UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

FINAL EXAMINATION

CHEMISTRY 353

April 27th, 2009 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 - 5 will be computer graded, and Parts 6 - 10 are to be answered in the booklet. Parts 1 - 5 consist of a series of multiple choice questions numbered 1 - 50 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.

Molecular models are permitted during the exam; calculators are also permitted, ***but NOT programmable calculators***. **Absolutely no other electronic devices are allowed.**

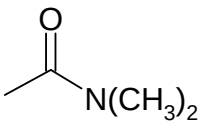
12% PART 1: RELATIVE PROPERTIES

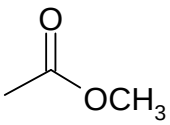
ANSWER ANY EIGHT (8) OF THE TEN (10) QUESTIONS 1-10.

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:

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 reactivity towards methyl magnesium bromide of each of the following:


i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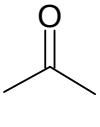
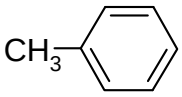

iii

2. The relative reactivity towards N-bromosuccinimde (NBS) of each of the following: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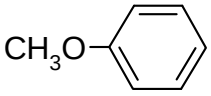
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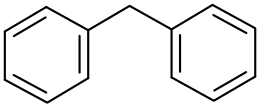
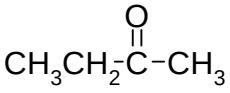
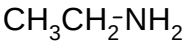

iii

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


i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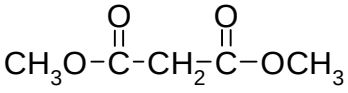
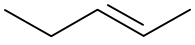

iii

4. The number of allylic hydrogens in each of the following: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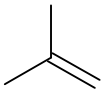
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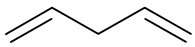
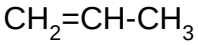

iii

5. The relative stability of the carbocations formed by the reaction of each of the following with H_2SO_4:


i


ii

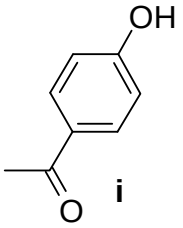

iii

CONTINUED -->

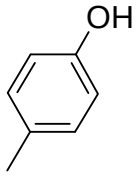
Use the following code to indicate your answers:

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

6. The relative acidity of each of the following:



i



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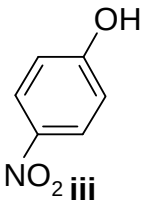
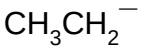
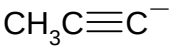


iii

7. The relative stability of the following carbanions:



i



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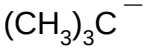
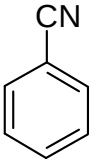


iii

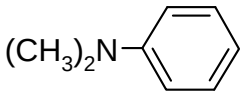
8. The number of enolisable hydrogens in each of the following:

i cyclopentanone **ii** benzaldehyde **iii** 2-pentanone

9. The relative reactivity towards Br_2 / Fe of each of the following:



i



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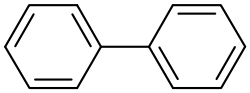
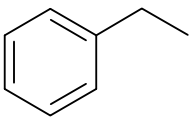


iii

10. The resonance energies of each of the following:



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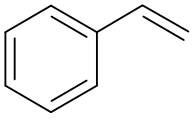

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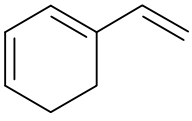

iii

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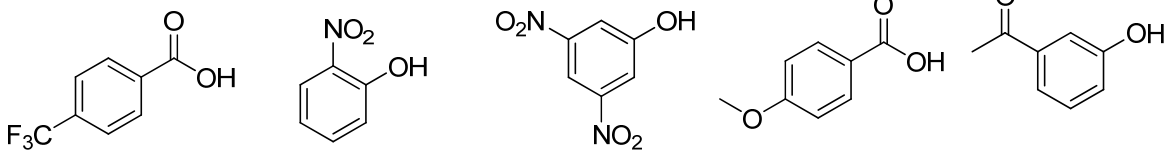
10 % PART 2: STRUCTURE AND PROPERTIES

ANSWER ANY TEN (10) OF THE TWELVE (12) QUESTIONS 11-22.

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 11-14 by selecting the compounds from SET 1 above.

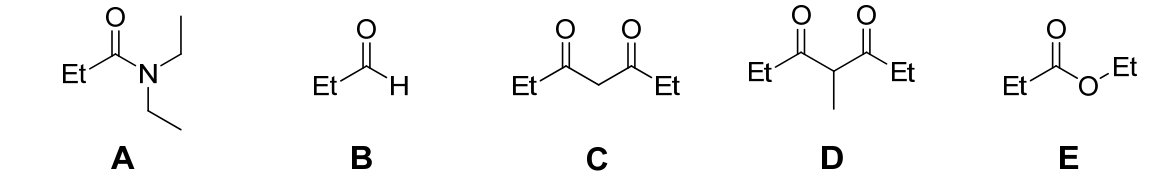
11. Which compound has the most acidic proton?

12. Which phenol is the most basic?

13. Which compound(s) become(s) less acidic when reduced with $SnCl_2$ /HCl?

14. Which compounds contain a substituent that only exerts inductive electronic effects?

SET 2



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

Answer questions 15-18 by selecting the compounds from SET 2 above.

15. Which compound(s) has(have) 4 or more enolizable protons?

16. Which compound will give the most stable enolate?

17. Which compound(s) react(s) with two equivalents of MeMgBr?

18. Which compound(s) will be reduced by $NaBH_4$?

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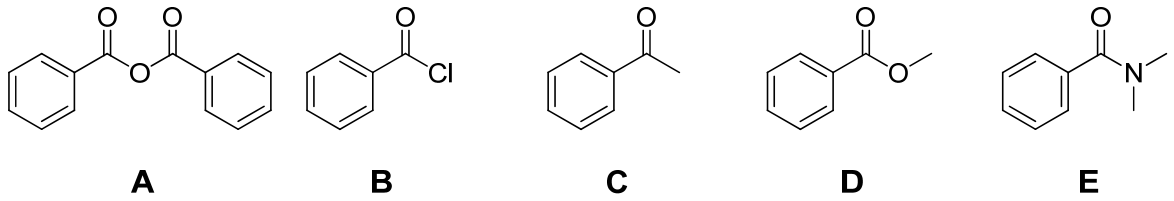
SET 3



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

Answer questions 19-22 by selecting the compounds from SET 3 above.

19. Which compound(s) will produce benzoic acid when heated in acidic water?

20. Which compound(s) will yield 1-phenylethanol when reacted with $NaBH_4$?

21. Which carboxylic acid derivative is the slowest to undergo hydrolysis?

22. Which compound(s) is(are) reduced to primary alcohols?

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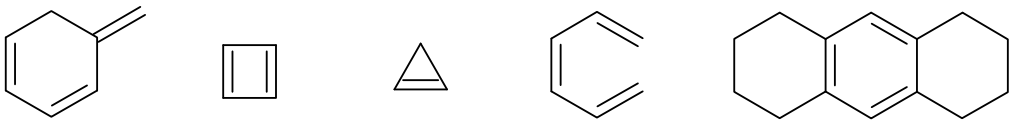
9% **PART 3: AROMATICITY AND RESONANCE**

ANSWER ANY SIX (6) OF THE SEVEN (7) QUESTIONS 23 - 29.

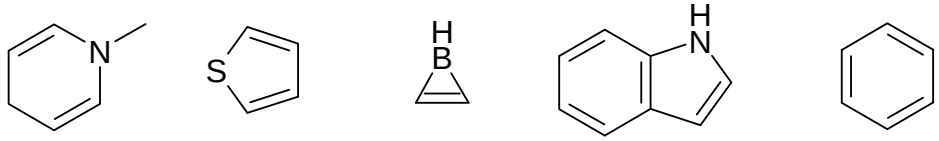
For each of the questions 23-29 select ALL the compounds from the lists provided that matches each of the specific descriptions:

23. Molecules that are aromatic as drawn.



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

24. Molecules that are heteroaromatic as drawn.

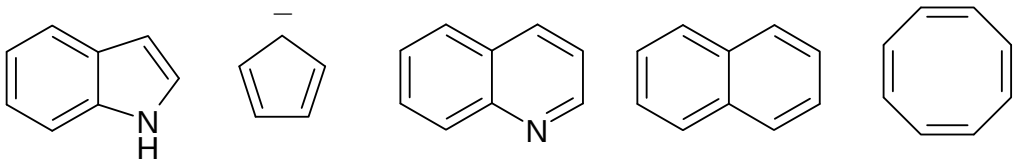


A **B** **C** **D** **E**

25. Molecules that are conjugated but non-aromatic as drawn.

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

26. Molecules that are aromatic hydrocarbons where n=2 in the Hückel rule.



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

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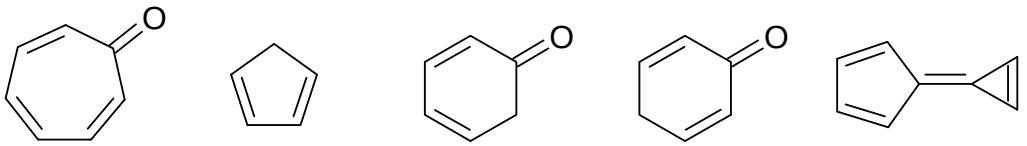
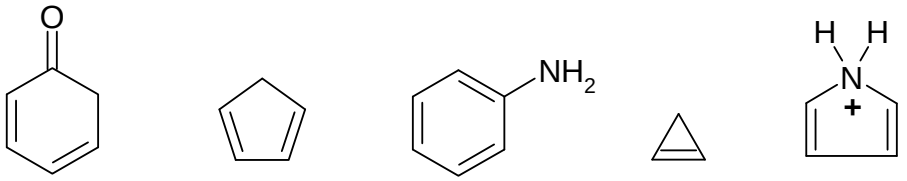
27. Molecules that are non-aromatic as drawn, but have an aromatic resonance contributor.



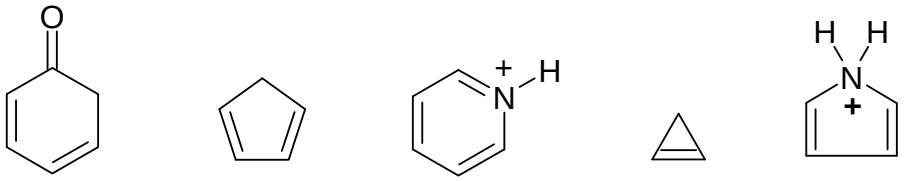
A **B** **C** **D** **E**

28. Molecules that are aromatic as drawn and have an aromatic conjugate base.



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

29. Molecules that are non-aromatic as drawn and have an aromatic conjugate base.



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

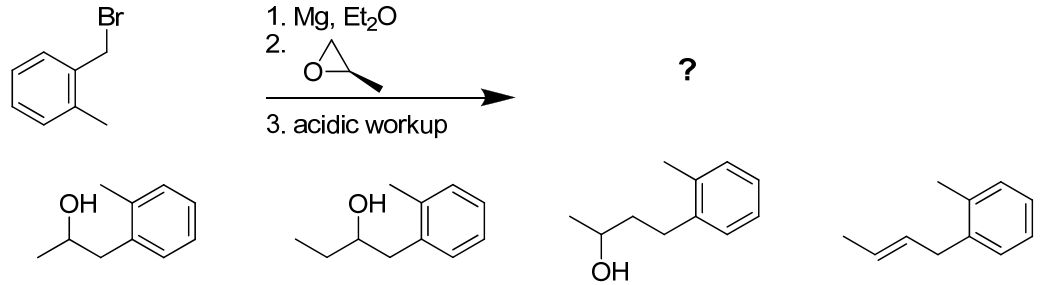
CONTINUED -->

16% PART 4: STARTING MATERIALS AND PRODUCTS OF SYNTHESIS

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

For each of the questions 30 - 38 identify the product(s) obtained or starting material(s) required in order to complete each of the reaction sequences shown by selecting from the list provided. In some cases more than one answer may be correct and ALL compounds that apply MUST be selected for full credit.

30.



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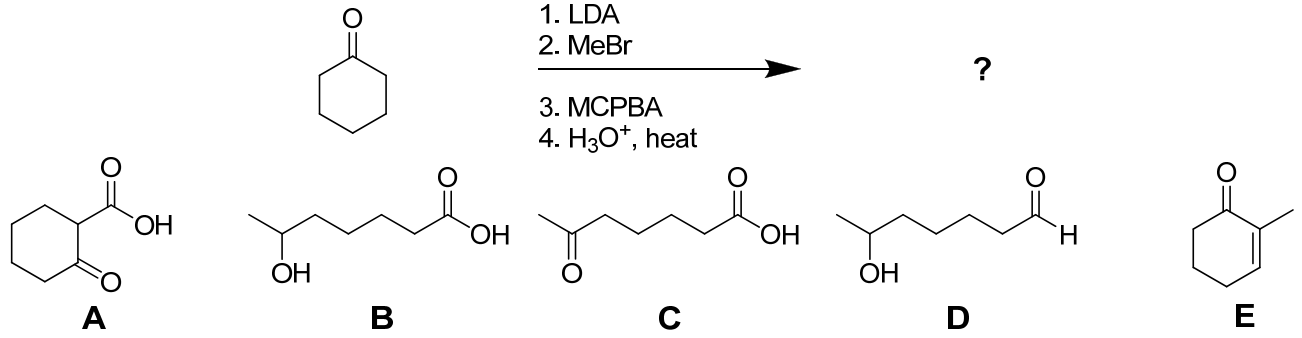

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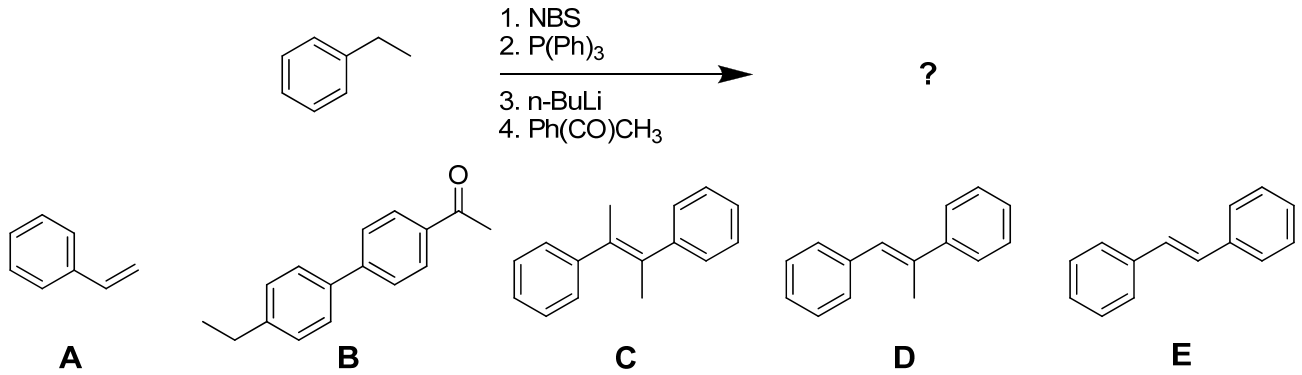

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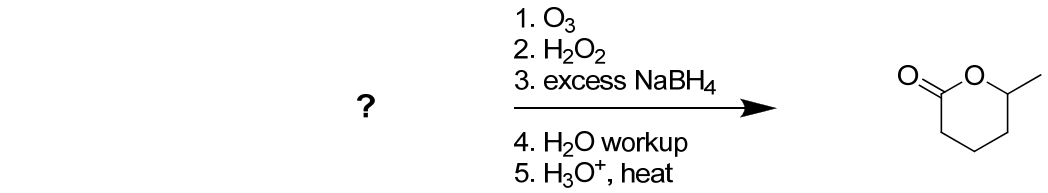
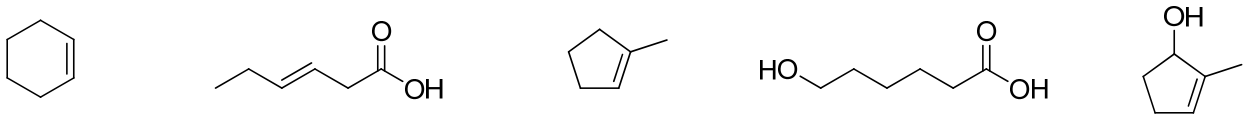
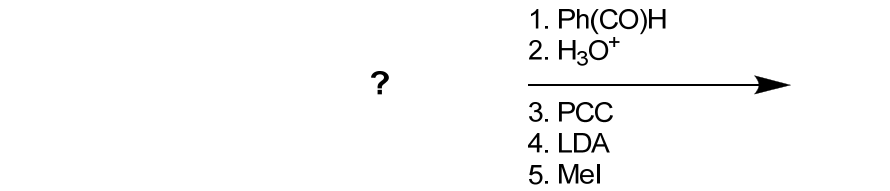
33.

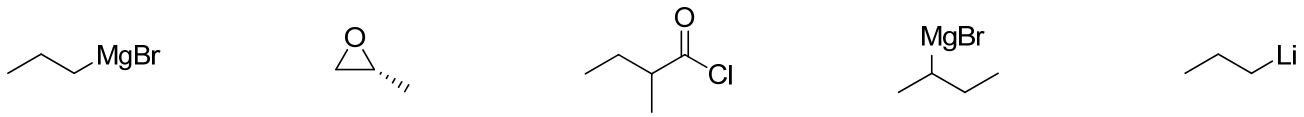




A **B** **C** **D** **E**

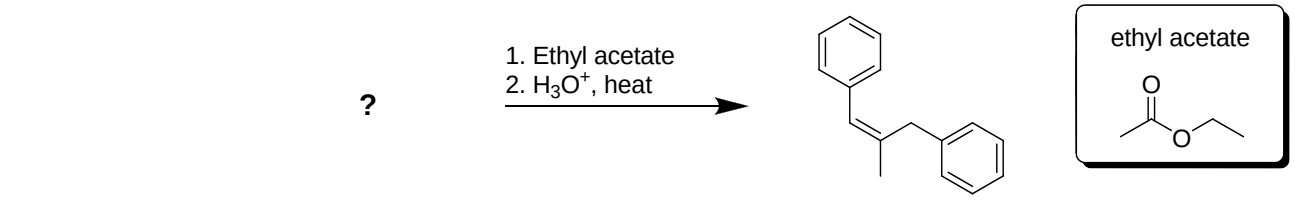
34.

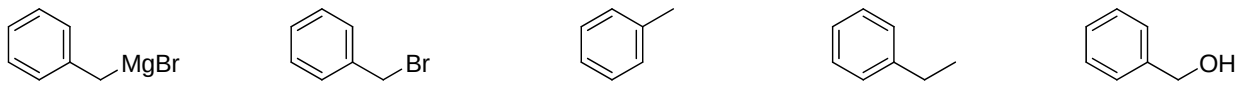




A **B** **C** **D** **E**

35.





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

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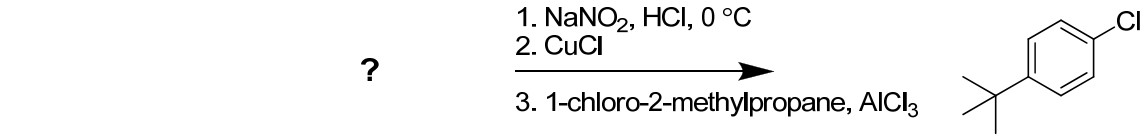
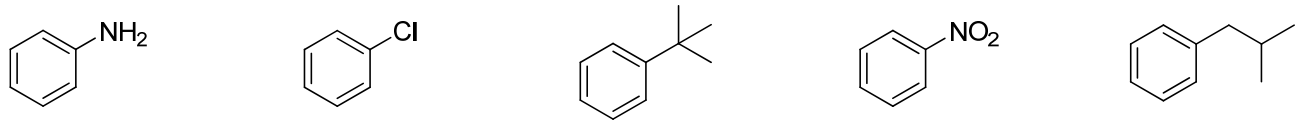
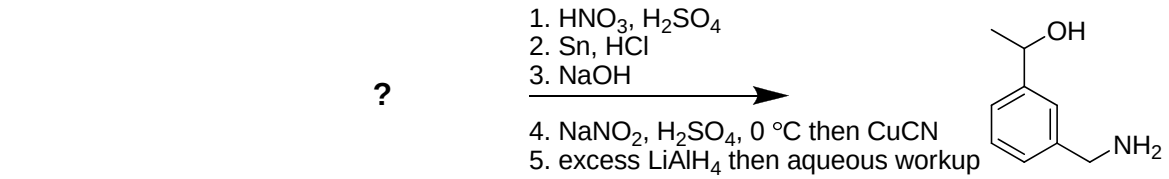
36.

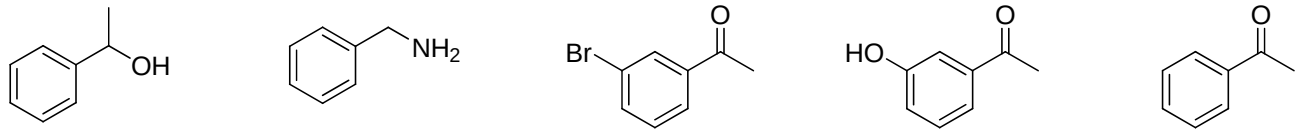




A **B** **C** **D** **E**

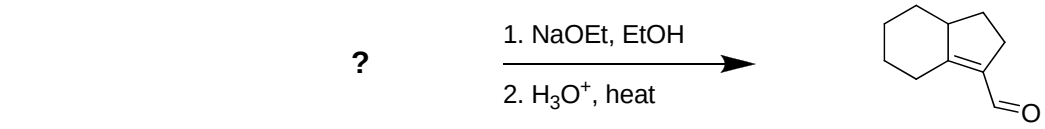
37.

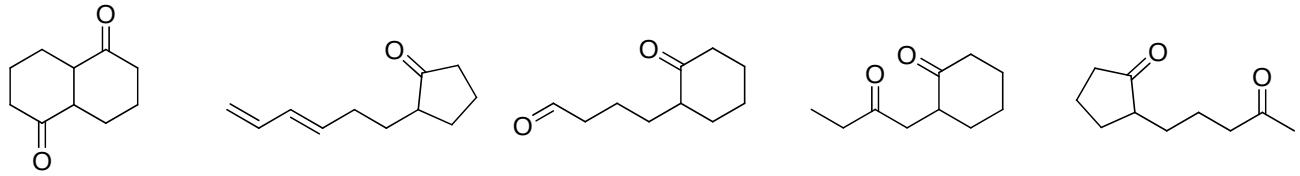




A **B** **C** **D** **E**

38.





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

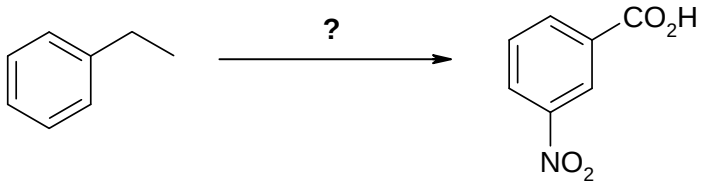
CONTINUED -->

7.5% 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. HNO_3 / H_2SO_4 ii. $KMnO_4$ / H_3O^+ / heat

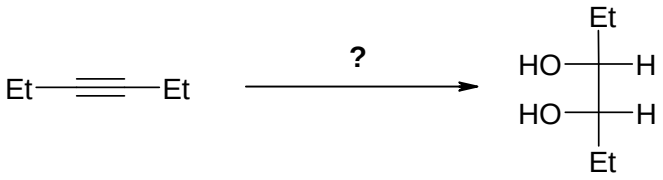
B i. $KMnO_4$ / H_3O^+ / heat ii. $NaNO_2$ / H_2SO_4

C. i. $KMnO_4$ / H_3O^+ / heat ii. HNO_3 / H_2SO_4

D. i. $NaNO_2$ / H_2SO_4 ii. $KMnO_4$ / H_3O^+ / heat

E. i. Mg / THF ii. CO_2 iii. H_3O^+ iv. HNO_3 / H_2SO_4

40.



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

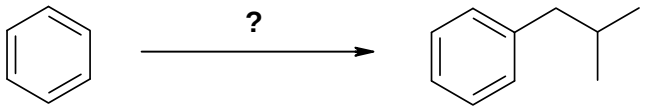
B. i. Na / NH_3, ii. aq. H_2SO_4

C. i. H_2 / Pd, ii. $KMnO_4$ / aq. NaOH / 0^oC

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

E. $KMnO_4$ / aq. NaOH / 0^o

41.



A. $(CH_3)_2C=CH_2$ / H_2SO_4

B. $(CH_3)_2CHCH_2MgCl$ / THF then H_3O^+

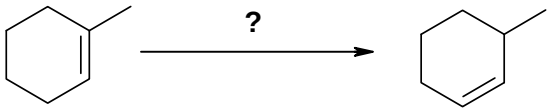
C. $(CH_3)_2CHCH_2Cl$ / $AlCl_3$

D. $(CH_3)_2CHC(=O)Cl$ / $AlCl_3$, ii. Zn/Hg / HCl

E. $(CH_3)_2CHC(=O)Cl$ / $AlCl_3$, ii. $NaBH_4$, iii. H_3O^+

CONTINUED -->

42.



A. H_2SO_4

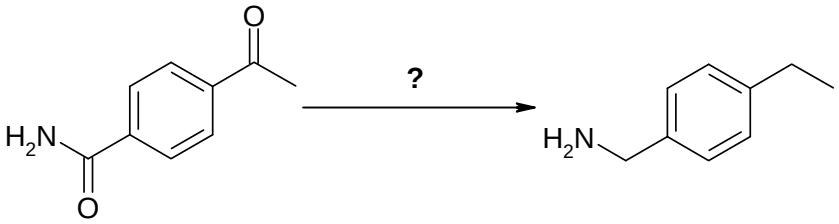
B. i. HBr, ii. $KOC(CH_3)_3$ / $(CH_3)_3COH$ / heat

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

D. i. aq. H_2SO_4, ii. Tosyl chloride / Et_3N iii. KOH / EtOH / heat

E. i. BH_3, ii H_2O_2 / aq. NaOH, iii. Tosyl chloride / Et_3N iv. KOH / EtOH / heat

43.



A. H_2NNH_2 / NaOH / heat

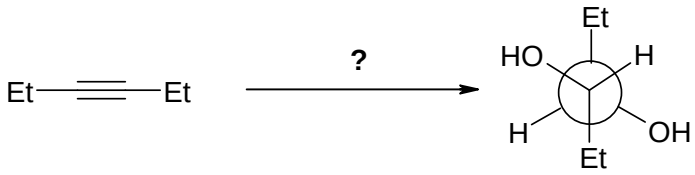
B. $LiAlH_4$ / THF then H_3O^+

C. $NaBH_4$

D. i. $HOCH_2CH_2OH$ / TsOH, ii. $LiAlH_4$ / THF then H_3O^+ iii. H_3O^+ / heat

E. i. Zn/Hg / HCl, ii. $LiAlH_4$ / THF then H_3O^+

44.



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

B. i. Na / NH_3, ii. aq. H_2SO_4

C. i. H_2 / Pd, ii. $KMnO_4$ / aq. NaOH / 0^oC

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

E. $KMnO_4$ / aq. NaOH / 0^o

CONTINUED -->

7.5% PART 6: EXPLANATION OF PHENOMENA

ANSWER ANY FIVE (5) OF THE SIX (6) QUESTIONS 45 - 50.

CHOOSE THE SINGLE EXPLANATION THAT BEST RATIONALISES THE PHENOMENON INDICATED.

45. Cyclopropane has a pKa = 46 and the allylic H in propene have a pKa = 43 while cyclopropene has a pKa = 61 This is because:

A. Cyclopropene is unstable due to high ring strain primarily due to angle strain.

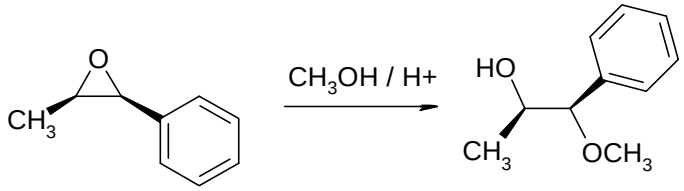
B. The cyclopropenyl carbocation is a 2π aromatic compound.

C. The cyclopropenyl carbocation is a 4π aromatic compound.

D. The cyclopropene conjugate base is a 4π aromatic compound.

E. The cyclopropene conjugate base is a 4π anti-aromatic compound.

46. The epoxide ring opening reaction proceeds with the regiochemistry shown below. This is because:



A. The reaction follows Markovnikov's rule.

B. The CH_3OH reacts as the nucleophile at the more substituted end.

C. The CH_3O- ion reacts as the nucleophile at the more substituted end.

D. The CH_3OH reacts as the nucleophile at the partially cationic benzylic end.

E. The CH_3O- ion reacts as the nucleophile at the partially cationic benzylic end.

47. The room temperature H-NMR of N,N-dimethyl ethanamide shows two peaks for the methyl groups attached to the nitrogen. This is because:

A. Nitrogen deshields the methyl groups because it is more electronegative than carbon.

B. The amide nitrogen is sp^3 hybridised.

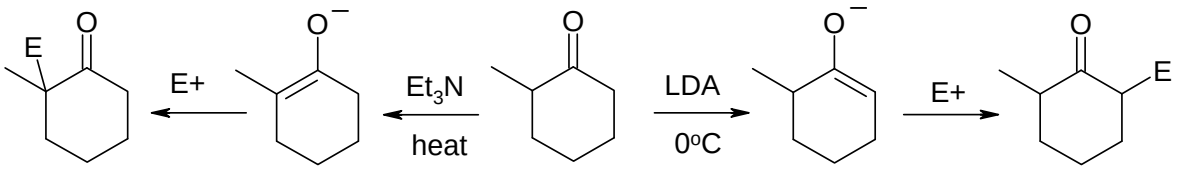
C. The amide has a tautomer so there are two types of N-methyl groups.

D. The carbonyl C to N bond has double bond character.

E. Amides are involved in intermolecular hydrogen bonding.

CONTINUED -->

48. When 2-methylcyclohexanone reacts with a base and is then treated with an electrophile, the product depends on the reaction conditions, see below. This is because:



A. Alkyl groups are weak electron donors due to inductive effects and hyperconjugation.

B. Lithium diisopropyl amide (LDA) promotes a Markovnikov type addition.

C. Lithium diisopropyl amide (LDA) promotes an anti-Markovnikov type addition.

D. Lithium diisopropyl amide (LDA) is a much stronger base than Et_3N.

E. The reaction with Et_3N is under thermodynamic control.

49. When methoxybenzene is alkylated using $(CH_3)_3CCl$ / $AlCl_3$, the *para* product is the major product. This is because:

A. The $–OCH_3$ group is an *ortho/para* director and *para* is statistically favoured.

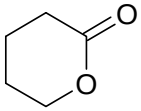
B. The $–OCH_3$ group is an *ortho/para* director and *para* is sterically favoured.

C. The -R (alkyl) group is an *ortho/para* director and *para* is statistically favoured.

D. The -R (alkyl) group is an *ortho/para* director and *para* is sterically favoured

E. Friedel-Crafts alkylations usually give the *para* position as the major product.

50. A chemist attempted to reduce the compound shown below with $LiAlH_4$ to give 1-pentanol but did not obtain the desired alcohol product. This is because:



A. $LiAlH_4$ is not reactive enough to reduce esters.

B. $LiAlH_4$ is not reactive enough to reduce ethers.

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

D. An intermediate was formed that reacted to give a cyclic hemi-ketal.

E. The actual product is 1,5-pentanediol.

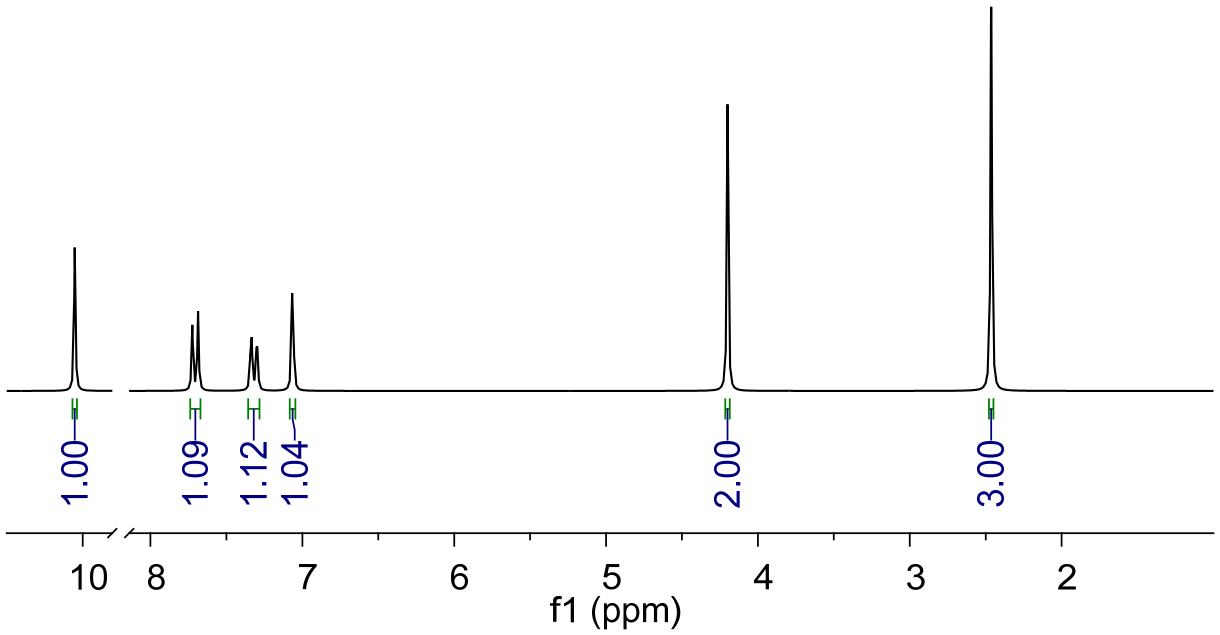
CONTINUED -->

6% **PART 7: LABORATORY**

WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED.

The H NMR of the unknown compound, **#854** and the functional group test results are shown below. In order to answer the question, draw **ONE** structure that is consistent with the experimental results in your exam booklet.

Compound #854 - **$C_9H_9NO_2$**



H-NMR : peak at 4.2ppm exchanges with D_2O.

Solubility Test results for compound #854 : dissolved in 5% HCl.

Chemical Test results for compound #854 :

2,4-D.N.P. **:** orange ppt formed
Tollen's **:** silver mirror observed
Schiff's **:** purple solution observed
$FeCl_3$ **:** not applied
I_2/KOH **:** yellow ppt formed

CONTINUED -->

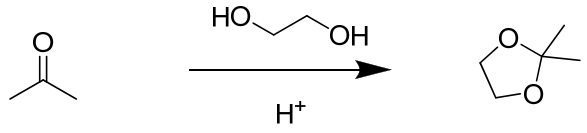
10% PART 8: MECHANISM

WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED.

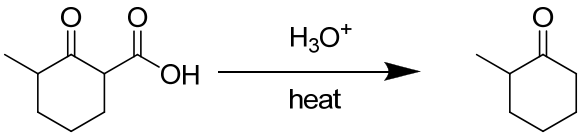
ANSWER TWO (2) QUESTIONS, ONE FROM PART A AND ONE FROM PART B.
NO REAGENTS OTHER THAN THOSE ALREADY SHOWN IN EACH QUESTION ARE REQUIRED.

(5%) PART A: Use a curly arrow mechanism to explain ONE of the following reactions:

i

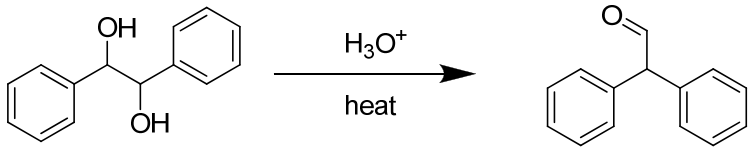


ii

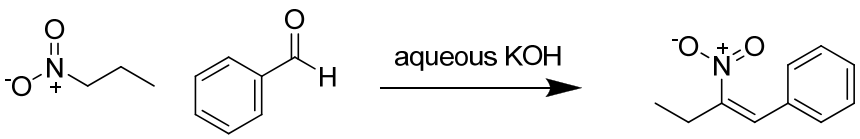


(5%) PART B: Use a curly arrow mechanism to answer ONE of the following:

i. Propose a mechanism for the rearrangement shown below that occurs when dibenzyl diol is heated in aqueous acid.



ii. Provide a detailed mechanism showing the steps involved in the following reaction that involves the reaction nitro-propane and benzaldehyde in aqueous KOH. This reaction is also known as the Henry reaction.



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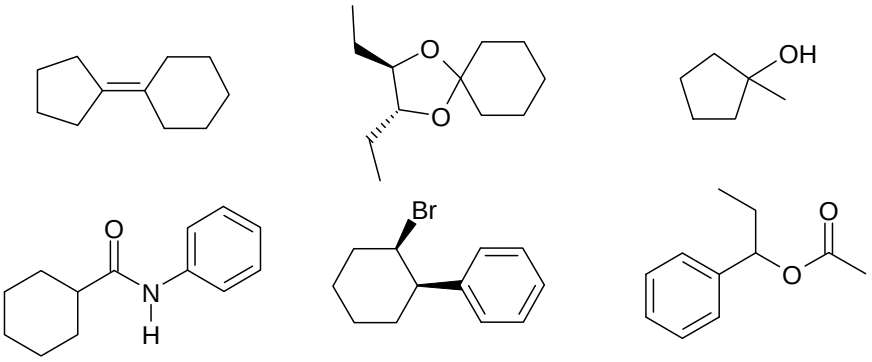
12% PART 9: TOTAL SYNTHESIS

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 Starting Materials*

- cyclohexene
- benzene
- any organic compounds with no more than three carbons

* **any materials that contribute carbon atoms to the target molecule *must* come from the starting material list**.

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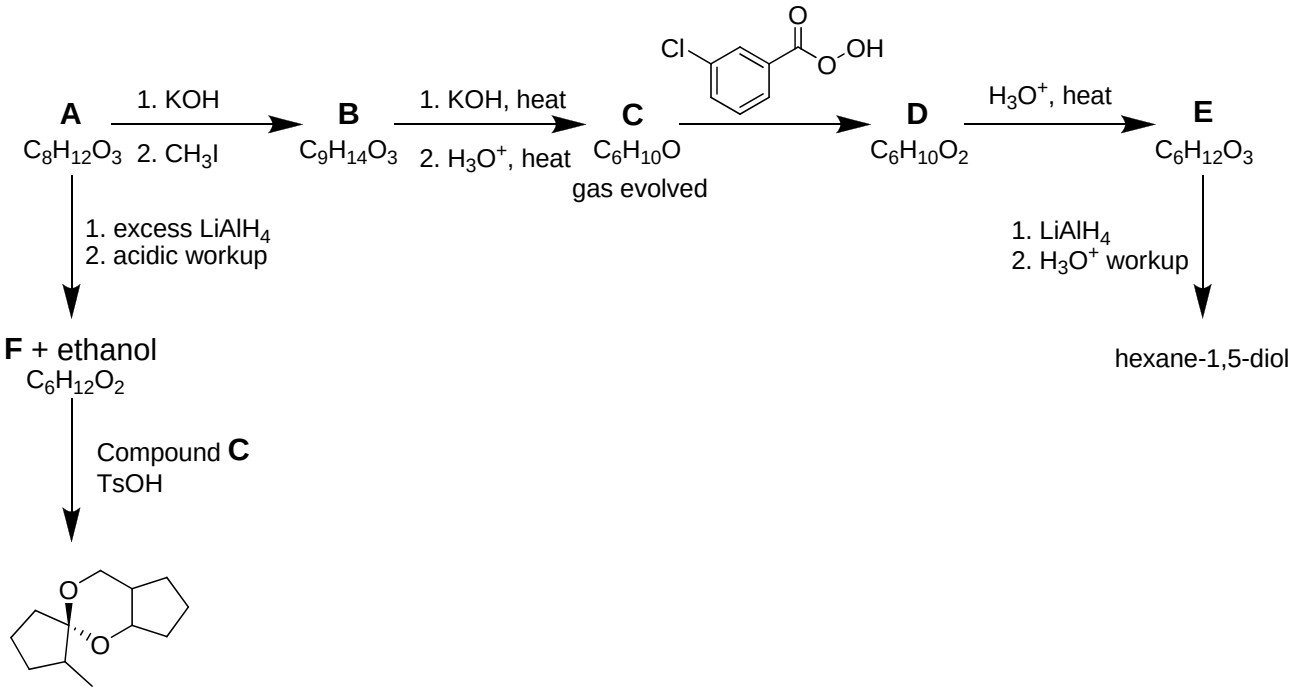
10% PART 10: STRUCTURE DETERMINATION

WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED



Identify the compounds **A**, **B**, **C**, **D**, **E** and **F**.

Give the IUPAC name for **C (1 mark)**.

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

IRH / TS W2009

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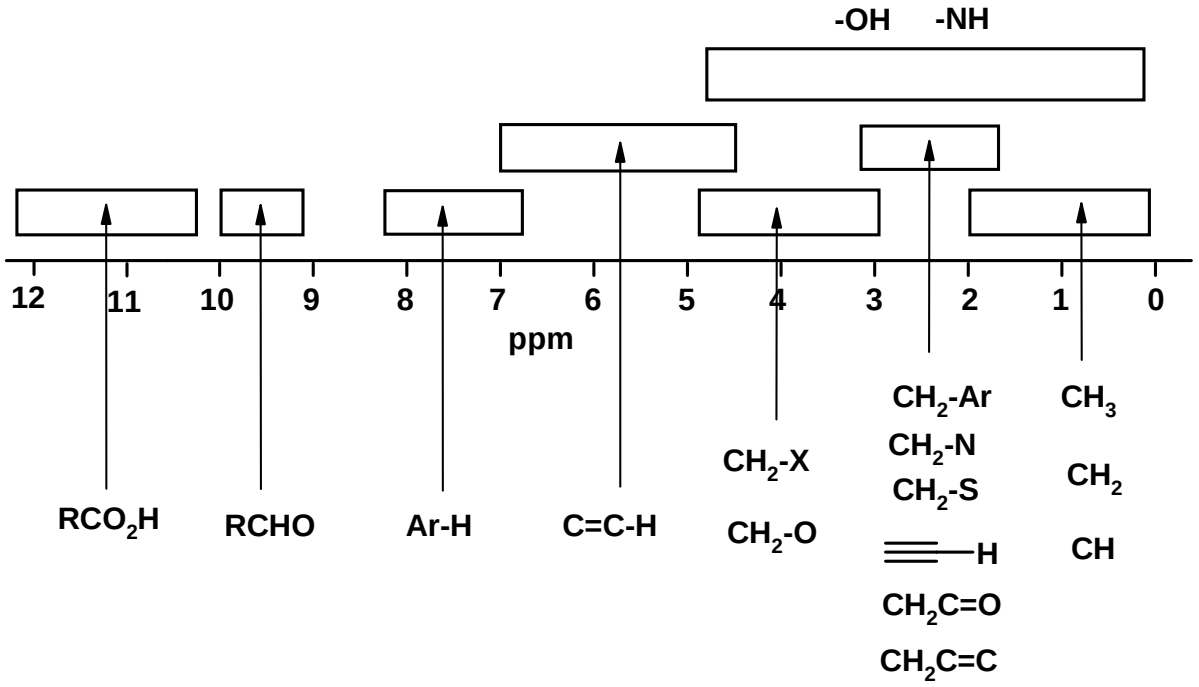
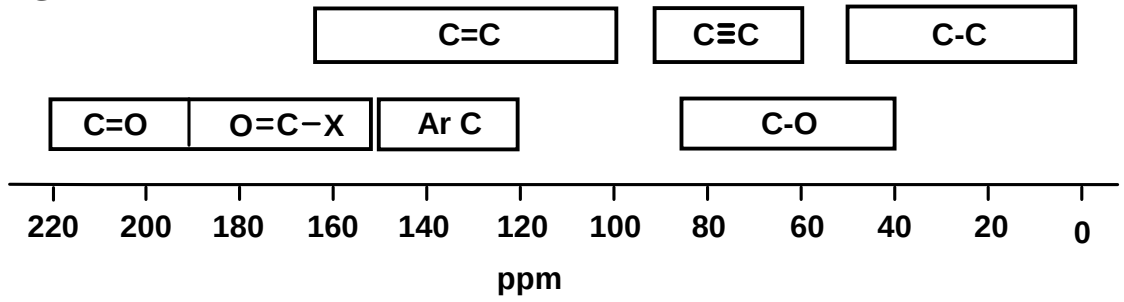
Schematic diagrams of NMR chemical shift data for H and ^{13}C NMR

^{1}H NMR



^{13}C NMR



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A Correlation Table of Infra-Red Group Absorption Frequencies

	TYPE OF VIBRATION		FREQUENCY (cm^{-1})	WAVELENGTH (μ)	INTENSITY
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 interpretatively useful			
C=C	Alkene		1680-1600	5.95-6.25	m-w
	Aromatic		1600-1400	6.25-7.14	m-w
C≡C	Alkyne		2250-2100	4.44-4.76	m-w
C=O	Aldehyde		1740-1720	5.75-5.81	s
	Ketone		1725-1705	5.80-5.87	s
	Carboxylic acid		1725-1700	5.80-5.88	s
	Ester		1750-1730	5.71-5.78	s
	Amide		1700-1640	5.88-6.10	s
	Anhydride		ca. 1810	ca. 5.52	s
			ca. 1760	ca. 5.68	s
C–O	Alcohols, Ethers, Esters, Carboxylic acids		1300-1000	7.69-10.0	s
O–H	Alcohols, Phenols				
	Free		3650-3600	2.74-2.78	m
	H-Bonded		3400-3200	2.94-3.12	m
	Carboxylic acids*		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

(* note that the -OH absorption of carboxylic acids which are solids and run as a nujol mull can be difficult to see as they maybe very broad)