

UNIVERSITY OF CALGARY
FACULTY OF SCIENCE
FINAL EXAMINATION
CHEMISTRY 353

Version

1

April 21st, 2023

Time: 2 Hours

READ ALL OF THE INSTRUCTIONS CAREFULLY

PLEASE WRITE YOUR NAME & STUDENT I.D. NUMBER ON BOTH YOUR BLUE ANSWER BOOKLET AND COMPUTER ANSWER SHEET.

ENTER VERSION NUMBER 1 ON THE COMPUTER ANSWER SHEET

The examination consists of Parts 1 - 8, 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 - 8 are to be answered in the blue answer booklet. Parts 1 - 5 consist of a series of multiple choice questions numbered 1 - 34 which are to be answered on your optical score 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.**

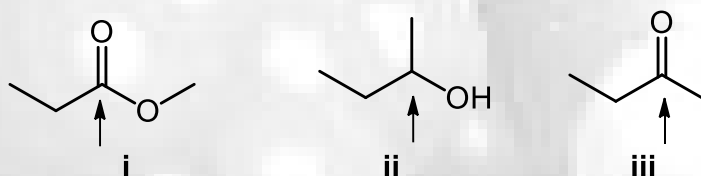
17.5% PART 1: RELATIVE PROPERTIES

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

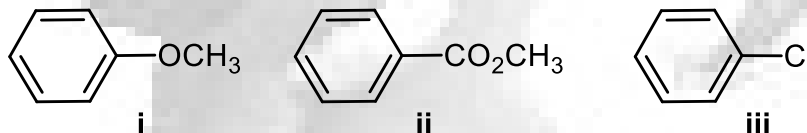
Arrange the items in questions 1-8 in **DECREASING ORDER** (*i.e.* greatest, most *etc.* first) with respect to the indicated property. Use the following code to indicate your answers in the box provided:

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

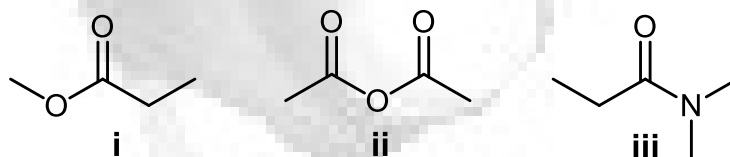
1. The relative oxidation state of the C atom indicated in each of the following :



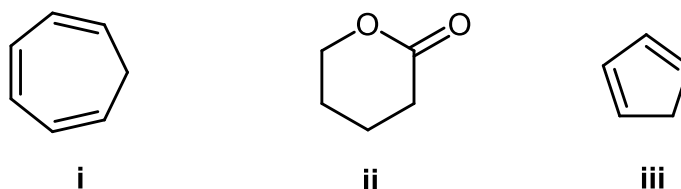
2. The relative rate of reaction of HNO₃ / H₂SO₄ with each of the following:



3. The relative reactivity of each of the following towards hydrolysis using H₃O⁺ :



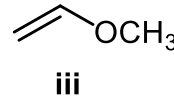
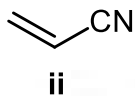
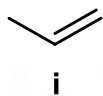
4. The relative acidity of the most acidic hydrogen in each of the following:



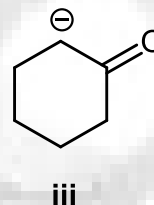
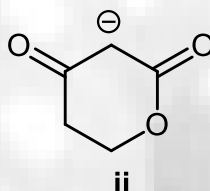
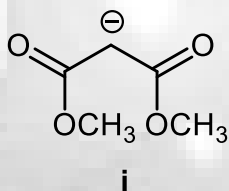
Use the following code to indicate your answers in the box provided:

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

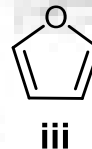
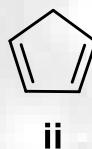
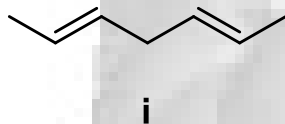
5. The relative rate of reaction of 1,3-butadiene with each of the following:



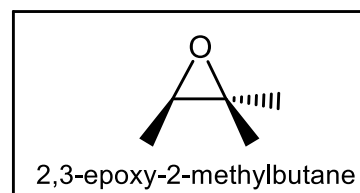
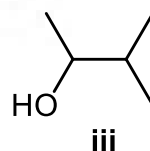
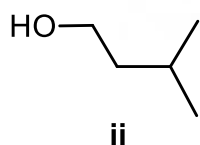
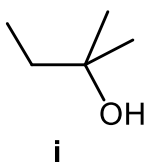
6. The relative basicity of the following anions:

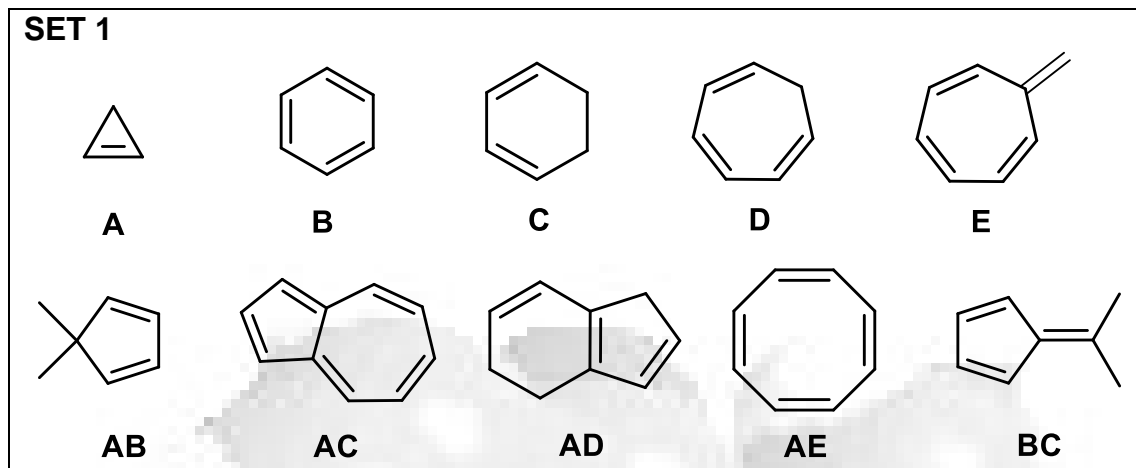


7. The resonance energies of the each the following:



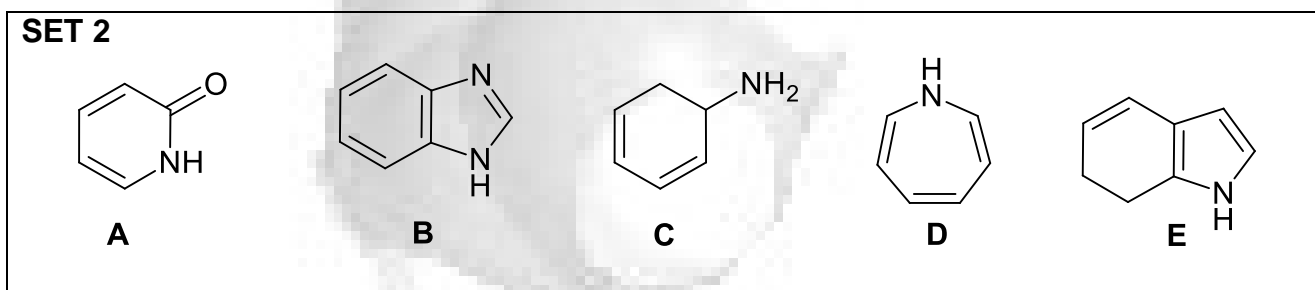
8. The relative yield of each the following when 2,3-epoxy-2-methylbutane is reacted with LiAlH_4 followed by an aqueous acid workup:



14% PART 2: AROMATICITY AND RESONANCE**ANSWER ANY SEVEN (7) OF THE EIGHT (8) QUESTIONS 9 - 16.**

Answer questions 9-12 by selecting a SINGLE compound from those shown above.

9. An aromatic compound where $n \neq 1$ when applying the Hückel rule
10. Non-aromatic as drawn, but has an aromatic resonance structure.
11. Non-aromatic as drawn, but becomes aromatic when protonated.
12. Non-aromatic as drawn, but becomes aromatic when deprotonated.



Answer questions 13-16 by selecting the compounds from SET 2 above.

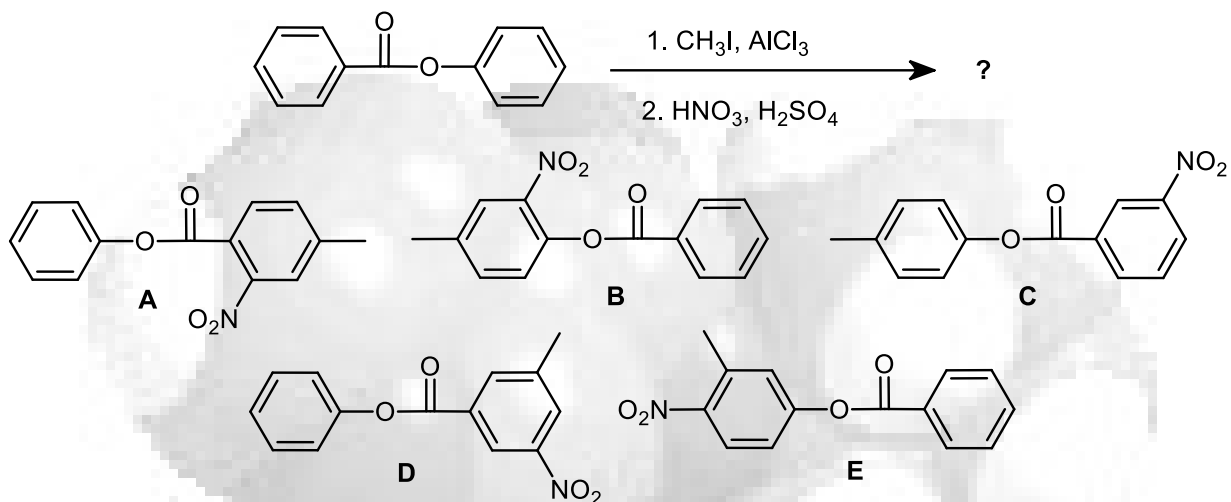
13. A compound that has an aromatic tautomer.
14. Select all compounds that are aromatic when deprotonated.
15. Anti-aromatic (assuming that it is planar).
16. An aromatic compound where $n \neq 1$ when applying the Hückel rule



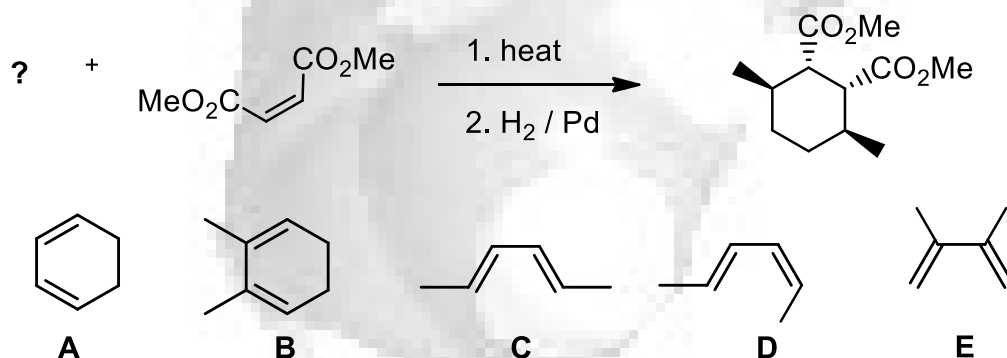
17.5% PART 3: STARTING MATERIALS AND PRODUCTS OF SYNTHESIS**ANSWER ANY SEVEN (7) OF THE EIGHT (8) QUESTIONS 17 - 24.**

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.

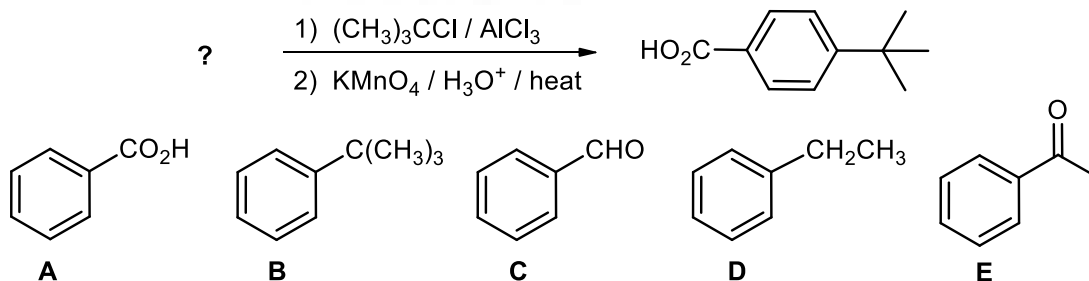
17.



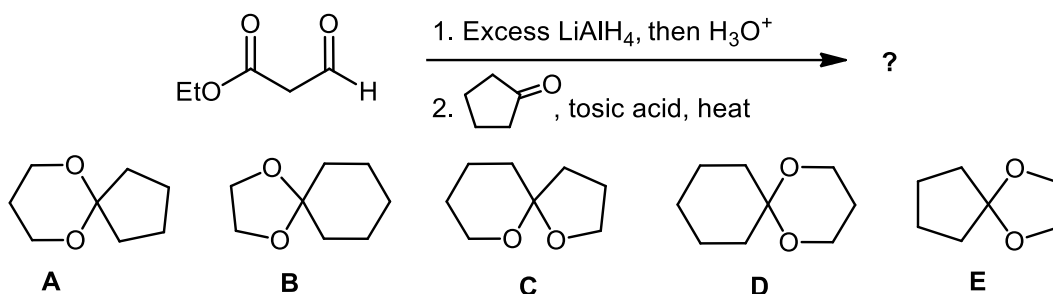
18.



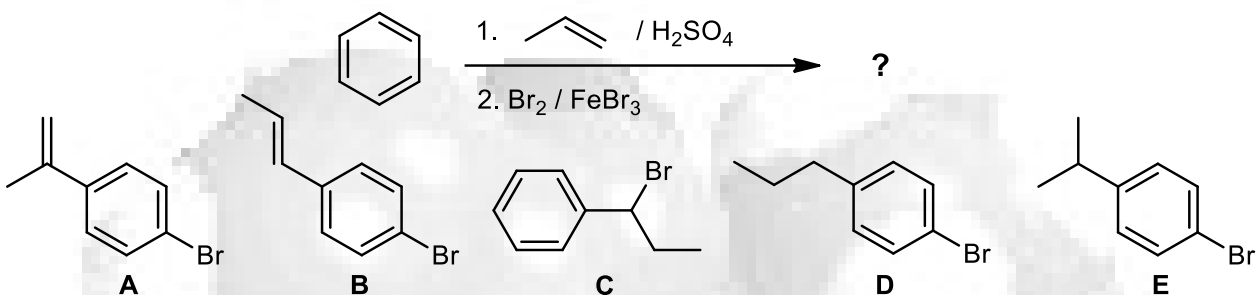
19.



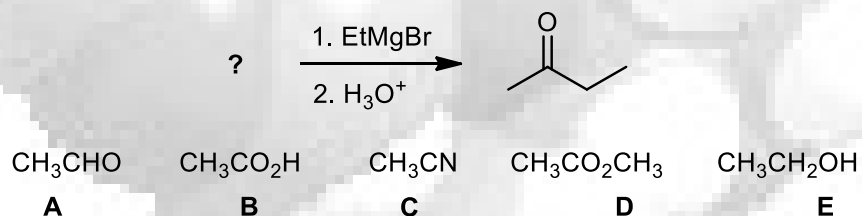
20.



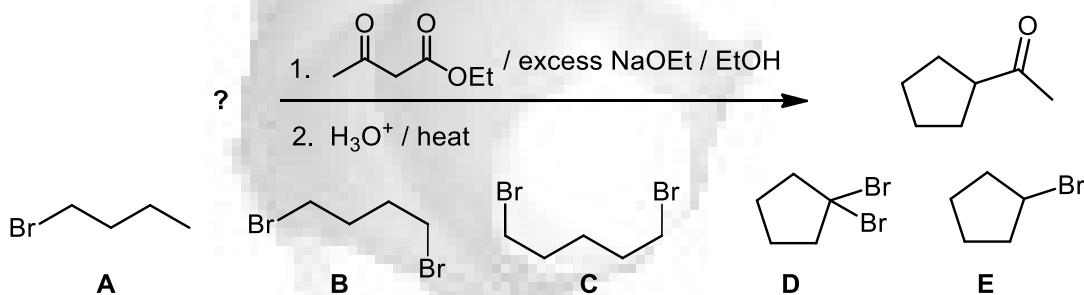
21.



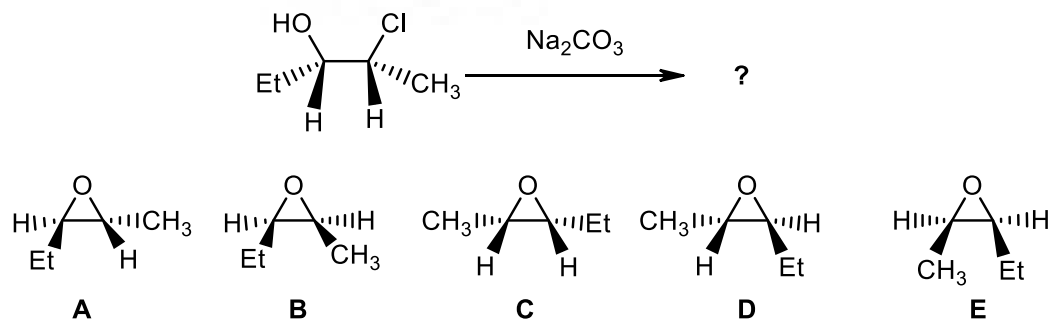
22.



23.



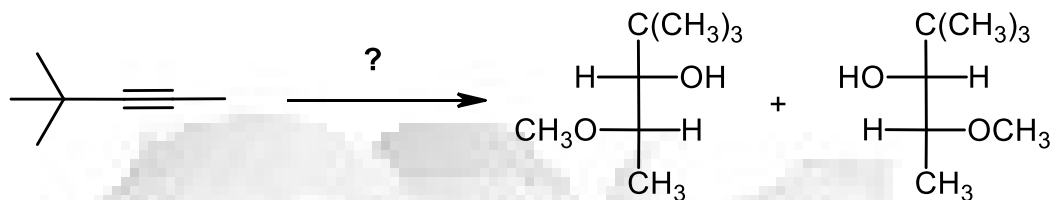
24.



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** 1. Na / NH₃ ii. CH₃CO₃H iii. CH₃OH, H⁺
B 1. Na / NH₃ ii. CH₃CO₃H iii. CH₃ONa, CH₃OH
C 1. H₂ / Lindlar's catalyst ii. CH₃CO₃H iii. CH₃OH, H⁺
D 1. H₂ / Lindlar's catalyst ii. CH₃CO₃H iii. CH₃ONa, CH₃OH
E CH₃OH, aq H₂SO₄, HgSO₄

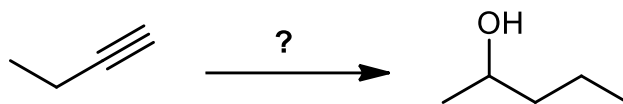
26.



- A.** aq. H₂SO₄, heat
B. i. Br₂, FeBr₃ ii. H₃O⁺, heat iii. aq NaOH (cold)
C. i. Sn, HCl ii. Na₂CO₃ iii. NaNO₂, HCl iv. H₃O⁺, heat
D. i. H⁺, NH₃ ii. NaNO₂, HCl iii. H₃O⁺, heat
E. i. CuBr ii. aq. NaOH

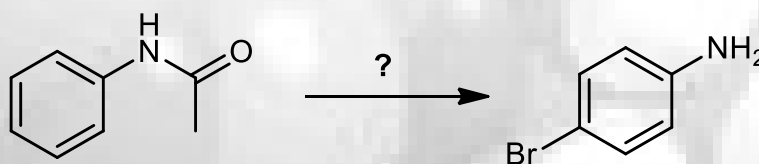


27.



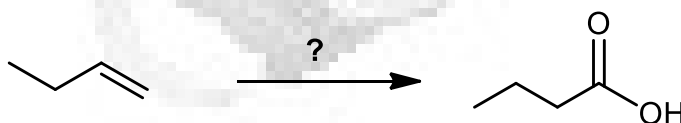
- A. i. H_2 / Lindlar's catalyst, ii. $\text{CH}_3\text{CO}_3\text{H}$, iii. CH_3MgBr , iv. H_3O^+
 B. i. O_3 , ii. H_2O , iii. $\text{CH}_3\text{CH}_2\text{MgBr}$, iv. H_3O^+
 C. i. BH_3 , ii. aq. NaOH , H_2O_2 , iii. LDA, iv. CH_3I
 D. i. HgSO_4 , aq. H_2SO_4 , ii. CH_3MgBr , iii. H_3O^+
 E. i. BH_3 , ii. aq. NaOH , H_2O_2 , iii. CH_3MgBr , iv. H_3O^+

28.



- A. i. H_3O^+ / heat, ii. HBr
 B. i. HBr / FeBr_3 , ii. H_3O^+ / heat
 C. i. Br_2 / FeBr_3 , ii. H_3O^+ / heat iii. NaNO_2/HCl , then CuCN iv. LiAlH_4 then H_3O^+
 D. i. Br_2 / FeBr_3 , ii. H_3O^+ / heat
 E. i. HCN / H_2SO_4 , ii. HBr / FeBr_3

29.



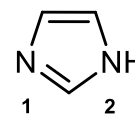
- A. i. HBr , peroxides ii. Mg iii. CO_2 iv. H_3O^+
 B. i. aq. H_2SO_4 , ii. aq. H_2CrO_4
 C. i. B_2H_6 , ii. H_2O_2 , aq. NaOH iii. PDC / CH_2Cl_2
 D. i. B_2H_6 , ii. H_2O_2 , aq. NaOH iii. aq. H_2CrO_4
 E. i. O_3 , ii. H_2O_2



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. Imidazole has a $pK_a = 7$ with respect to its conjugate acid.

Which N is protonated in this conjugate acid and why?

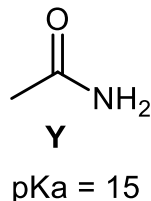
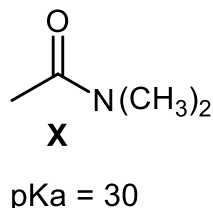
imidazole



- A. Either because imidazole is an aromatic heterocycle where $n=1$ in the Huckel rule.
- B. N1 is protonated because it is sp^2 hybridised.
- C. N2 is protonated because it is sp^3 hybridised.
- D. N1 is protonated because the lone pair is part of the aromatic pi system.
- E. N1 is protonated because the lone pair is not part of the aromatic pi system.
- AB.** N2 is protonated because the lone pair is not part of the aromatic pi system.
31. Tertiary alcohols are not easily oxidised by aqueous potassium dichromate but secondary alcohols are. This is because:
- A. Ketones are less electrophilic than aldehydes
- B. The tertiary alcohol lacks the appropriate H atom for the oxidation step.
- C. The tertiary alcohol is too hindered to react to form the chromate ester.
- D. The secondary carbocation is less stable and therefore more reactive.
- E. Tertiary alcohols are insoluble in the reaction medium.
- AB.** Oxidation occurs via an SN_2 mechanism that is too unfavourable for tertiary alcohols.
32. When an internal alkyne reacts with excess HCl, the product is a geminal dichloride because:
- A. This is a radical hydrohalogenation and proceeds via the most stable radical.
- B. A carbocation rearrangement occurs.
- C. Halogens can stabilise carbocations by resonance.
- D. An intermediate cyclic halonium ion forms that is then opened when chloride attacks.
- E. The reaction shows anti-Markovnikov selectivity.
- AB.** Steric effects control the attack of the chloride ion to control the regiochemistry.



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



- A. The conjugate base of **X** is better stabilized by resonance.
B. The conjugate base of **X** is better stabilized by an electronegative atom
C. The conjugate base of **Y** is better stabilized by resonance
D. The conjugate base of **Y** is better stabilized by an electronegative atom
E. The N atom in **X** is sp² hybridised.
AB. The N atom in **Y** is sp³ hybridised.
34. When 2-methylbuta-1,3-diene was reacted with HCl, the major product was as shown below. This indicates that:



- A. the addition reaction was performed under anti-Markovnikov conditions.
B. the addition reaction was performed under Markovnikov conditions.
C. the reaction was at lower temperature and under thermodynamic control.
D. the reaction was at lower temperature and under kinetic control.
E. the reaction was at higher temperature and under thermodynamic control.
AB. the reaction was at higher temperature and under kinetic control.

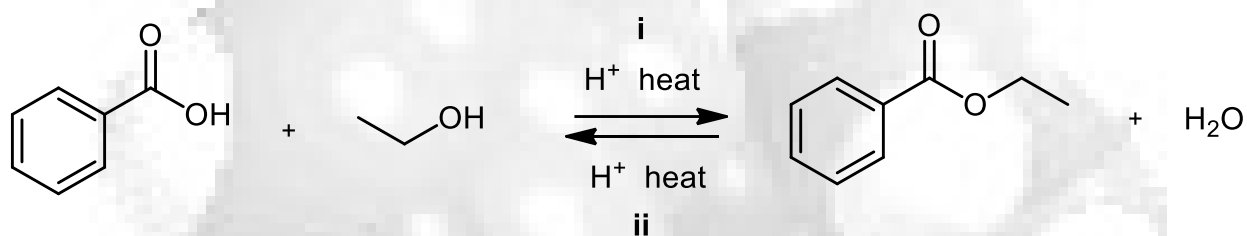


10% **PART 6: MECHANISM**

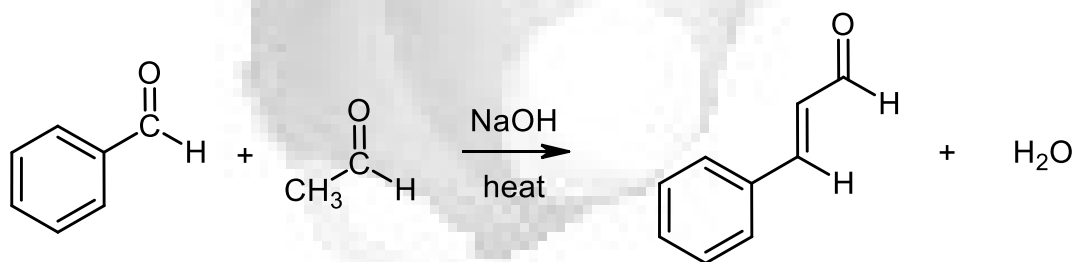
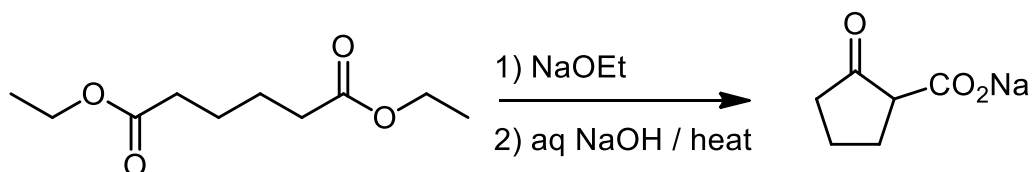
ANSWER TWO (2) QUESTIONS, ONE FROM PART A AND ONE FROM PART B. WRITE YOUR ANSWERS IN THE BLUE ANSWER BOOKLET PROVIDED. NO REAGENTS OTHER THAN THOSE ALREADY SHOWN IN EACH QUESTION ARE REQUIRED.

(5) PART A:

Draw the curly arrow mechanism for EITHER the reaction (i) from left to right OR (ii) from right to left of the following transformation:

**AND****(5) PART B : Draw the curly arrow mechanism for ONE of the following transformations:**

i. Provide a mechanism for EITHER of the reactions shown below:

**OR**

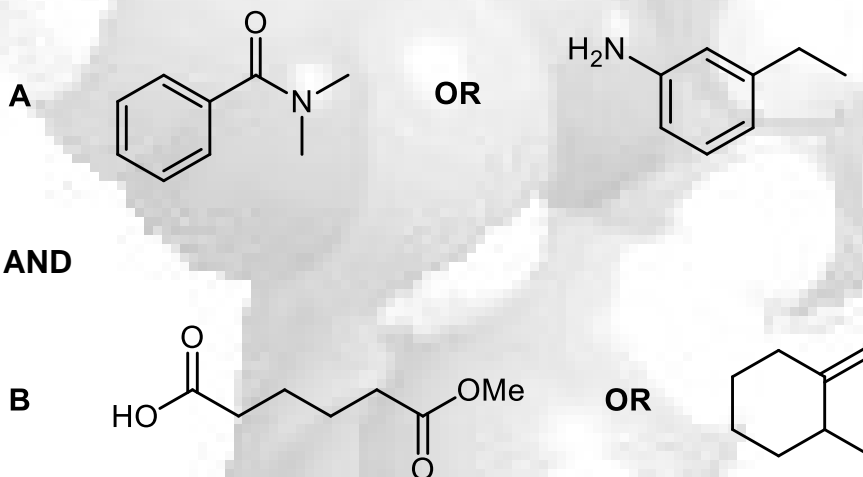
10% PART 7: TOTAL SYNTHESIS

WRITE YOUR ANSWERS IN THE BLUE ANSWER BOOKLET PROVIDED.

Design an efficient synthesis from the starting materials in the list below for TWO (2) of the following target molecules. Choose ONE target from each of the sections A and B.

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:

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



13% PART 8: STRUCTURE DETERMINATION**WRITE YOUR ANSWERS IN THE BLUE ANSWER BOOKLET PROVIDED**

Compound **A** (C_5H_8), primarily found in gasoline, was reacted with Br_2 in the dark under nitrogen to produce compound **B**. Heating **B** with an excess of sodium ethoxide in ethanol led to compound **C**, a hydrocarbon, which when heated in the presence of ethene gave bicyclo[2.2.1]hept-2-ene.

When either **A** or **C** were catalytically hydrogenated, the same compound, **D**, was formed which has the following spectral data: H NMR (ppm) 1.51 (s) and ^{13}C NMR (ppm) 26.

When compound **A** was reacted with aqueous sulfuric acid, it generated **E**, which had a characteristic IR stretch at 3345 cm^{-1} .

When **E** was reacted with *either* aqueous chromic acid, or with pyridinium chlorochromate in dichloromethane it provided **F**, (C_5H_8O), which has the following spectral data: H NMR (ppm) 2.16 (t, 1H), 1.97 (t, 1H).

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

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

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



PERIODIC TABLE

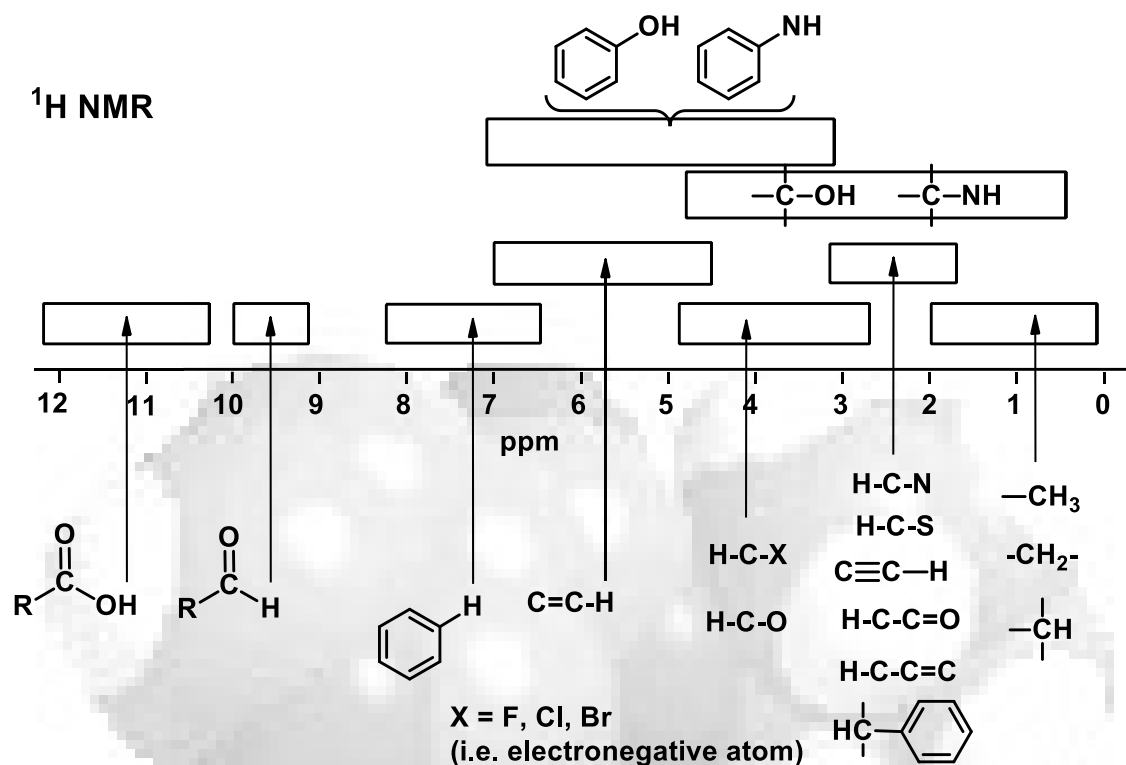
1 1A																	18 8A
1 H 1.008	2 2A											13 3A	14 4A	15 5A	16 6A	17 7A	2 He 4.003
3 Li 6.941	4 Be 9.012										5 B 10.81	6 C 12.01	7 N 14.01	8 O 16.00	9 F 19.00	10 Ne 20.18	
11 Na 22.99	12 Mg 24.31	3	4	5	6	7	8	9	10	11	12	13 Al 26.98	14 Si 28.09	15 P 30.97	16 S 32.07	17 Cl 35.45	18 Ar 39.95
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
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)

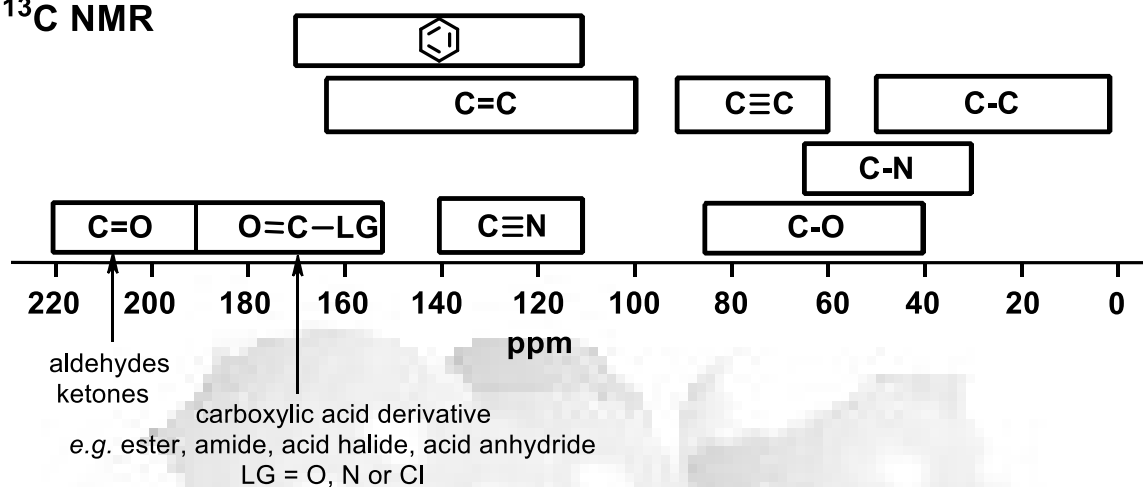
Actinides **



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
	2.1	2.4	2.5	C≡CH 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	9-10
				9-12



^{13}C NMR ^{13}C 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 10-40	—C(=O)—OH 160-185
 110-170		—C—Cl 20-50	—C(=O)—H 190-210
		—C—OH 45-75	—C(=O)— 190-220
		—C—N 30-65	$\text{—C}\equiv\text{N}$ 110-140



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	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.

