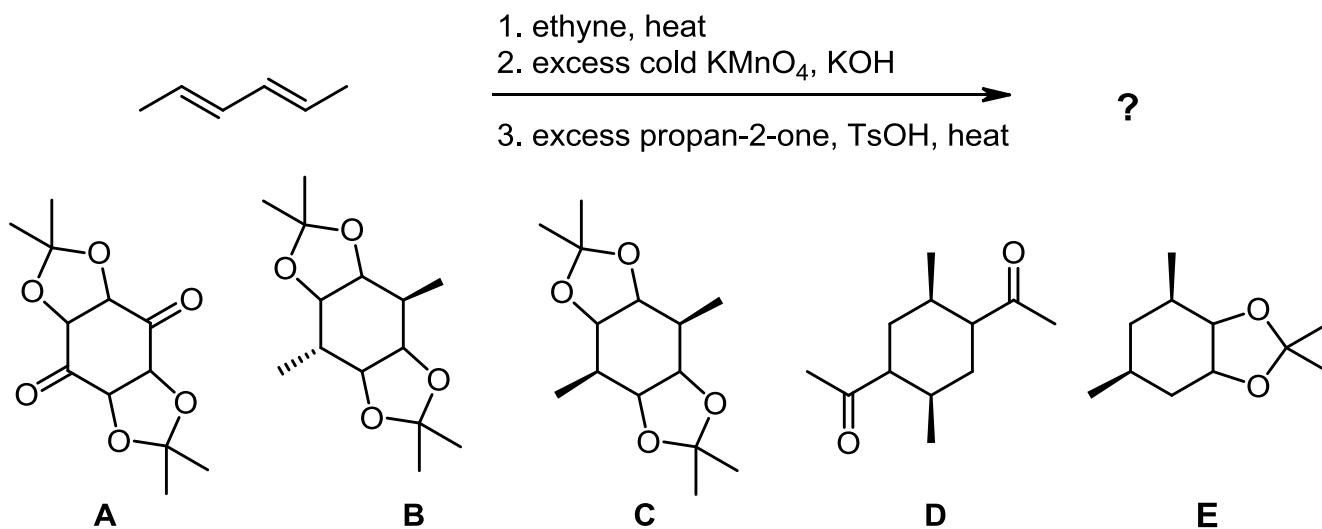
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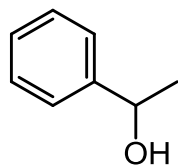
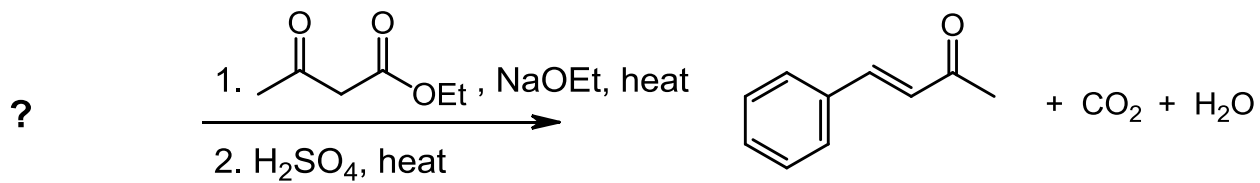
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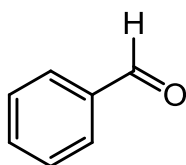
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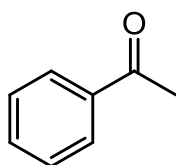
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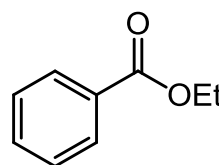
A



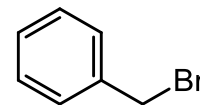
B



C

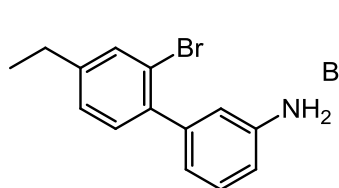
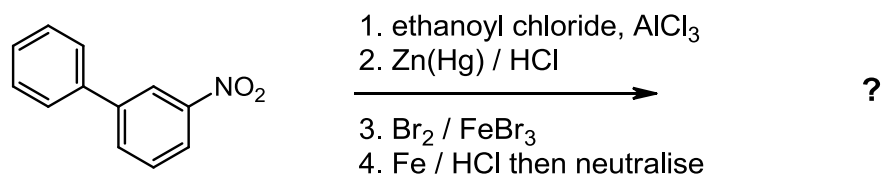


D

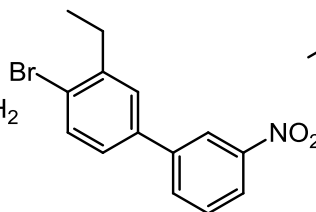


E

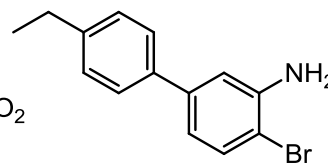
37.



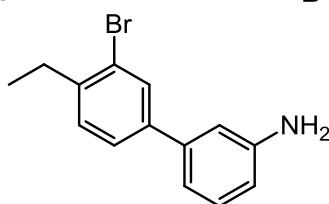
A



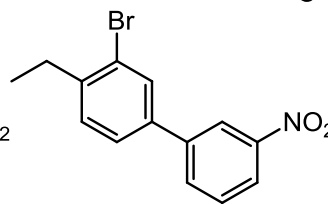
B



C

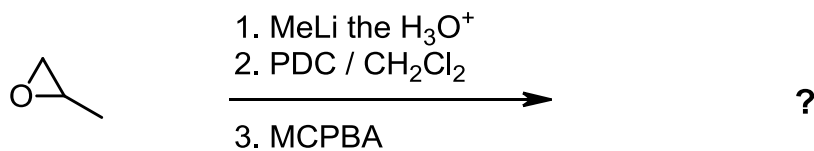


D

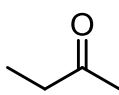


E

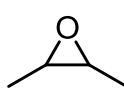
38.



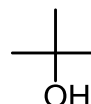
A



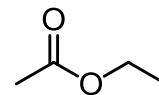
B



C



D

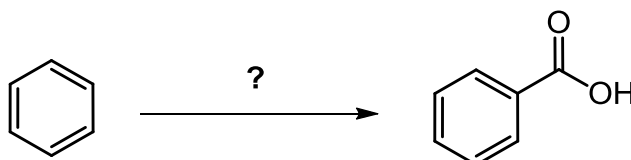


E

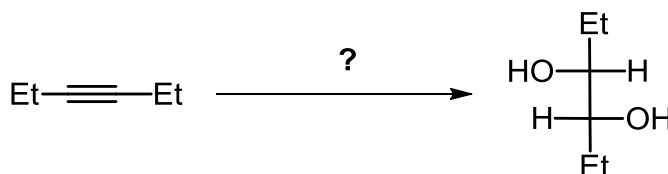
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10% PART 5: REAGENTS FOR SYNTHESIS**ANSWER ANY FIVE (5) OF THE SIX (6) QUESTIONS 39-44**

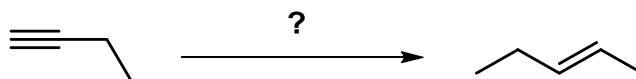
For each of the questions **39-44** identify the **reagent(s)** required in order to complete each of the reaction sequences shown by selecting from the list provided.

39.

- A. i. $\text{CH}_3\text{C}(=\text{O})\text{Cl} / \text{AlCl}_3$ ii. LiAlH_4 then H_3O^+
 B. i. $\text{CH}_3\text{C}(=\text{O})\text{Cl} / \text{AlCl}_3$ ii. cold H_2O
 C. i. $\text{CH}_3\text{Cl} / \text{AlCl}_3$ ii. $\text{KMnO}_4 / \text{H}_3\text{O}^+ / \text{heat}$
 D. i. CH_3MgBr ii. $\text{KMnO}_4 / \text{H}_3\text{O}^+ / \text{heat}$
 E. i. Mg / THF ii. CO_2 iii. H_3O^+

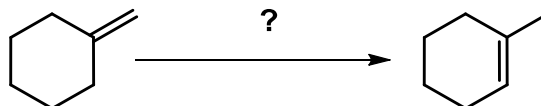
40.

- A. i. Na / NH_3 , ii. O_3 iii. Zn / H^+
 B. i. Na / NH_3 , ii. $\text{CH}_3\text{CO}_3\text{H}$ iii. H_3O^+
 C. i. H_2 / Pd , ii. $\text{KMnO}_4 / \text{aq. NaOH} / 0^\circ\text{C}$
 D. i. $\text{H}_2 / \text{Lindlar's catalyst}$ ii. $\text{KMnO}_4 / \text{aq. NaOH} / 0^\circ\text{C}$
 E. i. $\text{H}_2 / \text{Lindlar's catalyst}$ ii. $\text{CH}_3\text{CO}_3\text{H}$ iii. H_3O^+

41.

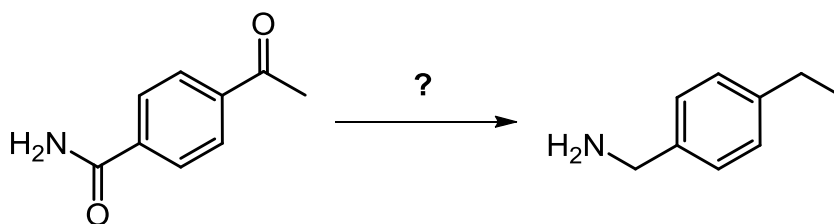
- A. NaNH_2 ii. CH_3Br
 B. NaNH_2 ii. $\text{CH}_3\text{CH}_2\text{Br}$
 C. NaNH_2 ii. CH_3Br iii. Na / NH_3
 D. NaNH_2 ii. $\text{CH}_3\text{CH}_2\text{Br}$ iii. Na / NH_3
 E. NaNH_2 ii. CH_3Br iii. $\text{H}_2 / \text{Lindlar's catalyst}$

42.



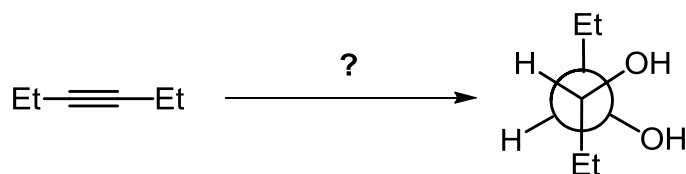
- A. H_2SO_4
 B. i. HBr ii. $\text{KOC}(\text{CH}_3)_3 / (\text{CH}_3)_3\text{COH} / \text{heat}$
 C. i. $\text{HBr} / \text{peroxides}$, ii. $\text{KOH} / \text{EtOH} / \text{heat}$
 D. i. Br_2 ii. $\text{KOC}(\text{CH}_3)_3 / (\text{CH}_3)_3\text{COH} / \text{heat}$
 E. i. Br_2 ii. $\text{KOH} / \text{EtOH} / \text{heat}$

43.



- A. $\text{H}_2\text{NNH}_2 / \text{NaOH} / \text{heat}$
 B. $\text{LiAlH}_4 / \text{THF}$ then H_3O^+
 C. NaBH_4
 D. i. $\text{HOCH}_2\text{CH}_2\text{OH} / \text{TsOH}$ ii. $\text{LiAlH}_4 / \text{THF}$ then H_3O^+ iii. $\text{H}_3\text{O}^+ / \text{heat}$
 E. i. $\text{Zn}/\text{Hg} / \text{HCl}$ ii. $\text{LiAlH}_4 / \text{THF}$ then H_3O^+

44.



- A. i. Na / NH_3 , ii. O_3 iii. Zn / H^+
 B. i. Na / NH_3 ii. $\text{CH}_3\text{CO}_3\text{H}$ iii. H_3O^+
 C. i. H_2 / Pd ii. $\text{KMnO}_4 / \text{aq. NaOH} / 0^\circ\text{C}$
 D. i. $\text{H}_2 / \text{Lindlar's catalyst}$ ii. $\text{KMnO}_4 / \text{aq. NaOH} / 0^\circ\text{C}$
 E. i. $\text{H}_2 / \text{Lindlar's catalyst}$ ii. $\text{CH}_3\text{CO}_3\text{H}$ iii. H_3O^+

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. The two nitrogen heterocycles shown below called pyridine and pyrrole are interesting because of their near equivalent, yet opposite dipole moments. This is because:



- A. pyridine contains an sp^2 nitrogen.
- B. pyrrole, being a 5-membered ring, has more strain.
- C. pyrrole contains an sp^3 nitrogen.
- D. resonance forms of pyrrole have more positive charge on the nitrogen.
- E. pyridine is aromatic and pyrrole is non-aromatic.
- AB.** the s-character difference between the two nitrogen atoms.

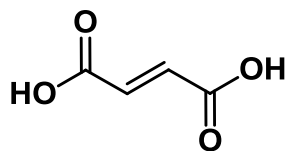
46. Aziridines of structure **1** have not been isolated, yet isomeric aziridines of structure **2** are rather common. This is because:



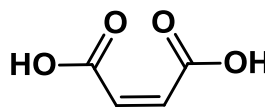
- A. Structure **1** has too much strain.
- B. Structure **1** is too sterically crowded.
- C. Structure **1** is anti-aromatic.
- D. Structure **2** is aromatic.
- E. The nitrogen atom in structure **2** is more basic.
- AB.** Bonding between R^1 and R^2 stabilize structure **2**.

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47. The two compounds shown below, fumaric and maleic acid, are geometric (E/Z) isomers of each other. Interestingly, maleic acid is more acidic with a pK_a of 1.9 as compared to fumaric acid's pK_a of 3.0. This is because:



fumaric acid

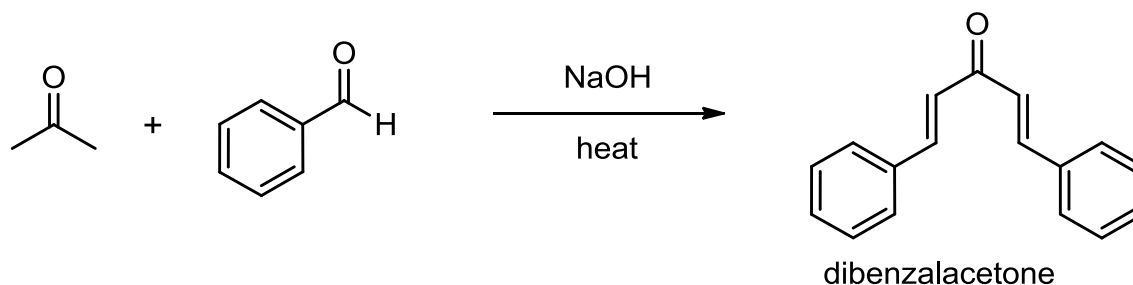


maleic acid

- A. maleic acid has more strain and is thus more acidic.
- B. E-double bonds are less electropositive, thus fumaric acid is a weaker proton donor.
- C. maleic acid has a larger molecular dipole and dissolves better in water.
- D. the conjugate base of fumaric acid is better stabilized through the pi-orbitals.
- E. the conjugate base of maleic acid has an intramolecular hydrogen bond.
- AB.** Z-double bonds stabilize conjugate bases better than E-double bonds.
48. Isolation of 5-bromocyclohexa-1,3-diene very difficult, while isolation of an isomeric form, 1-bromocyclohexa-1,3-diene, is very easy. This is because:
- A. conjugated dienes are more stable than isolated dienes.
- B. vinyl bromides are simple to synthesize.
- C. allylic bromides are easy to synthesize.
- D. vinylic bromides are very stable.
- E. 5-bromocyclohexa-1,3-diene readily eliminates to give benzene.
- AB.** The 5-bromo derivative spontaneously undergoes a rearrangement to the 1-bromo derivative. .
49. Propanal is more reactive than 2,2-dimethylpropanal towards MeMgBr . This is because:
- A. The α -protons of propanal are less acidic.
- B. The α -protons of propanal are more acidic
- C. The α -protons of propan-2-one are more acidic than the α -protons of propanal.
- D. Propanal is less sterically hindered.
- E. The aldehyde proton in 2,2-dimethylpropanal is less acidic.
- AB.** The methyl group in propanal makes the carbonyl C less electrophilic.

5% PART 7: LABORATORY**WRITE YOUR ANSWERS IN THE BLUE BOOKLET PROVIDED.**

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



Benzaldehyde (1.5 g) and propan-2-one (*i.e.* acetone) (0.75 ml, density = 0.791g/ml) were stirred at 50°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 (1.25 g).

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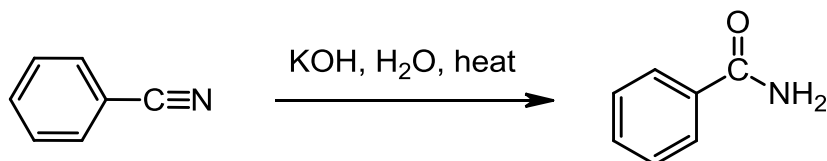
8% PART 8: MECHANISMANSWER TWO (2) QUESTIONS, ONE FROM PART A AND ONE FROM PART B.

WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED.

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

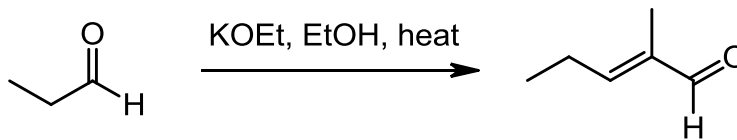
(4) PART A: Draw the curly arrow mechanism for ONE of the following transformations :

i.



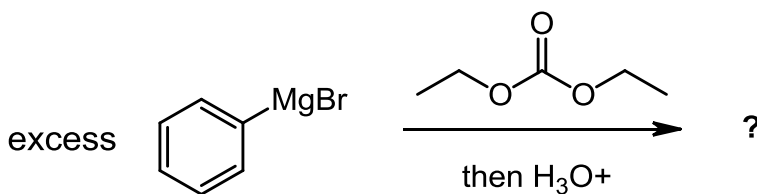
OR

ii.



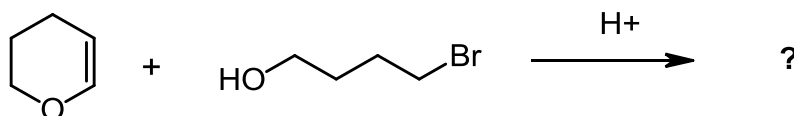
(4) PART B : Draw the curly arrow mechanism for ONE of the following transformations:

i. :



OR

ii.



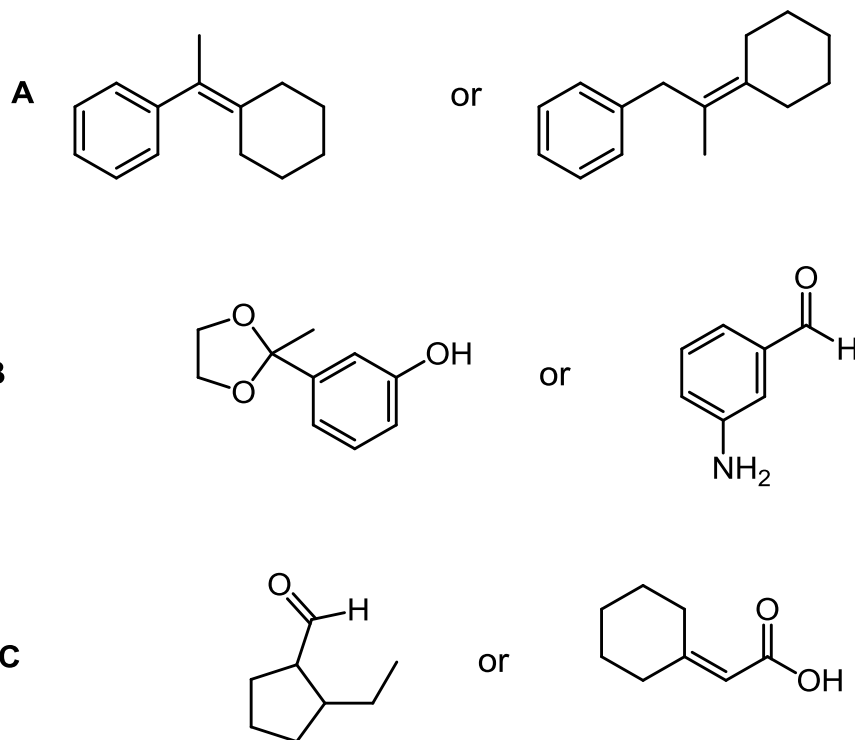
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12% PART 9: TOTAL SYNTHESIS**WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED.**

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.



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 BOOKLET PROVIDED**

Compound **A**, C_8H_{12} , was treated with O_3 followed by H_2O_2 work-up to form a single compound **B**, $C_4H_6O_3$. When **B** was reacted with Na_2CO_3 then CH_3CH_2I , it gave a new compound **C**, $C_6H_{10}O_3$.

Reaction of **A** with H_2 / Pd gave a dimethylcyclohexane as a mixture of *cis* and *trans* isomers.

C was also obtained via a separate reaction sequence by reaction of ethyl ethanoate with $NaOEt$

When **C** was heated with $HOCH_2CH_2OH / H^+$, product **D**, $C_8H_{14}O_4$ was obtained.

When **D** was reacted with excess phenyl magnesium bromide followed by the usual acid work-up it gave **E**, $C_{18}H_{20}O_3$. **E** was then heated with H_3O^+ to provide **F**, $C_{16}H_{16}O_2$ which was easily dehydrated to give **G**, $C_{16}H_{14}O$. **G** could also be obtained by the reaction of propan-2-one with diphenyl ketone (also known as benzophenone) in hot ethanolic $NaOH$.

All the compounds **A-G** were achiral.

What are the structures **A - G** ?

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

PERIODIC TABLE

1																18	
1A																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)							

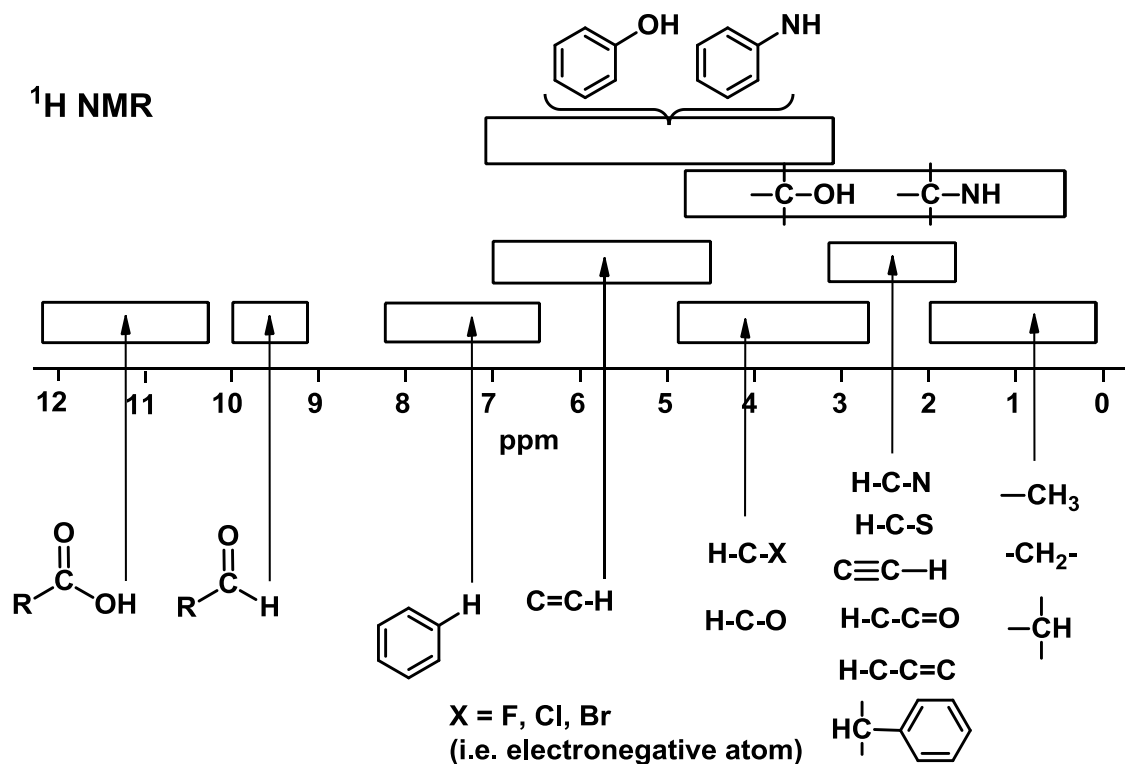
Lanthanides *

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
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Actinides **

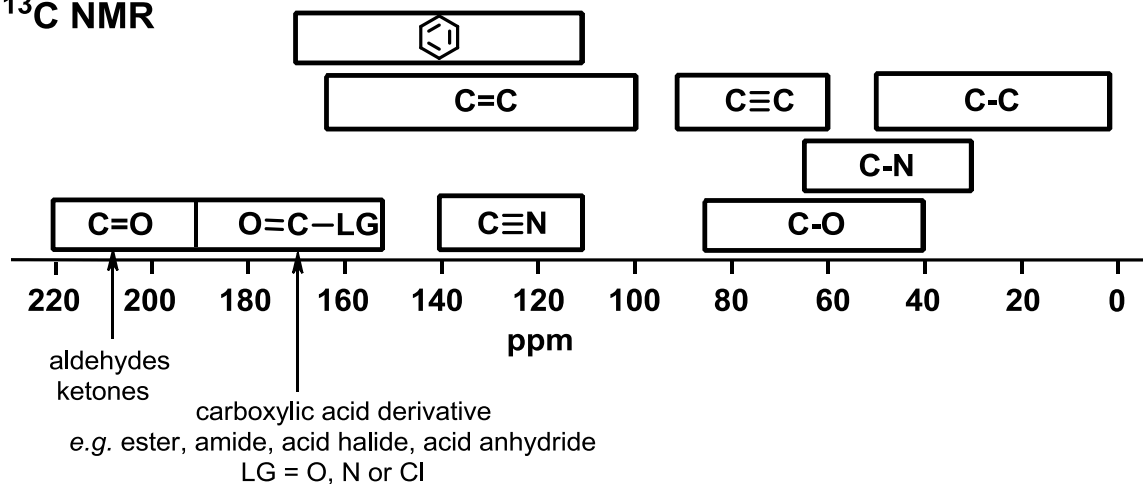
90 Th 232.0	91 Pa 231.0	92 U 238.0	93 Np 237.0	94 Pu (244)	95 Am (243)	96 Cm (247)	97 Bk (247)	98 Cf (251)	99 Es (252)	100 Fm (257)	101 Md (258)	102 No (259)	103 Lr (260)
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
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SPECTROSCOPIC TABLES**¹H NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm**

	R = methyl	methylene	methyne	other
	-CH ₃	-CH ₂ -	-CH	
	0.9	1.4	1.5	sp ³ C-OH 1-5
	1.6	2.3	2.6	sp ³ C-NH 1-3
	1.6	2.3	2.6	C≡CH 2.5
	2.1	2.4	2.5	
	2.2	2.5	2.9	
	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	

CONTINUED -->

¹³C NMR¹³C NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm

—CH_3 0-30	>CH_2 10-50	—C—H 25-60	—C(=O)—O— 155-180
$\text{—C}\equiv\text{C—}$ 65-90	>C=C< 80-145	—C—Br 10-25	—C(=O)OH 160-185
 110-170		—C—Cl 15-30	—C(=O)H 190-210
		—C—OH 45-75	—C(=O)— 190-220
		—C—N 30-65	$\text{—C}\equiv\text{N}$ 110-140

CONTINUED -->

INFRA-RED GROUP ABSORPTION FREQUENCIES

	<u>TYPE OF VIBRATION</u>	<u>FREQUENCY (cm⁻¹)</u>	<u>WAVELENGTH (μ)</u>	<u>INTENSITY (1)</u>			
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 Ketone Carboxylic acid Ester Amide Anhydride Acyl chloride	1740-1720	5.75-5.81	s			
		1725-1705	5.80-5.87	s			
		1725-1700	5.80-5.88	s			
		1750-1730	5.71-5.78	s			
		1700-1640	5.88-6.10	s			
		ca. 1810	ca. 5.52	s			
		ca. 1760	ca. 5.68	s			
		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
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 Chloride Bromide, Iodide	1400-1000	7.14-10.0	s			
		800-600	12.5-16.7	s			
		<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 may be very broad.

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