UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

FINAL EXAMINATION

CHEMISTRY 353

Version 1

April 17th, 2025 **Time: 2 Hours**

READ ALL OF THE INSTRUCTIONS CAREFULLY

WRITE YOUR **NAME**, **STUDENT I.D. NUMBER** AND **VERSION NUMBER 1** ON ***BOTH*** **YOUR MULTIPLE CHOICE ANSWER SHEET** AND **WRITTEN ANSWER SHEET**.

The exam consists of **Parts 1 - 8**, each of which should be attempted. Some Parts provide you with a choice of questions, *e.g*. answer any 5 out of 6. These will be graded in numerical order 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 - 8** must be answered **IN THE APPROPRIATE BOX ON THE WRITTEN ANSWER SHEET PROVIDED**.

Parts 1 - 5 consist of a series of multiple choice questions **1 - 35** to be answered on the multiple choice answer sheet. Indicate your answer by completely blackening out the appropriate space, A, B, C, D and / or E on the answer sheet at the line for the corresponding question number. Use a soft pencil only, ***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***. For 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 spectroscopic data tables and pages of scrap paper for rough work are included with this examination paper.

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

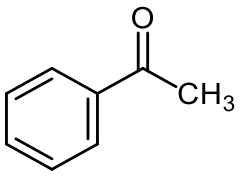
17.5% PART 1: RELATIVE PROPERTIES

ANSWER ANY SEVEN (7) OF THE EIGHT (8) QUESTIONS 1-8.

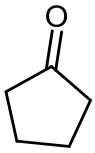
Arrange the items in questions 1-8 in DECREASING ORDER (*i.e.* greatest, most *etc*. *first*) with respect to the indicated property. Use the following code to indicate your answers in the box provided:

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

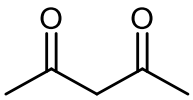
1. The number of enolisable protons in each of the following :



i

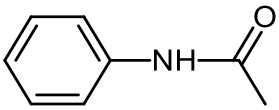


ii

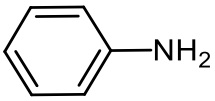


iii

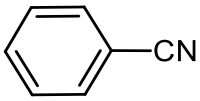
2. The relative rate of reaction of Br_2 / Fe with each of the following:



i

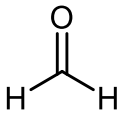


ii

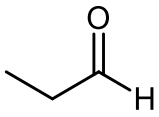


iii

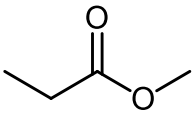
3. The relative reactivity of each of the following towards $LiAlH_4$:



i



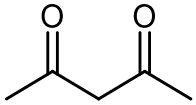
ii



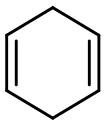
iii

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

i



ii

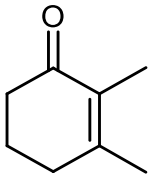


iii

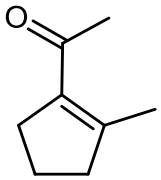
Use the following code to indicate your answers in the box provided:

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

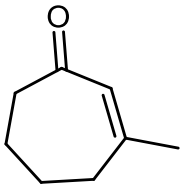
5. The relative yield of the following products by reacting 2,7-octadione with hot KOH:



i

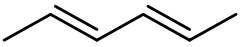


ii

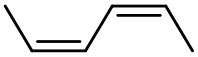


iii

6. The relative reactivity of each the following when reacted with propenal :



i



ii

iii

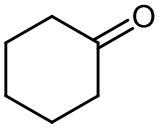
7. The relative reactivity of each of the following towards HCl:

$H_2C{=}CHCH{=}CH_2$ **i**

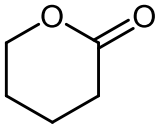
$H_2C{=}CH_2$ **ii**

$CH_3CH_2CH{=}CH_2$ **iii**

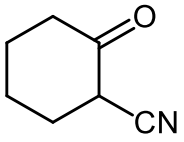
8. The relative acidity of the most acidic hydrogen in each of the following:



i



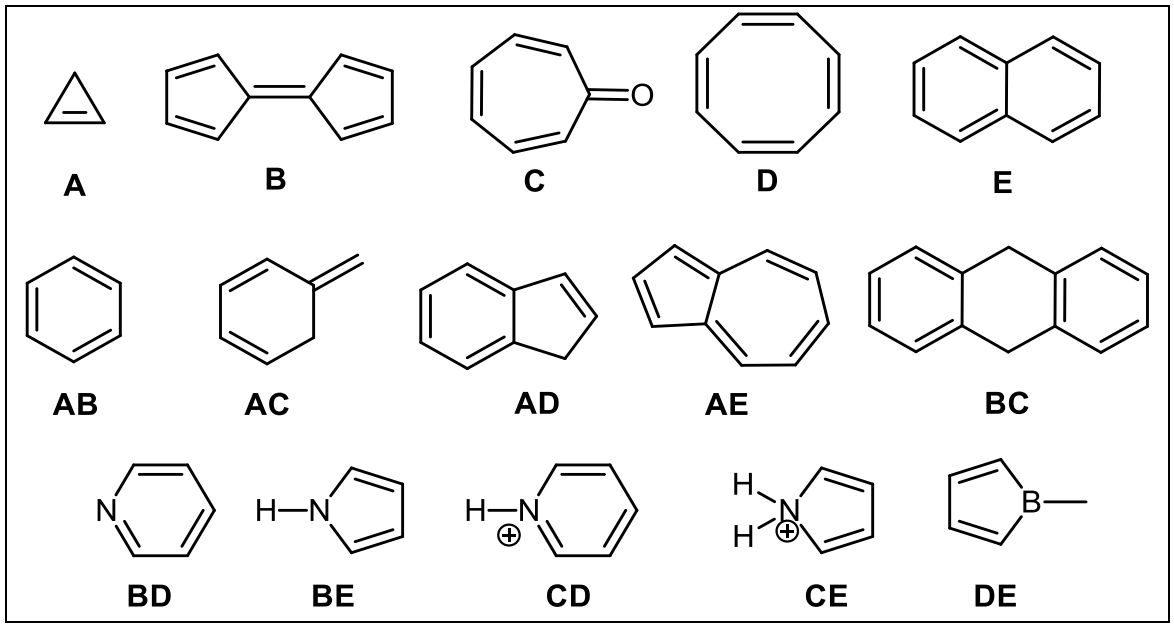
ii



iii

14% PART 2: AROMATICITY AND RESONANCE

ANSWER ANY SEVEN (7) OF THE EIGHT (8) QUESTIONS 9 - 16.



Answer questions 9-16 by selecting a SINGLE compound from those shown above.

9. A compound that is non-aromatic because it adopts a non-planar conformation.

10. The compound with the highest resonance energy.

11. Aromatic as drawn where n ≠ 1 when applying the Hückel rule for aromaticity.

12. Non-aromatic as drawn, but has an aromatic conjugate acid.

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

14. Select the compound that contains the **most** acidic proton.

15. A compound with an sp^3 hybridised heteroatom.

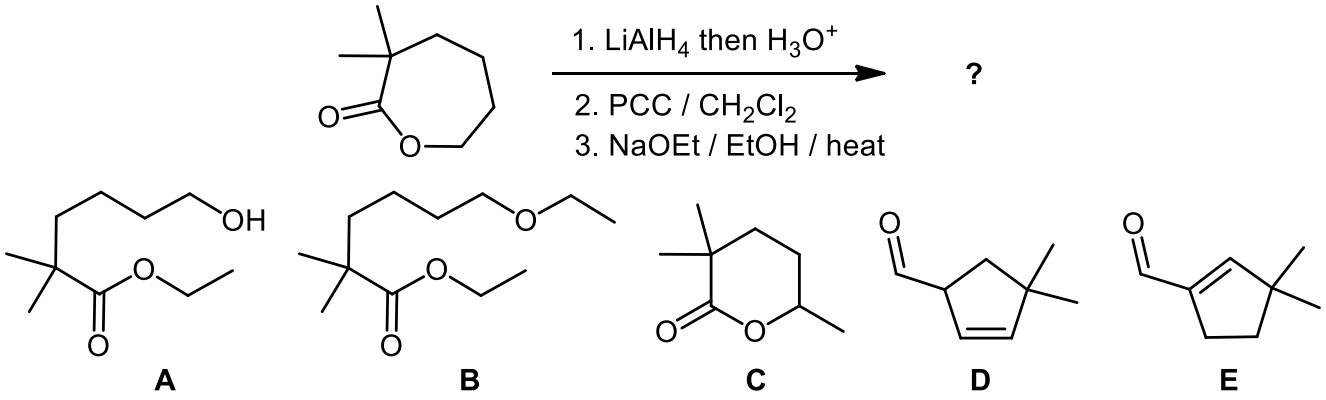
16. A heterocyclic compound that is anti-aromatic as drawn.

17.5% **PART 3: STARTING MATERIALS AND PRODUCTS OF SYNTHESIS**

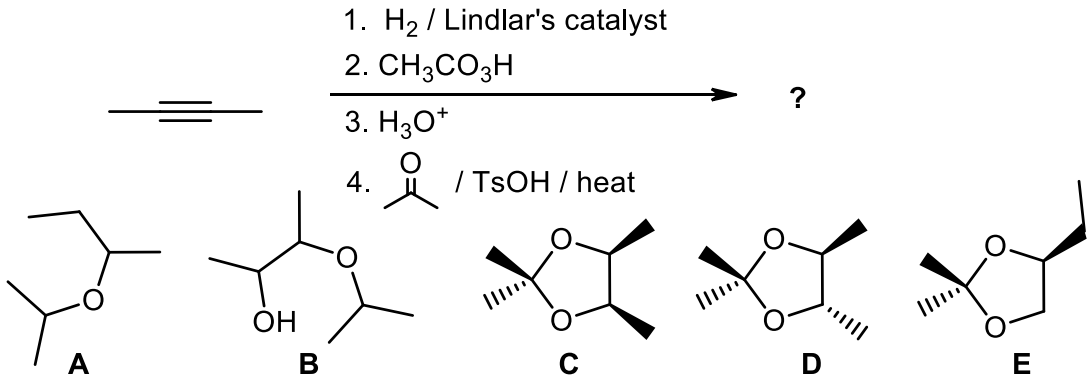
ANSWER ANY SEVEN (7) OF THE EIGHT (8) QUESTIONS 17 - 24.

For each of the questions 17 - 24 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.

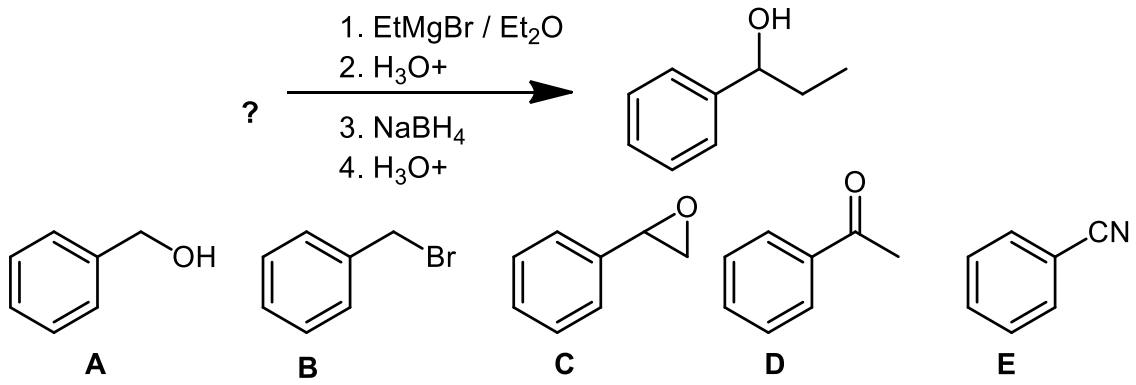
17.



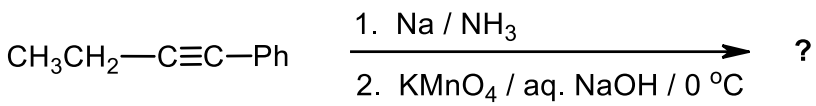
18.

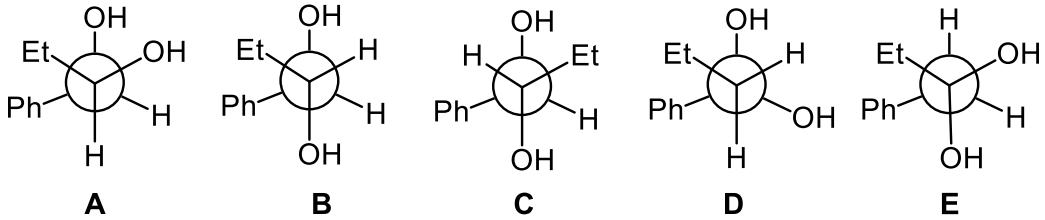


19.

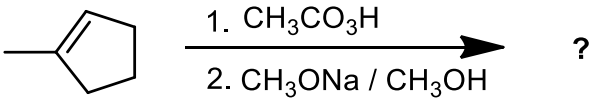


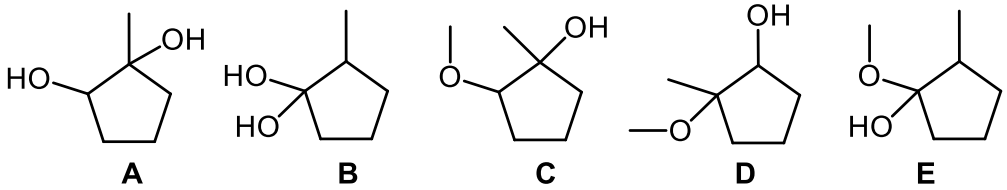
20.



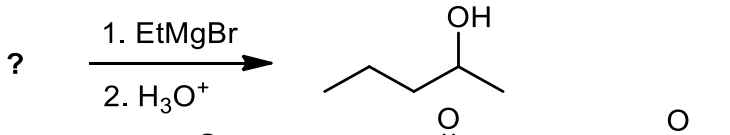


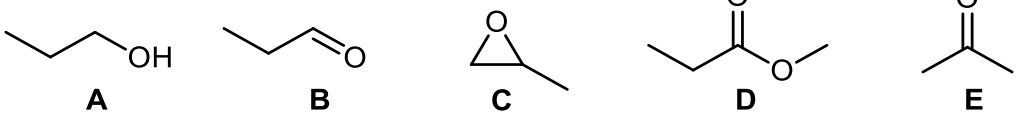
21.



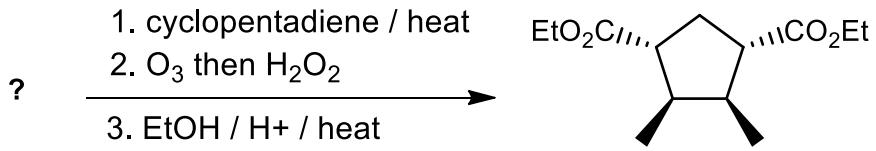


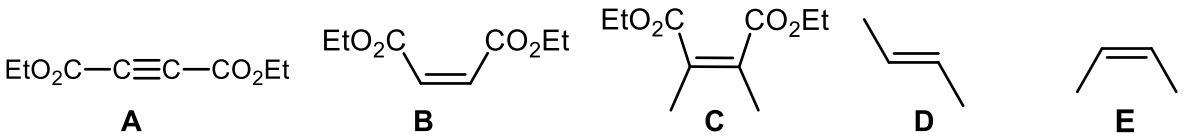
22.



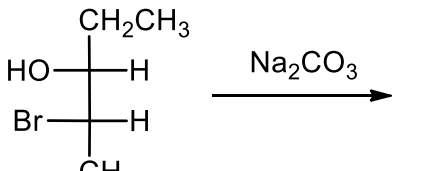


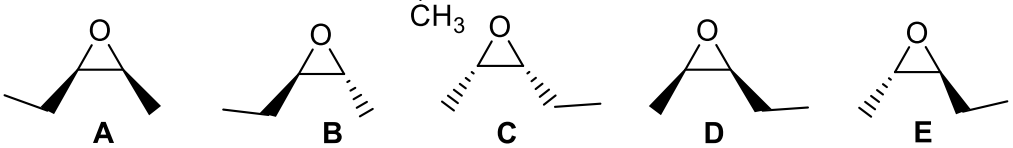
23.





24.



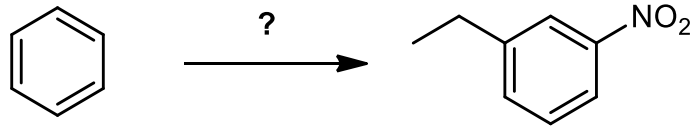


10% PART 4: REAGENTS FOR SYNTHESIS

ANSWER ANY FIVE (5) OF THE SIX (6) QUESTIONS 25 - 30

For each of the questions 25 - 30 identify the reagent(s) required in order to BEST complete each of the reaction sequences shown by selecting from the list provided.

25.



A. i. HNO_3 / H_2SO_4 / heat, ii. ethyl chloride / $AlCl_3$ / heat

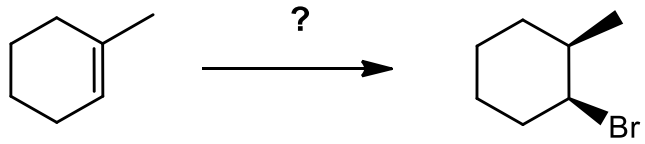
B. i. HNO_3 / H_2SO_4 / heat, ii. ethanoyl chloride / $AlCl_3$ / heat iii. H_2 / Pd

C. i. ethyl chloride / $AlCl_3$ / heat, ii. HNO_2 / HCl

D. i. ethanoyl chloride / $AlCl_3$ / heat, ii. HNO_3 / H_2SO_4 / heat iii. NH_2NH_2 / KOH/ heat

E. i. ethanoyl chloride / $AlCl_3$ / heat, ii. HNO_2 / HCl iii. Zn / Hg / HCl

26.



A. HBr / peroxides / uv light

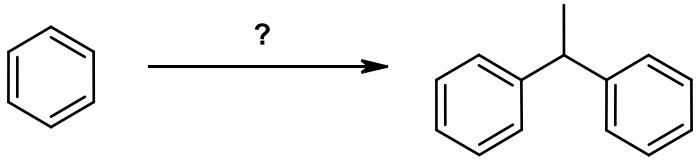
B. HBr / dark / N_2

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

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

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

27.



A. i. Br_2 / $FeBr_3$ ii. Mg iii. benzyl bromide

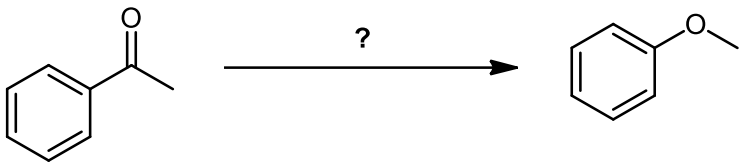
B i. Ethanoyl chloride, $AlCl_3$ ii. $KMnO_4$, H_3O^+, heat iii. benzene

C. i. Ethyl chloride, $AlCl_3$ ii. NBS iii. H_2SO_4, heat

D. i. Ethyl chloride, $AlCl_3$ ii. H_2CrO_4 iii. PhMgBr, then H^+ workup

E. i. Ethanoyl chloride, $AlCl_3$ ii. $NaBH_4$ iii. H^+, benzene

28.



A. i. $NaBH_4$, ii. H_3O^+, iii. H_2SO_4, MeOH

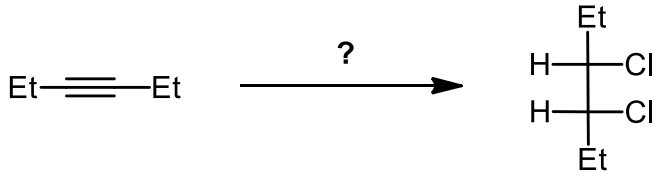
B. i. MeOH, heat, ii. H_3O^+

C. i. CH_3CO_3H , ii. NaOMe, MeOH, heat iii. Na_2CO_3, MeI

D. i. $NaBH_4$, ii. H_3O^+, iii. CH_3CO_3H

E. i. $NaBH_4$, ii. LDA, MeI, iii. CH_3CO_3H

29.



A. i. Na / NH_3, ii. Cl_2

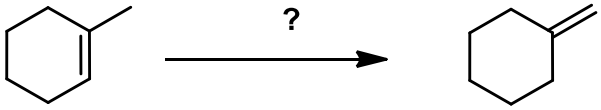
B. i. Na / NH_3, ii. CH_3CO_3H iii. $SOCl_2$ / Et_3N

C. i. H_2 / Pd, ii. Cl_2

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

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

30.



A. H_2SO_4

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

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

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

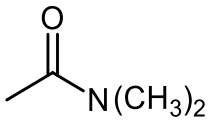
E. i. Br_2 ii. KOH / EtOH / heat

10% PART 5: EXPLANATION OF PHENOMENA

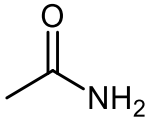
ANSWER ALL FIVE (5) OF THE QUESTIONS 31-35.

Choose the single explanation that best rationalises the phenomenon indicated.

31. Two amides are shown to the right.
Which is the more acidic and why ?



A



B

A. **A** because the conjugate base of **A** is better stabilized by resonance

B. **A** because the conjugate base of **A** is better stabilized by an electronegative atom

C. **B** because the conjugate base of **B** is better stabilized by resonance

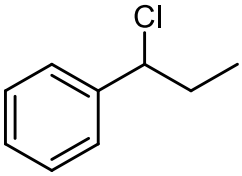
D. **B** because the conjugate base of **B** is better stabilized by an electronegative atom

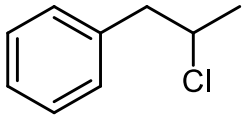
E. **B** because the N atom in **B** is sp^2 hybridised

AB. Since they are both amides, they are essentially equally acidic

32. 1-Phenylprop-1-ene reacts with HCl to give either **G** or **H**. Which is the major product and why?

G





H

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

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

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

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

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

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

33. What is the product of the reaction of benzoic acid with methyl amine ?

A. N-methyl benzamide because the carboxylic acid undergoes nucleophilic addition

B. N-methyl benzamide because the carboxylic acid undergoes nucleophilic acyl substitution

C. Phenyl methanamide because the carboxylic acid undergoes nucleophilic addition

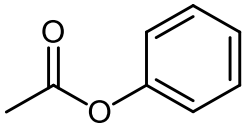
D. Phenyl methanamide because the carboxylic acid undergoes nucleophilic acyl substitution

E. An ammonium benzoate salt because the amine protonates

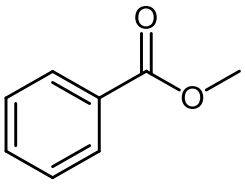
AB. N-methylaniline because the amine undergoes nucleophilic substitution

34. Two aromatic esters are shown below. Which of the following statements about the reaction of **M** and **N** with ethanoyl chloride / $AlCl_3$ / heat best describes what happens ?

M



N



A. Only **M** reacts because the substituent is an electron donating group

B. Only **N** reacts because the substituent is an electron donating group

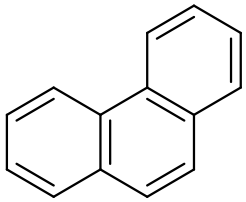
C. Both **M** and **N** react readily because esters are electron donating groups

D. Both react but **M** reacts more rapidly than **N** because **M** is more electron donating

E. Both react but **N** reacts more rapidly than **M** because **N** is more electron donating

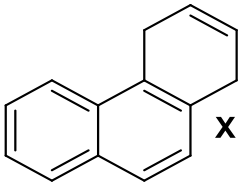
AB. Neither **M** nor **N** react because esters are electron withdrawing groups

35. Phenanthrene (right) reacts with 1 eq. of H_2 / catalyst to give one of the following products **X**, **Y** or **Z**. Which is the major product and why ?

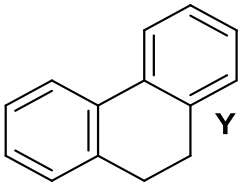


phenanthrene

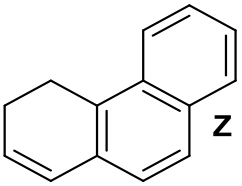
X



Y



Z



A. **X** because it gives a naphthalene, a larger aromatic molecule (n=2 in the Huckel rule)

B. **X** because it gives the fewest double bonds (5) in conjugation

C. **Y** because H_2 adds to the double bond that is the least sterically hindered for the catalyst

D. **Y** because it has the highest aromatic stabilisation

E. **Z** because it gives has the longest (6 C=C) conjugated system

AB. **Z** because it gives a naphthalene with a conjugated alkene

10% PART 6: SYNTHESIS

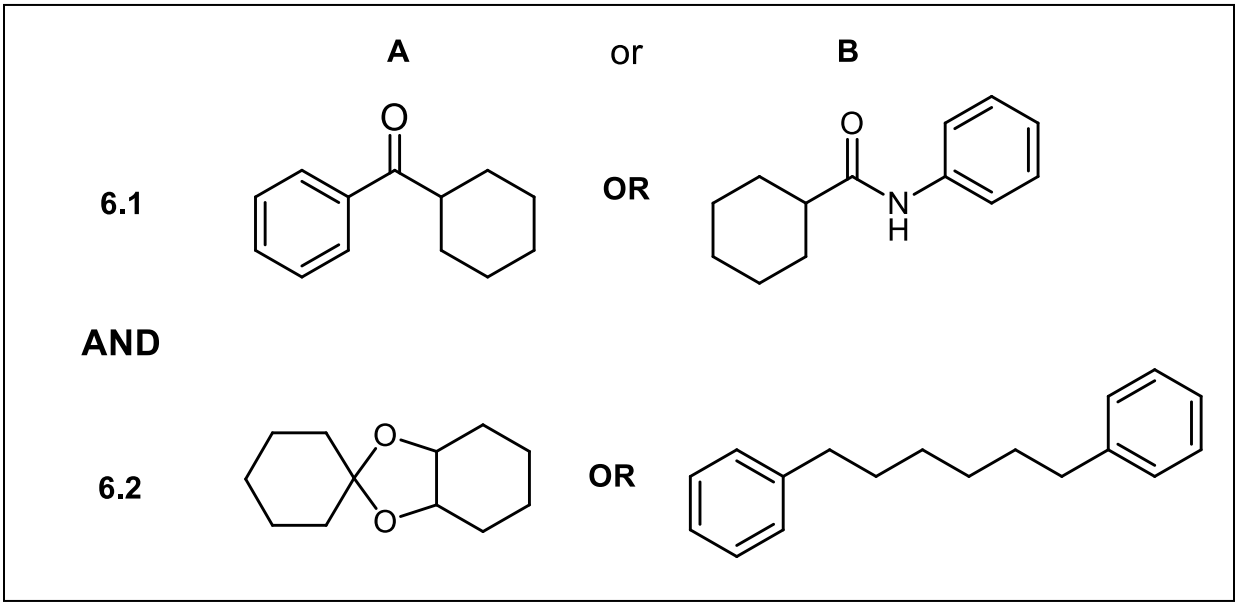
WRITE YOUR ANSWER IN THE APPROPRIATE BOX ON THE WRITTEN ANSWER SHEET PROVIDED.

ANSWER TWO (2) QUESTIONS, ONE (1) FROM EACH OF PART 6.1 AND PART 6.2

Design an efficient synthesis of TWO (2) of the following target molecules

SHOW YOUR ANSWER AS A STEPWISE REACTION SCHEME SHOWING THE REAGENT REQUIRED AND PRODUCT OF EACH STEP

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



Permitted Materials and Reagents

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

- any organic compounds with no more than **FOUR** carbons
- benzene
- cyclohexene
- you can use any solvents or other reagents for the reactions provided that they do not contribute carbon atoms to the target.

10% PART 7: MECHANISM

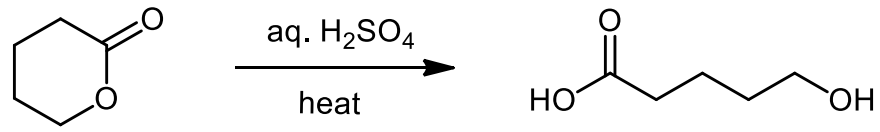
WRITE YOUR ANSWER IN THE APPROPRIATE BOX ON THE WRITTEN ANSWER SHEET PROVIDED

ANSWER TWO (2) QUESTIONS, ONE (1) FROM EACH OF PART 7.1 AND PART 7.2

Draw curly arrow mechanisms to explain the following reactions / observations. No other reagents are required.

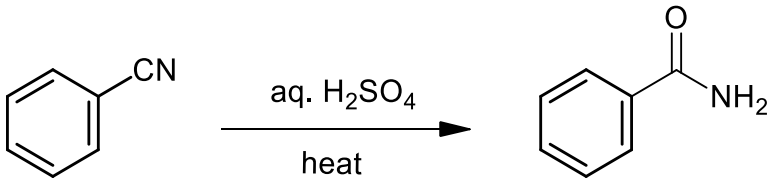
7.1. Draw the curly arrow mechanism for ONE (1) of the following reactions:

A



OR

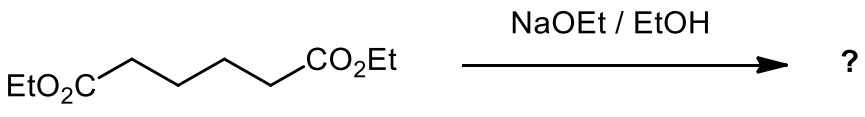
B



AND

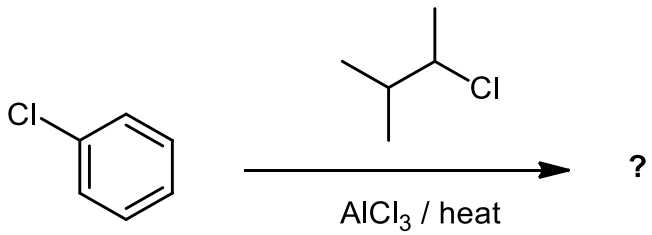
7.2. Predict the product and provide the curly arrow mechanism for ONE (1) of the following reactions:

A



OR

B



11% PART 8: STRUCTURE DETERMINATION

WRITE YOUR ANSWERS IN THE APPROPRIATE BOXES ON THE WRITTEN ANSWER SHEET PROVIDED

Use the information in the following paragraph to answer the questions below.

Compound **A** (C_5H_8O, 13C NMR / ppm: 220, 38, and 23) was reacted with lithium diisopropylamide and then ethyl bromide to give compound **B**.

Reaction of **B** with CH_3CO_3H led to compound **C** ($C_7H_{12}O_2$, IR stretch at 1735 cm^{-1}).

When **C** was reacted with $LiAlH_4$ / THF followed by a normal acidic work-up, compound **D** ($C_7H_{16}O_2$, IR stretch at 3330 cm^{-1}, strong, broad) was produced.

When compound **D** was reacted with excess pyridinium chlorochromate in dichloromethane, it gave compound **E**, an isomer of **C**. When **E**, was heated EtONa / EtOH then worked up with acid it yielded compound **F** ($C_7H_{10}O$) with water as the by-product.

(9%) Identify the compounds **A** to **F** (drawn structures are sufficient).

(1%) Given the IUPAC name for **B**.

(1%) The transformation of **E** to **F** is a named reaction. What is it named ?

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

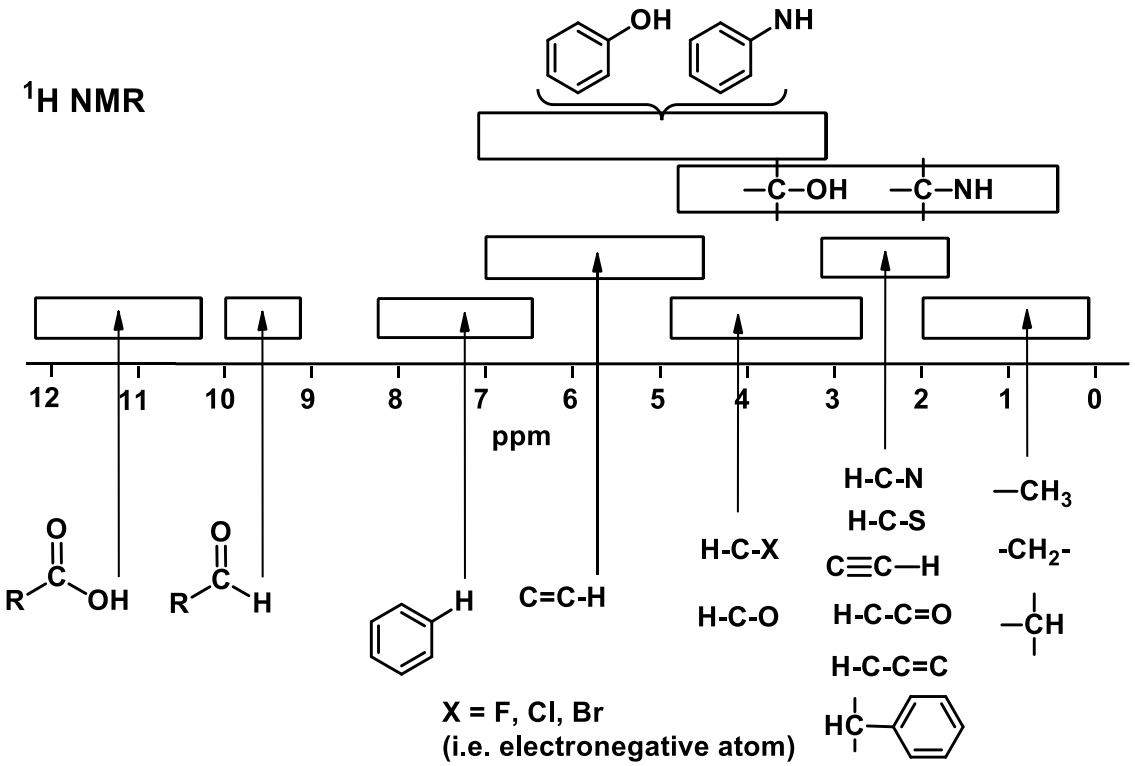
IRH W2025

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)

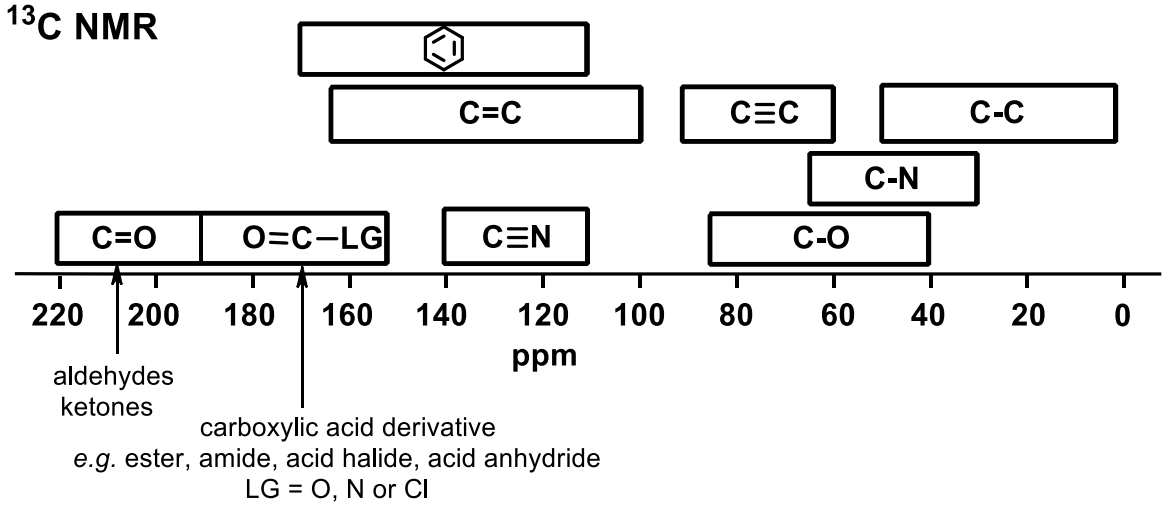
SPECTROSCOPIC TABLES



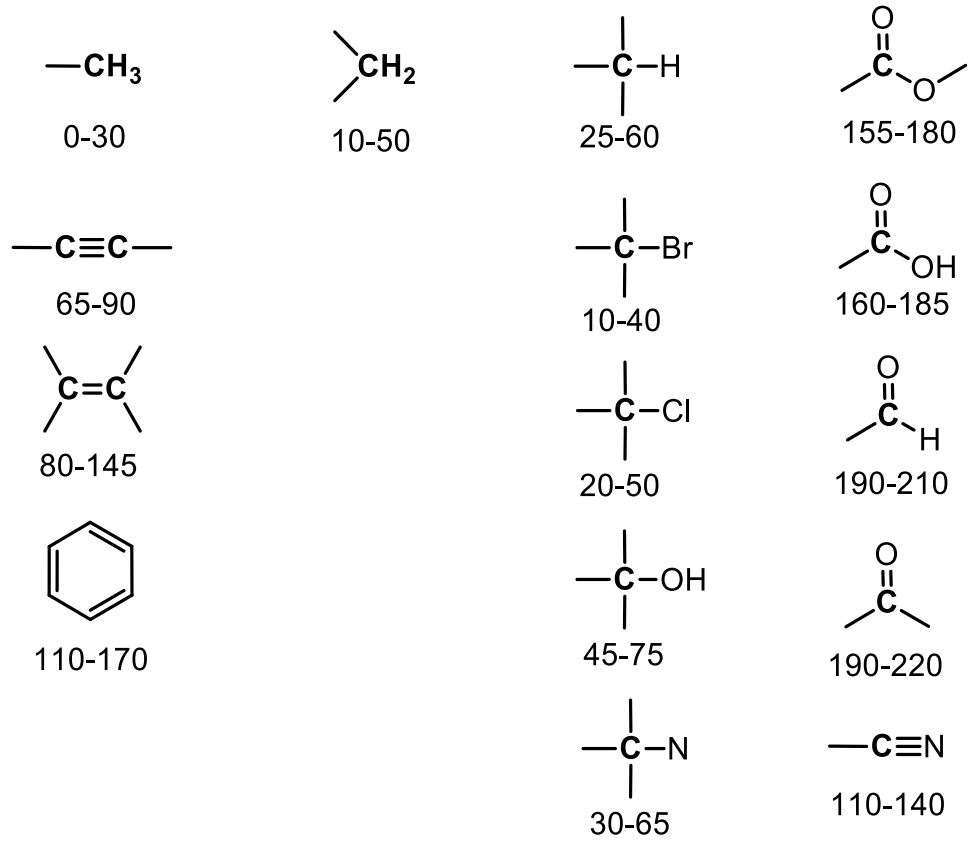
^{1}H NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm

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–Ar	2.3	2.7	3.0
R–Br	2.7	3.3	4.1
R–Cl	3.1	3.4	4.1
R–O—	3.3	3.4	3.7

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



^{13}C NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm



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 run as a nujol mull can be difficult to see as they may be very broad.

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