UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

FINAL EXAMINATION

CHEMISTRY 353

Version 1

April 16th, 2024 **Time: 2 Hours**

READ ALL 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** are to be answered **IN THE APPROPRIATE BOX ON THE WRITTEN ANSWER SHEET PROVIDED**.

Parts 1 - 5 consist of a series of multiple choice questions numbered **1 - 34** to be answered on the multiple choice answer sheet. Indicate your answer by completely blackening out the appropriate space, A, B, C, D or E on the answer sheet. 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***. 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 spectroscopic data tables and 2 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.**

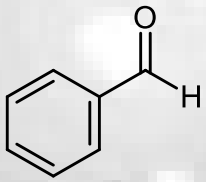
17.5% PART 1: RELATIVE PROPERTIES

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

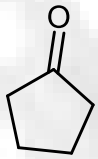
Arrange the items in questions 1-8 in DECREASING ORDER (*i.e.* greatest, most *etc*. *first*) with respect to the indicated property. Use the following code to indicate your answers in the box provided:

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

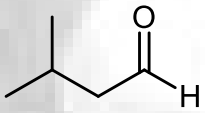
1. The number of enolisable protons in each of the following :



i

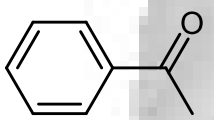


ii

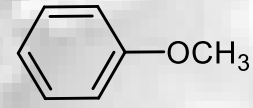


iii

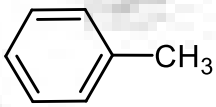
2. The relative rate of reaction of HNO_3 / H_2SO_4 with each of the following:



i

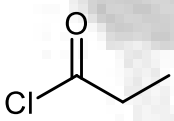


ii

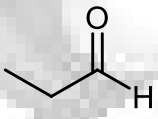


iii

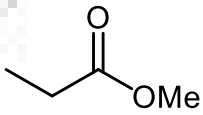
3. The relative reactivity of each of the following towards CH_3MgBr :



i

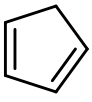


ii

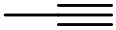


iii

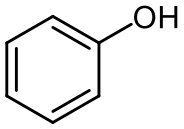
4. The relative acidity of the most acidic hydrogen in each of the following:



i



ii

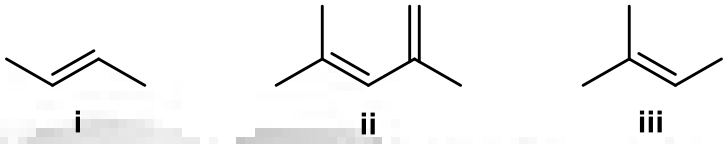


iii

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

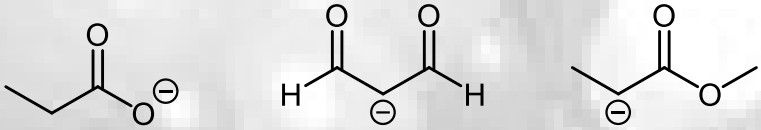
A	**i > ii > iii**	**D**	**ii > iii > i**
B	**i > iii > ii**	**E**	**iii > i > ii**
C	**ii > i > iii**	**AB**	**iii > ii > i**

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



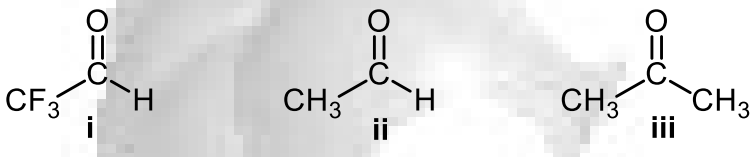
i **ii** **iii**

6. The relative basicity of each the following anions:



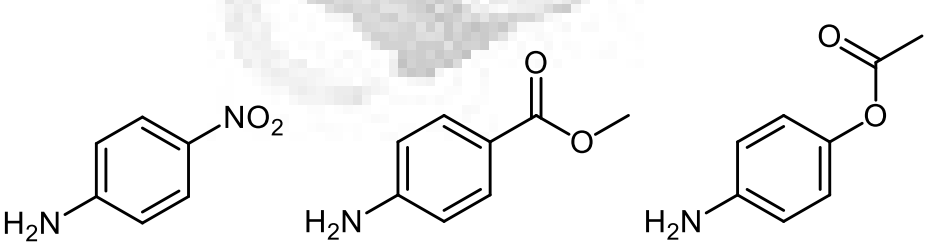
i **ii** **iii**

7. The equilibrium constant, *K*, for the formation of the hydrate produced when each of the following is dissolved in water:



i **ii** **iii**

8. The relative basicity of the following:



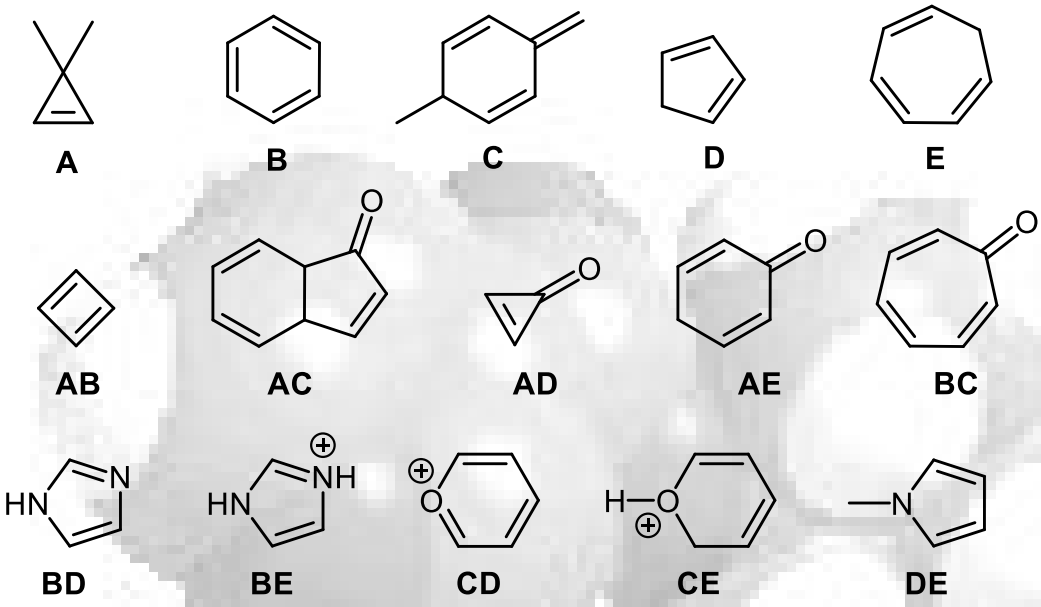
i **ii** **iii**

14% PART 2: AROMATICITY AND RESONANCE

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

For each question, select a SINGLE compound from those shown below.

SET 1



9. A non-conjugated molecule

10. Non-aromatic as drawn, but has an important aromatic resonance structure where n ≠ 1 when applying the Hückel rule.

11. The structure that contains the most acidic proton.

12. Non-aromatic as drawn, but becomes aromatic when deprotonated.

13. A compound that has an aromatic tautomer.

14. An anti-aromatic (assuming that it is planar) molecule.

15. A neutral, aromatic heterocycle that become non-aromatic when protonated.

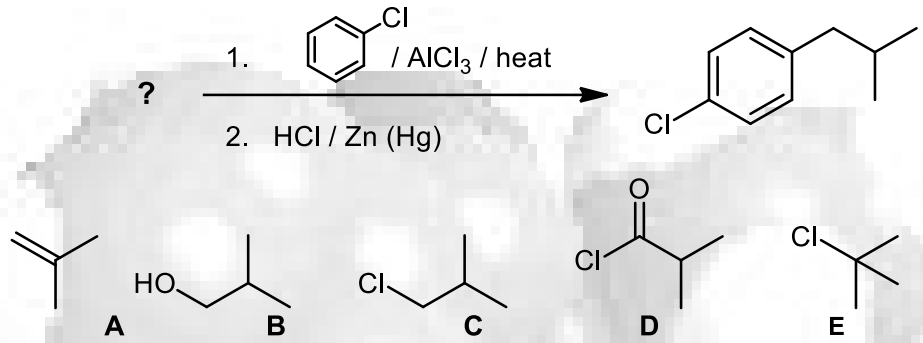
16. A non-aromatic hydrocarbon that would be anti-aromatic if deprotonated (assuming planarity).

17.5% PART 3: STARTING MATERIALS AND PRODUCTS OF SYNTHESIS

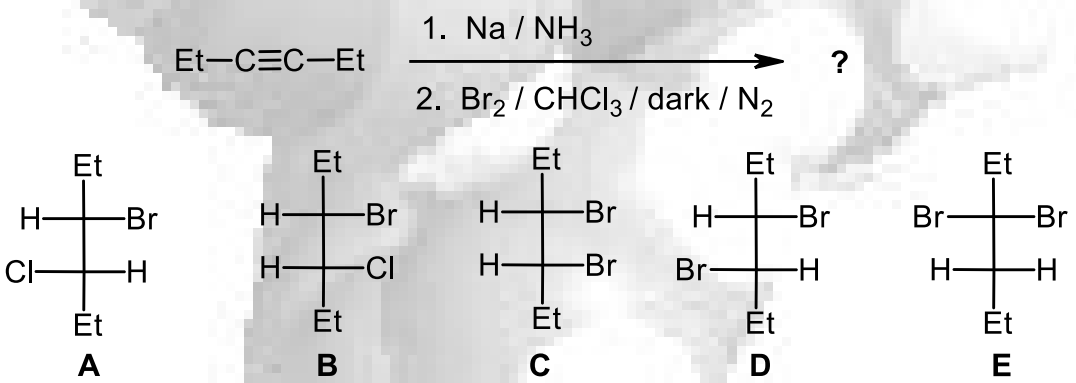
ANSWER ANY SEVEN (7) OF THE EIGHT (8) QUESTIONS 17 - 24.

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.

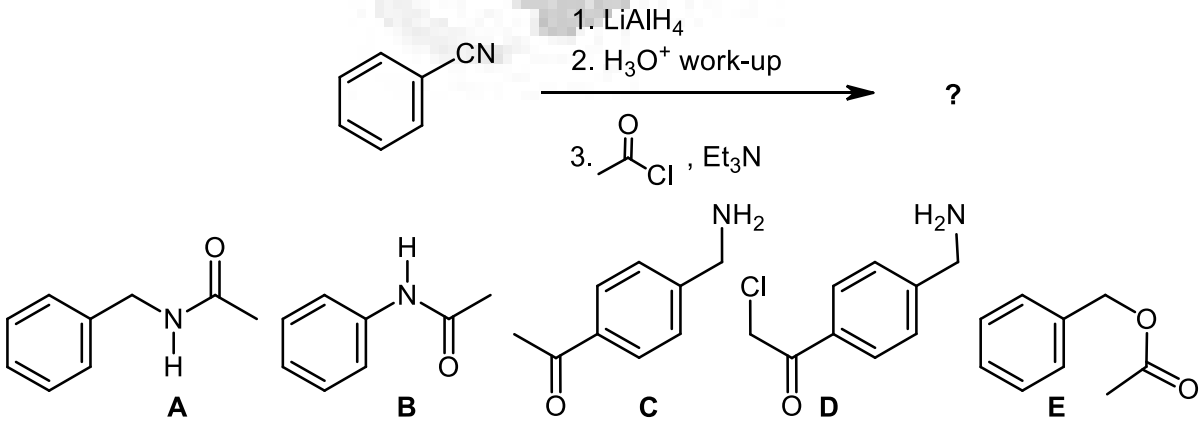
17.



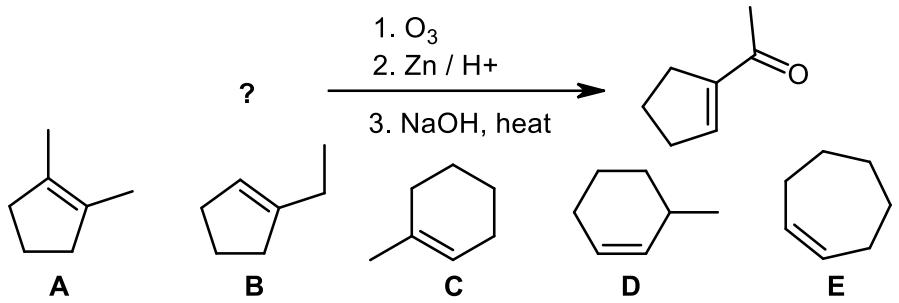
18.



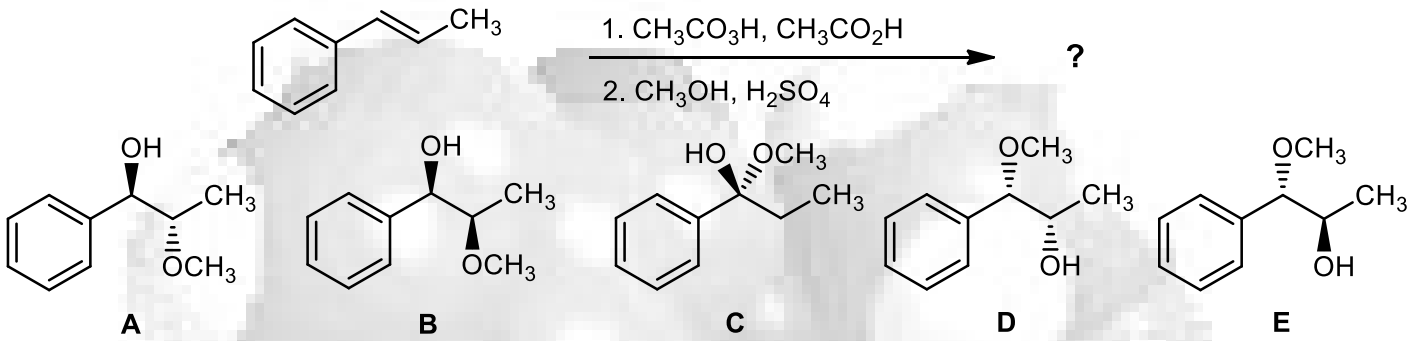
19.



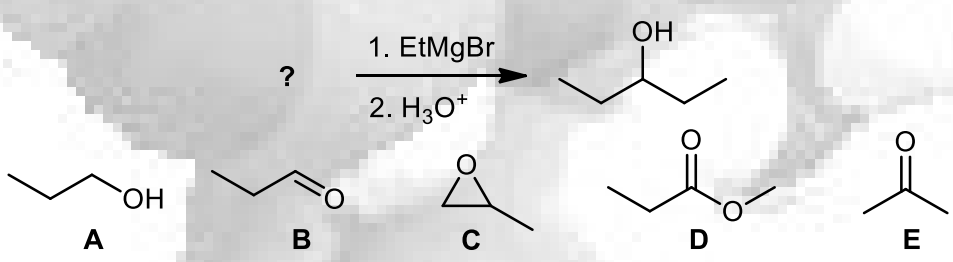
20.



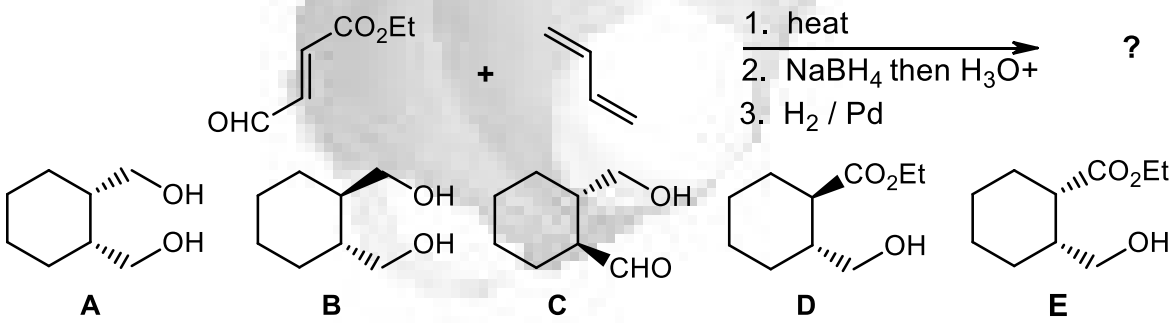
21.



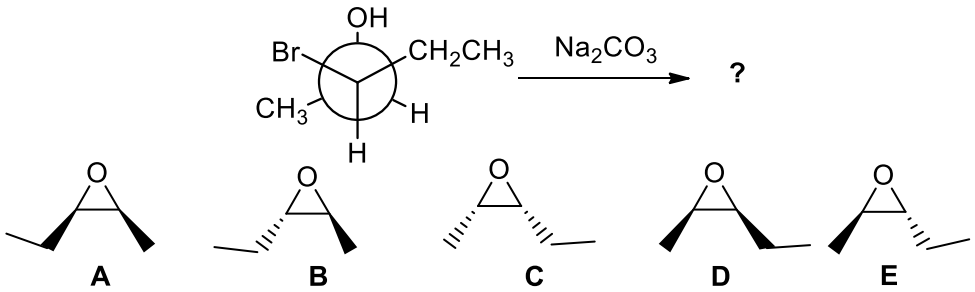
22.



23.



24.

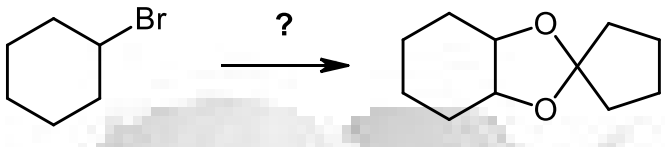


8% PART 4: REAGENTS FOR SYNTHESIS

ANSWER ANY FOUR (4) OF THE FIVE (5) QUESTIONS 25 - 29

For each of the questions 25 - 29 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. H_2SO_4, heat ii. $KMnO_4$, aq KOH, heat iii. 1,2-cyclopentanediol

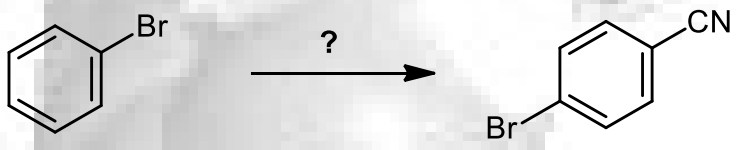
B i. $NaOC(CH_3)_3$, heat ii. CH_3CO_3H, CH_3CO_2H iii. cyclopentanone, TsOH

C i. NaOEt, heat ii. $KMnO_4$, aq KOH, 0 °C iii. cyclopentanone, TsOH

D i. NaOEt, heat ii. CH_3CO_3H, CH_3CO_2H iii. aq. H_2SO_4 iv. 1,2-cyclopentanediol, TsOH

E i. H_2SO_4, heat ii. 1,2-cyclopentanediol, aq H_2SO_4, $HgSO_4$ iii. TsOH

26.



A. i. CH_3MgBr ii. H_2CrO_4, H_2SO_4, heat iii. $NaNH_2$ iv. $LiAlH_4$, then water

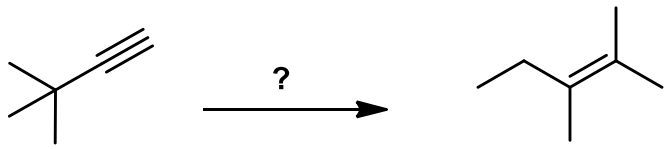
B. i. HNO_3, H_2SO_4, heat ii. Sn, HCl iii. $NaNO_2$, HCl, cold iv. CuCN

C. i. KCN, DMSO ii. Br_2, $FeBr_3$

D. i. CuCN ii. Mg then H^+ iii. Br_2, $FeBr_3$

E. i. HNO_3, H_2SO_4, heat ii. $NaNO_2$, HCl, cold iii. KCN iv. Sn, HCl

27.



A. i. H_2 / Lindlar's catalyst, ii. CH_3CO_3H, iii. CH_3MgBr, iv. H_3O^+

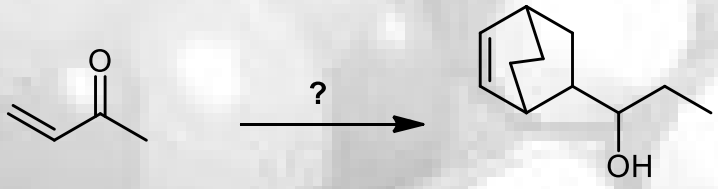
B. i. O_3, ii. H_2O, iii. CH_3CH_2MgBr, iv. H_3O^+

C. i. H_2 / Lindlar's cat. ii. BH_3, then aq. H_2O_2 / NaOH iii. PCC iv. MeMgBr then H^+ workup

D. i. $HgSO_4$, aq. H_2SO_4, ii. CH_3MgBr, iii. H_3O^+

E. i. BH_3, then aq. H_2O_2 / NaOH ii. $H_2C{=}P(Ph)_3$ iii. H^+, heat

28.



A. i. 1,3-cyclohexadiene, heat ii. MeMgBr iii. H_3O^+ iv. $LiAlH_4$ then H_2O

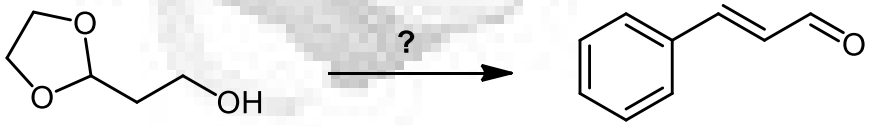
B. i. 1,3-cyclohexadiene, heat ii. $NaBH_4$, EtOH iii. PDC iv. MeMgBr v. H_3O^+

C. i. $NaBH_4$ ii. Na, CH_3I iii. 1,3-cyclohexadiene, heat

D. i. MeMgBr ii. H_3O^+ iii. cyclohexene, heat iv. PCC

E. i. LDA ii. Me-Br iii. 1,3-cyclohexadiene, heat iv. $NaBH_4$

29.



A. i. PCC ii. PhLi iii. H_3O^+, heat

B. i. aq. H_2SO_4 ii. PDC iii. PhMgBr iv. H_3O^+

C. i. $LiAlH_4$ ii. H_2O iii. Na, PhBr iv. H_3O^+

D. i. PhMgBr ii. H_3O^+ iii. PCC iv. $HgSO_4$, H_2SO_4, H_2O

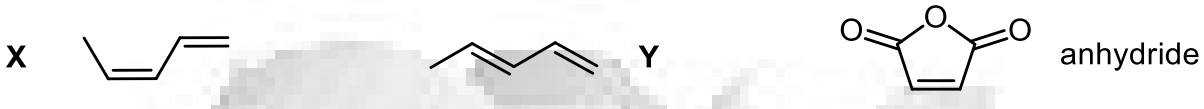
E. i. PDC ii. PhMgBr iii. H_3O^+ iv. $NaBH_4$

10% PART 5: EXPLANATION OF PHENOMENA

ANSWER ALL FIVE (5) OF THE QUESTIONS 30-34.

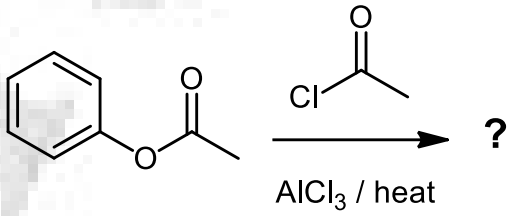
Choose the single explanation that best rationalises the phenomenon indicated.

30. The two pentadienes shown below are geometric (E/Z) isomers. One of them undergoes reaction with the anhydride shown significantly faster than the other. Which isomer is more reactive and why ?



A. **X** because it is the less stable isomer
B. **X** because steric effects destabilise its s-cis conformation
C. **X** because it has a more stable s-cis conformation
D. **Y** because it is the less stable isomer
E. **Y** because steric effects destabilise its s-cis conformation
AB. **Y** because it has a more stable s-cis conformation

31. When the aromatic ester is reacted as shown (right), which of the following best describes the major product and why it is formed ?

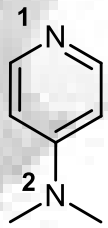


A. *para* because the ester group is electron donating directing *ortho/para*
B. *meta* because the ester group is electron donating directing *meta*
C. *para* because the ester group is electron withdrawing directing *ortho/para*
D. *meta* because the ester group is electron withdrawing directing *meta*
E. *meta* because the acyl group is electron withdrawing directing *meta*
AB. *no reaction* because the ester group is too deactivating for the Friedel-Crafts to work

32. What is the product of the reaction of butanoic acid with CH_3ONa / CH_3OH followed by work-up with aqueous acid ?

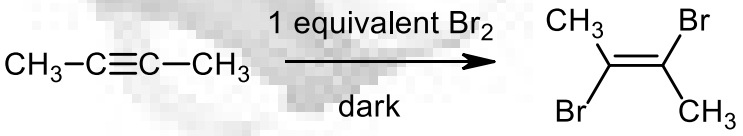
A. methyl butanoate because the carboxylic acid undergoes nucleophilic addition
B. methyl butanoate because the carboxylic acid undergoes nucleophilic acyl substitution
C. butyl methanoate because the carboxylic acid undergoes nucleophilic addition
D. butyl methanoate because the carboxylic acid undergoes nucleophilic acyl substitution
E. butanoic acid because the initial reaction forms a carboxylate that reprotonates
AB. pentan-2-one because the carboxylic acid undergoes nucleophilic acyl substitution

33. Dimethylaminopyridine has two basic nitrogen atoms labeled as **1** and **2** (shown below). Which N atom is more basic and why ?



A. N1 because the N1 lone pair is in an sp^2 hybrid orbital
B. N1 because the N1 lone pair is in a p orbital
C. N1 because its conjugate acid is resonance stabilised
D. N2 because the N2 lone pair is in an sp^3 hybrid orbital
E. N2 because its conjugate acid is resonance stabilised
AB. N2 because the N2 lone pair is in a p orbital

34. (E)-2,3-dibromobut-2-ene is the major product in the following reaction because:



A. *Trans* double bonds are generally more stable than *cis*
B. The stepwise reaction involves a vinyl cation
C. The stepwise reaction involves a cyclic bromonium ion
D. The stepwise reaction involves a vinyl radical
E. The two bromine atoms add in a concerted manner
AB. The reaction occurs in accord with Markovnikov's rule

10% PART 6: SYNTHESIS

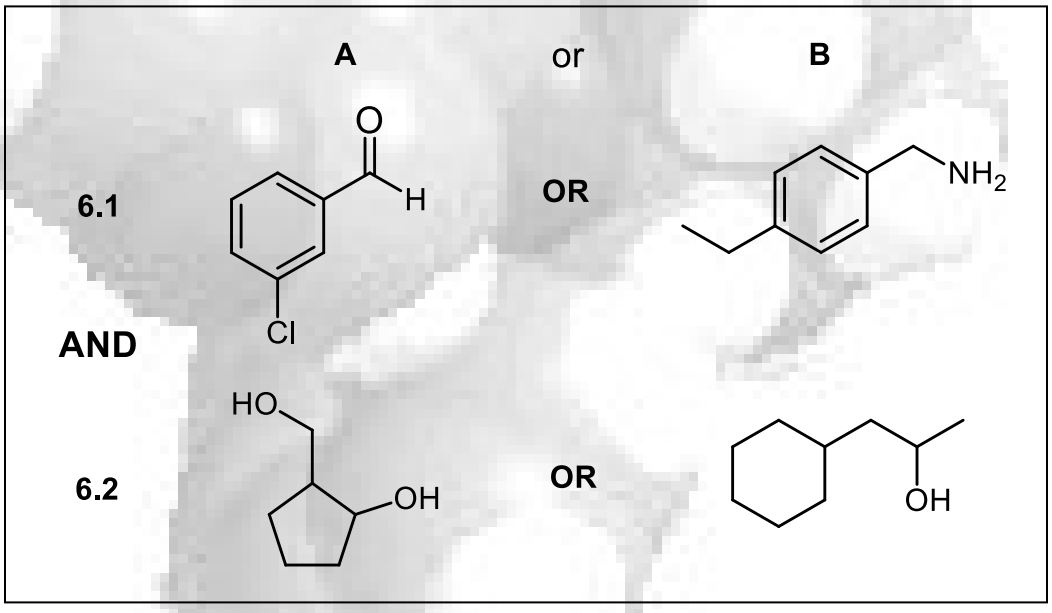
WRITE YOUR ANSWER IN THE APPROPRIATE BOX ON THE WRITTEN ANSWER SHEET PROVIDED.

ANSWER TWO (2) QUESTIONS, ONE 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

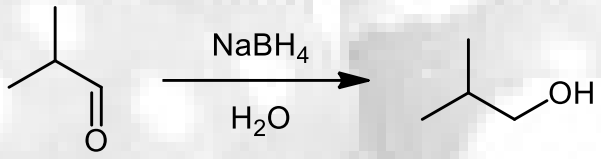
WRITE YOUR ANSWER IN THE APPROPRIATE BOX ON THE WRITTEN ANSWER SHEET PROVIDED

ANSWER TWO (2) QUESTIONS, ONE 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.

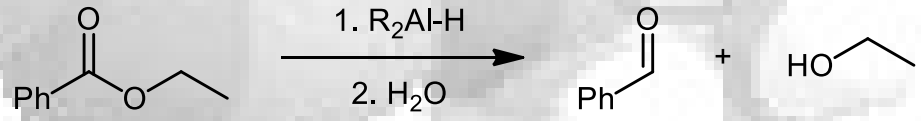
7.1. Draw the curly arrow mechanism for **one** of the following reactions:

A



OR

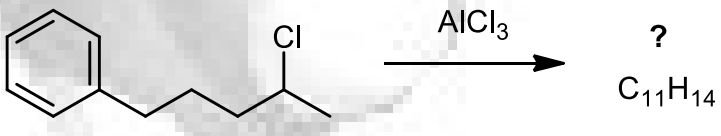
B



AND

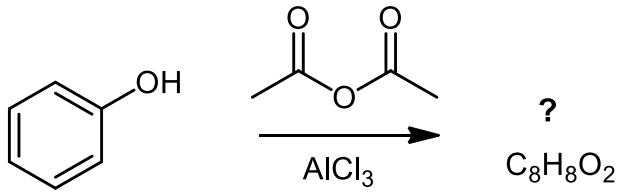
7.2. Predict the product and provide the curly arrow mechanism for **one** of the following reactions:

A



OR

B



13% 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.

An unknown compound **A** was heated with **B** (C_4H_7OCl) and $AlCl_3$ to give compound **C** as the major product (IR : approx. 1685 cm^{-1}).

When **C** was then reacted with CH_3CO_3H, two isomeric products were isolated in about 2:1 ratio where **D** was the major isomer.

When **D** was subsequently reacted with $LiAlH_4$ / THF followed by an aqueous acid work up, extraction with Et_2O and then removal of the volatile components on a rotary evaporator, the major product obtained was **E** (mass spec : M+ = 122, 13C NMR / ppm = 6 peaks total with 4 peaks 140-125 range, and 65, 21. IR : broad 3370 cm^{-1}). When **E** was heated with acidic aq. $KMnO_4$ it gave **F** ($C_8H_6O_4$, H-NMR / ppm = 12.0 (1H broad singlet, D_2O exchangeable); 8.1 (2H singlet)) as the major product.

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

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

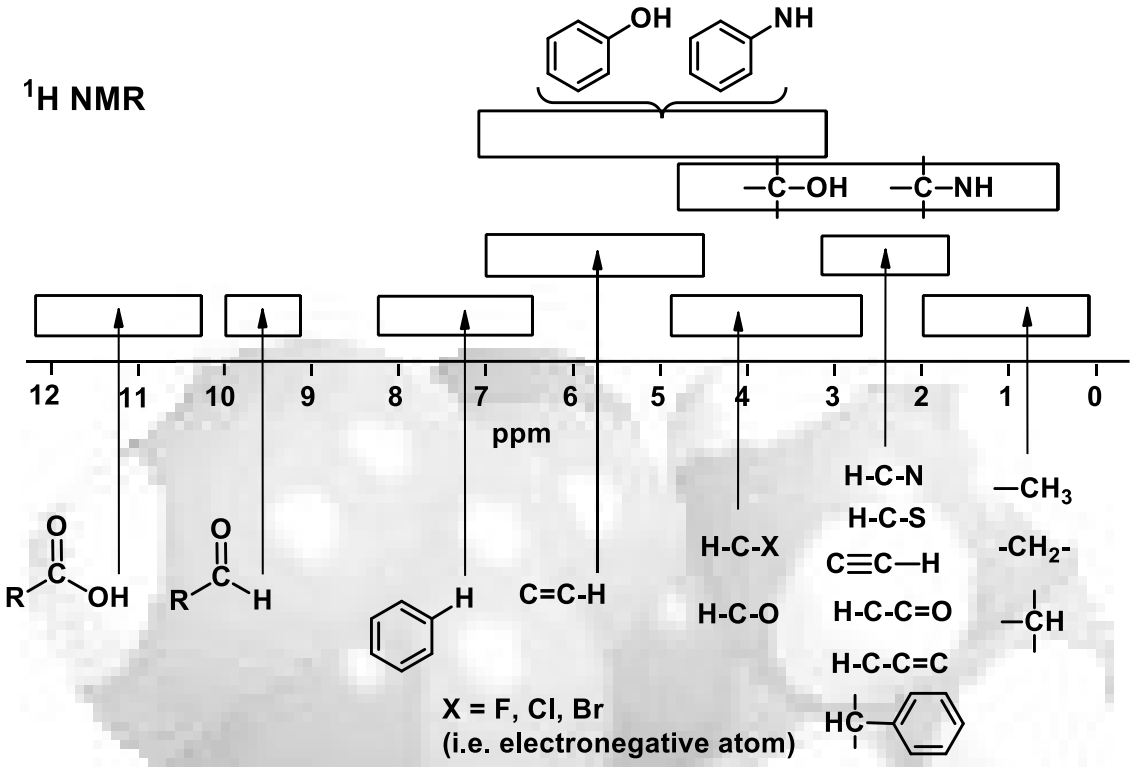
*****THE END*****

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

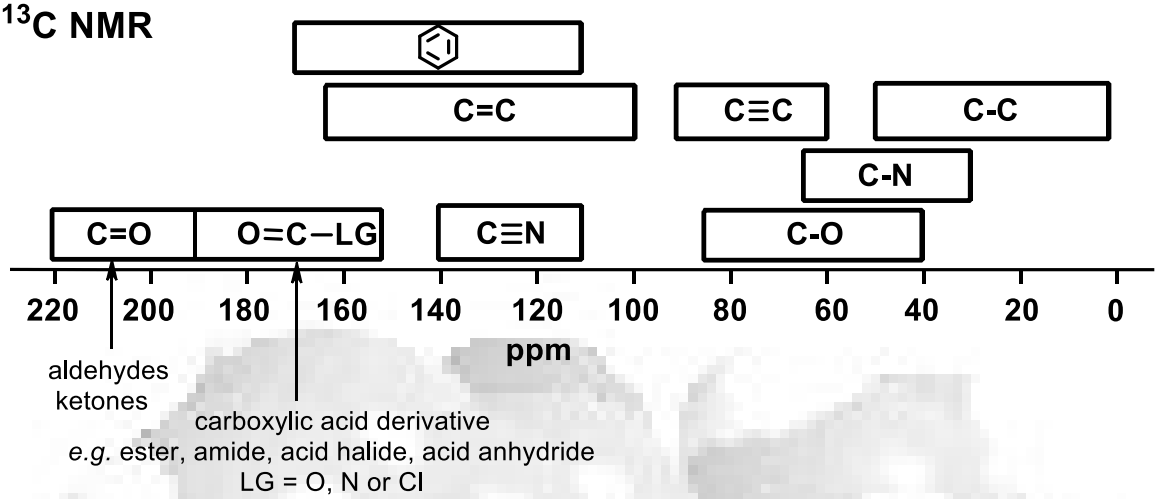


^{1}H NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm

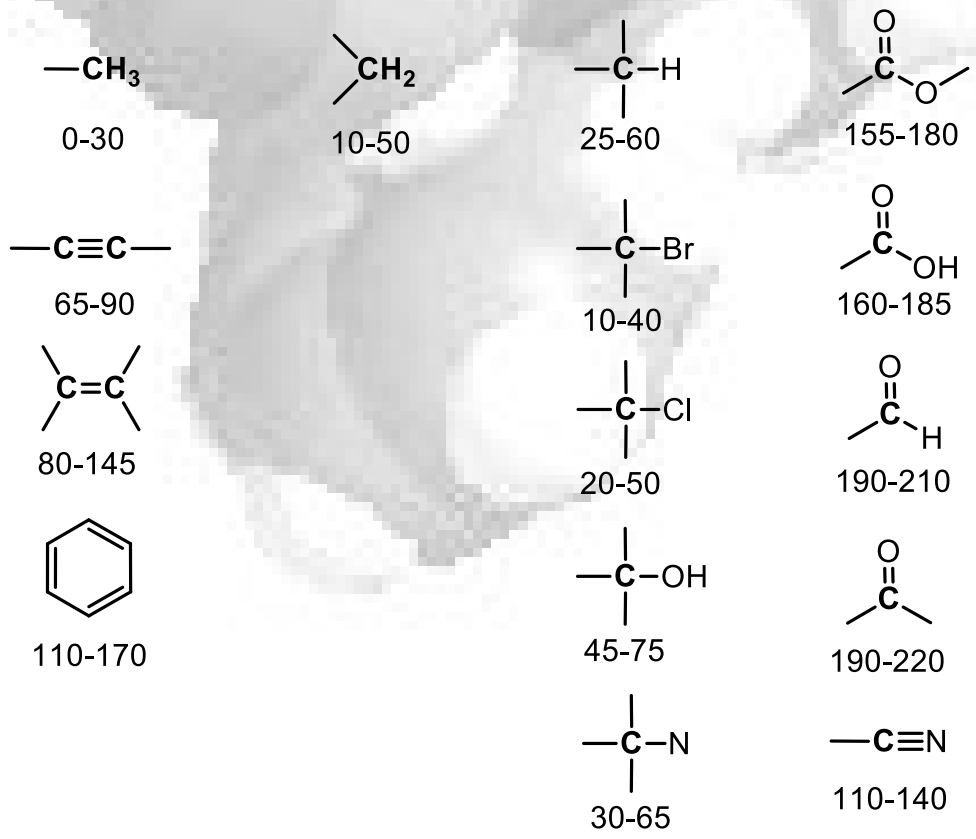
R =	methyl —CH$_3$	methylene -CH$_2$-	methyne —CH
R–C—	0.9	1.4	1.5
R–C=C	1.6	2.3	2.6
R–C(=O)—	2.1	2.4	2.5
R–N	2.2	2.5	2.9
R–Ar	2.3	2.7	3.0
R–Br	2.7	3.3	4.1
R–Cl	3.1	3.4	4.1
R–O—	3.3	3.4	3.7

other	
sp^{3}C-OH	1-5
sp^{3}C-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



^{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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