UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

FINAL EXAMINATION

CHEMISTRY 353

Version

1

April 20th, 2022 **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 - 33** 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.

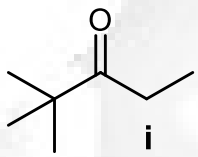
17.5% PART 1: RELATIVE PROPERTIES

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

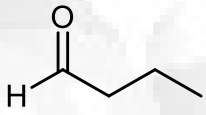
Arrange the items in questions 1-8 in DECREASING ORDER (*i.e.* greatest, most *etc*. *first*) with respect to the indicated property. Use the following code to indicate your answers in the box provided:

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 reactivity of each of following towards methyl magnesium iodide :



i



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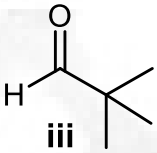
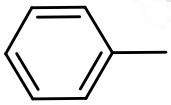
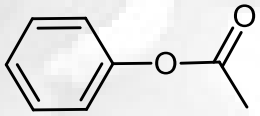


iii

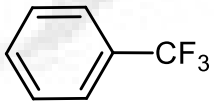
2. The relative rate of reaction of $(CH_3)_3CCl$ / $AlCl_3$ with each of the following:



i

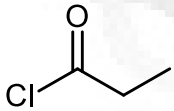


ii

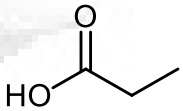


iii

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



i



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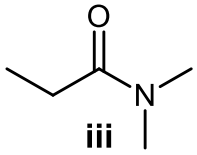
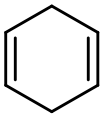
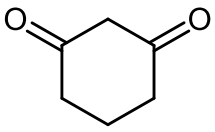


iii

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



i



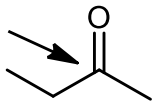
ii

iii

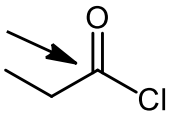
Use the following code to indicate your answers in the box provided:

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 oxidation state of the C atom indicated in each of the following:



i



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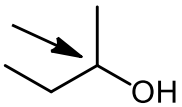
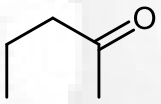
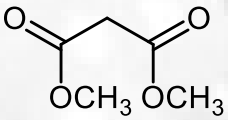


iii

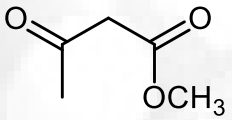
6. The relative acidity of the most acidic hydrogen in each of the following:



i

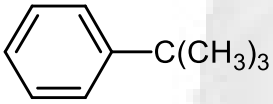


ii

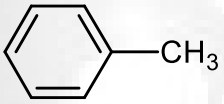


iii

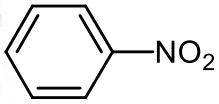
7. The % yield of the *<u>para</u>* product from the reaction of Br_2 / $FeBr_3$ with each of the following:



i

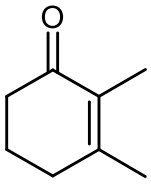


ii

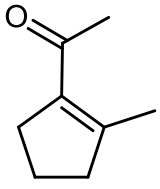


iii

8. The relative yield of the following products from the reaction of 2,7-octadione with hot KOH:



i



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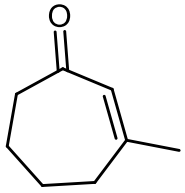
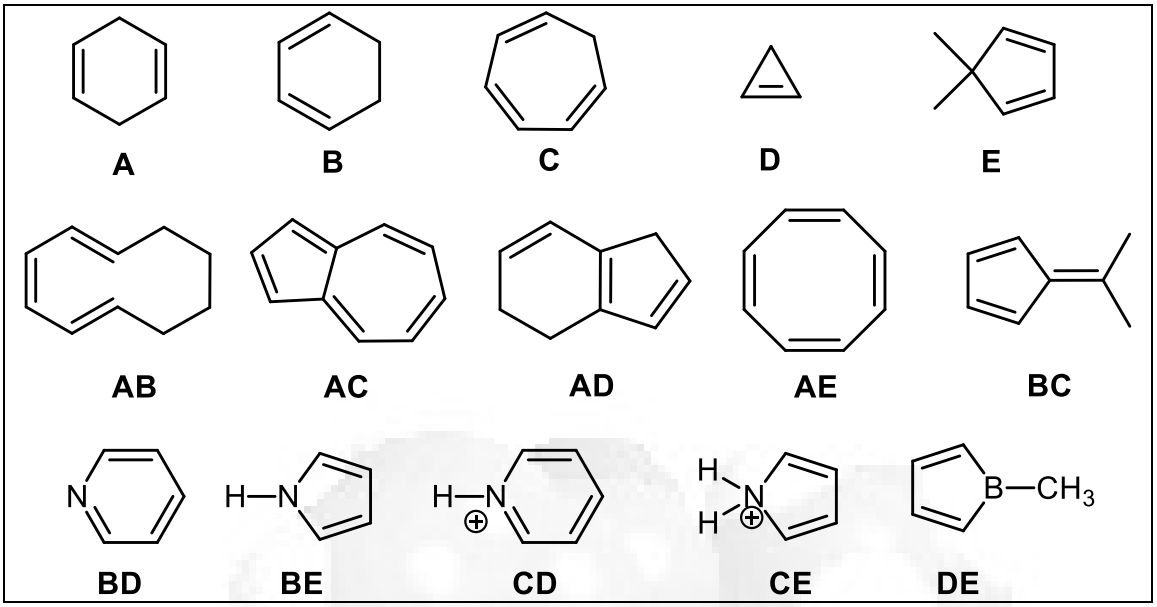


iii

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 hydrocarbon polyene with no resonance energy stabilization.

10. A polyene with the most resonance energy stabilization.

11. An aromatic compound where $n \neq 1$ when applying the Hückel rule.

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

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

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

15. Select the compound with the **most** basic heteroatom.

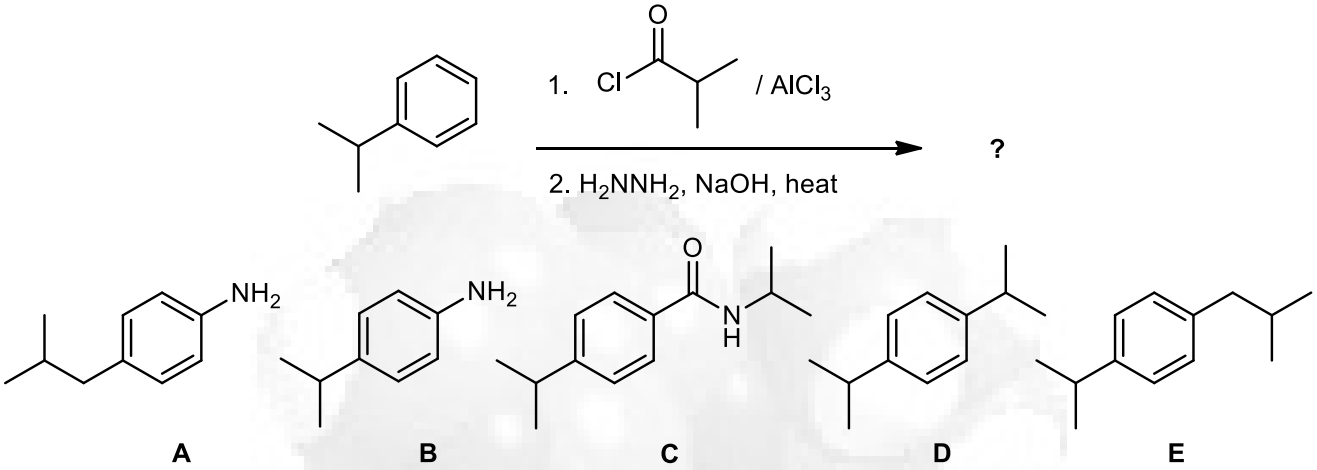
16. An antiaromatic heterocyclic compound.

17.5% PART 3: STARTING MATERIALS AND PRODUCTS OF SYNTHESIS

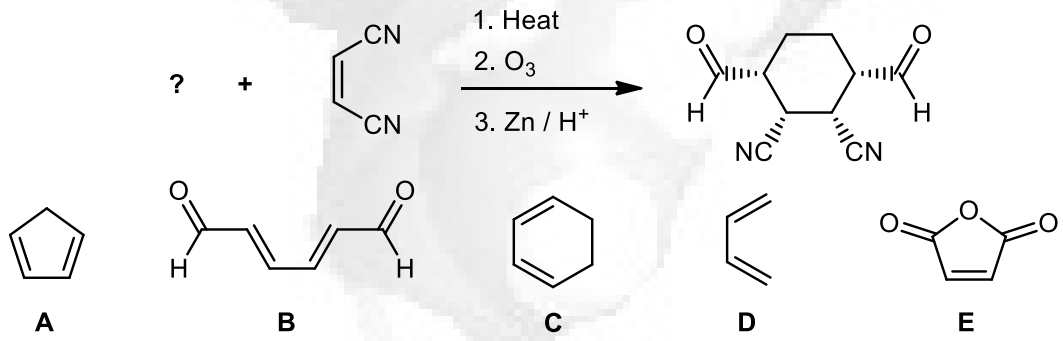
ANSWER ANY SEVEN (7) OF THE EIGHT (8) QUESTIONS 17 - 24.

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.

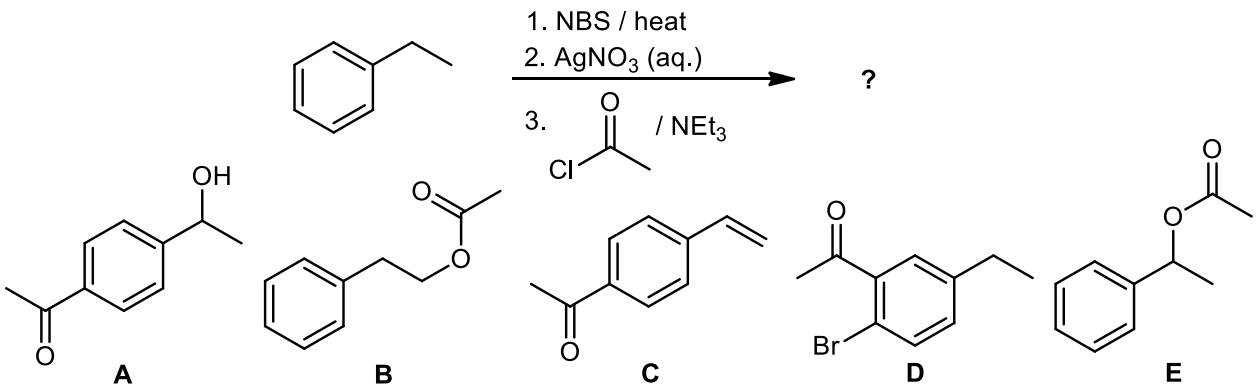
17.



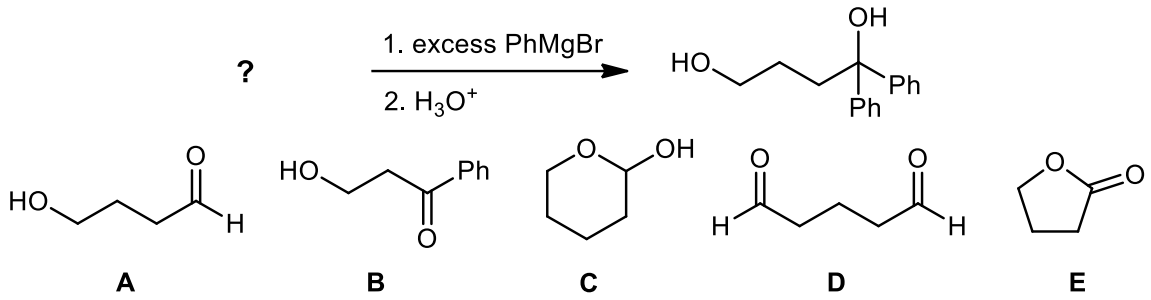
18.



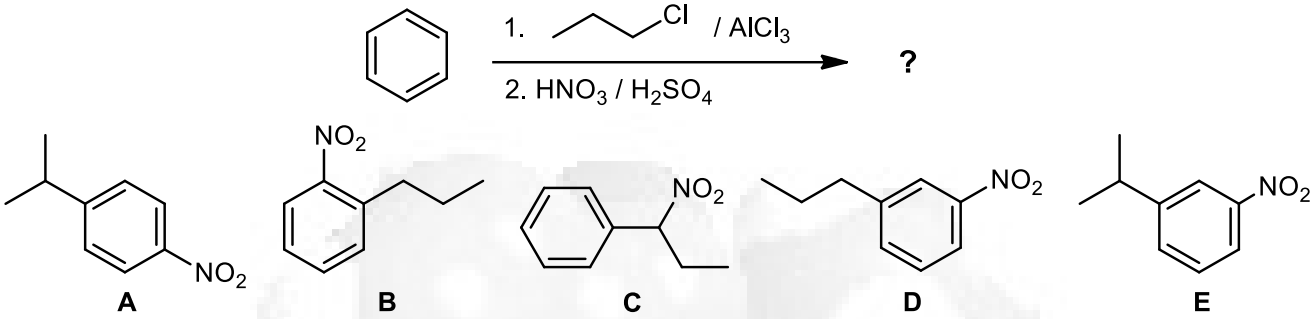
19.



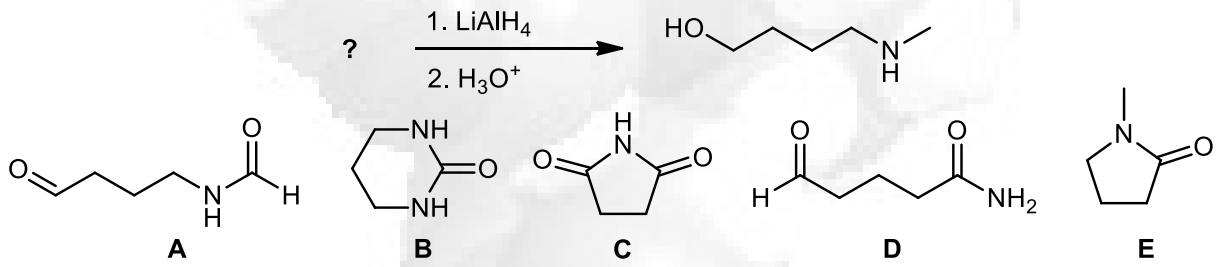
20.



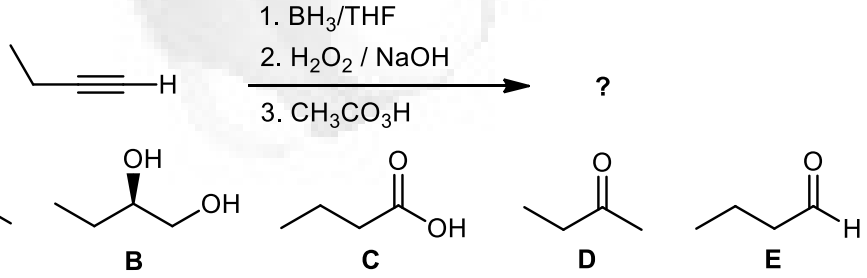
21.



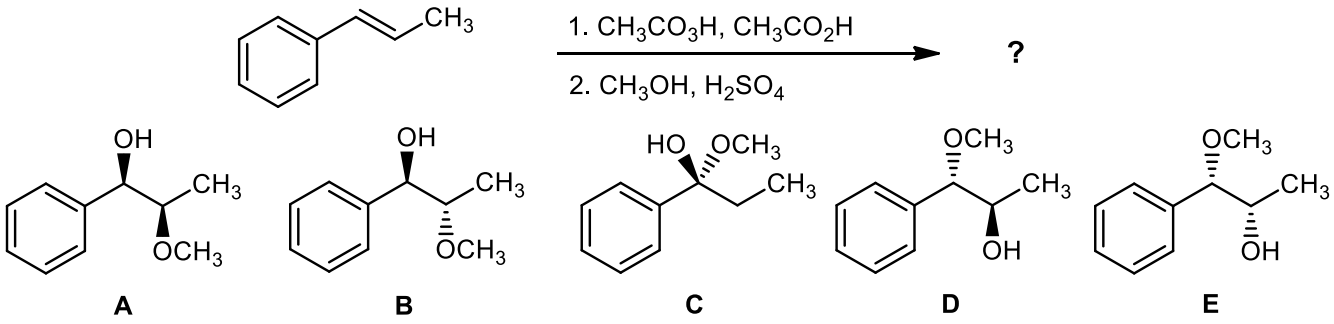
22.



23.



24

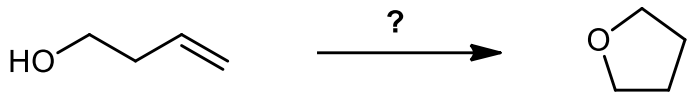


8% PART 4: REAGENTS FOR SYNTHESIS

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. HCl, ii. LDA

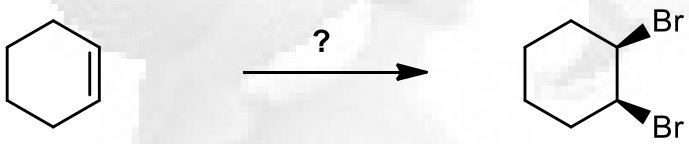
B. i. aq. H_2SO_4, ii. PBr_3, iii. NaH

C. i. PBr_3, Et_3N ii. 9-BBN, iii. H_2O_2, aq. NaOH, iv. NaH, cold

D. i. aq. Br_2, ii. NaH, iii. PCC / CH_2Cl_2

E. i. O_3, ii. H_2O_2, iii. H_2SO_4, heat

26.



A. Br_2

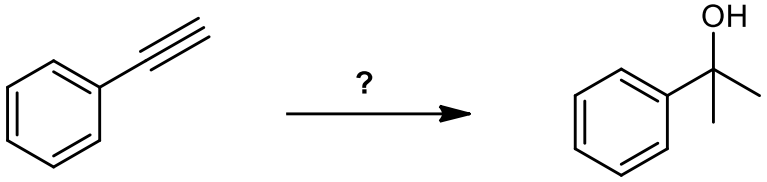
B. i. HOBr, ii. PBr_3, Et_3N

C. i. CH_3CO_3H, ii. H_3O^+, iii. PBr_3, Et_3N (excess)

D. i. HOBr, ii. Br_2

E. i. $KMnO_4$, NaOH, cold, ii. NBS

27.



A. i. CH_3CO_3H, ii. CH_3OH, H_2SO_4

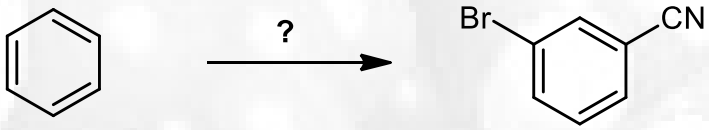
B. i. O_3, ii. $(CH_3)_2S$, iii. CH_3MgBr, iv. H_3O^+

C. i. LDA, ii. CH_3I, iii. H_3O^+

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

E. i. O_3, ii. H_2O_2, iii. CH_3MgBr, iv. H_3O^+

28.



A. i. HNO_3/H_2SO_4, ii. Sn/HCl, iii. Br_2, iv. $NaNO_2$/HCl, then CuCN

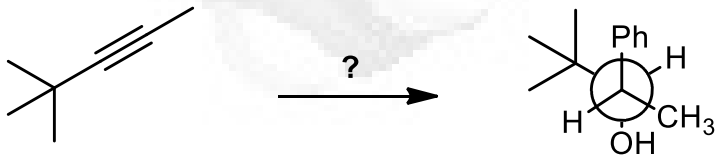
B. i. NBS / heat, ii. HNO_3/H_2SO_4, iii. Sn/HCl, iv. $NaNO_2$/HCl then CuCN

C. i. HNO_3/H_2SO_4, ii. Sn/HCl, iii. $NaNO_2$/HCl, then CuCN, iv. Br_2 / $FeBr_3$

D. i. HCN / H_2SO_4, ii. NBS / $FeBr_3$

E. i. Br_2 / $FeBr_3$, ii. HCN / H_2SO_4

29.



A. i. H_2/Lindlar's catalyst, ii. $KMnO_4$, NaOH, cold, iii. PhBr

B. i. Na/NH_3, ii. CH_3CO_3H, CH_3CO_2H, iii. PhMgBr, iv. H_3O^+

C. i. Na/NH_3, ii. aq. H_2SO_4, iii. PhMgBr, iv. H_3O^+

D. i. 9-BBN, ii. H_2O_2, NaOH, iii. PhMgBr, iv. H_3O^+

E. i. H_2/Lindlar's catalyst, ii. CH_3CO_3H, CH_3CO_2H, iii. PhMgBr, iv. H_3O^+

10% PART 5: EXPLANATION OF PHENOMENA

ANSWER ALL FOUR (4) OF THE QUESTIONS 30-33.

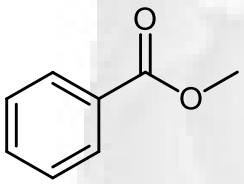
Choose the single explanation that best rationalises the phenomenon indicated.

30. When benzoic acid is reacted with a Grignard reagent (such as CH_3MgBr), **no** new C-C bond is formed. This is because:

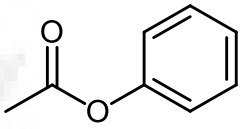
A. The carboxylic acid functional group does not have a good leaving group attached.
B. The phenyl ring of benzoic acid is sterically large, and blocks the carbonyl carbon.
C. Carboxylic acids are deactivating and meta-directing, so the reaction does not work.
D. Proton transfer is kinetically more favorable than C-C bond formation.
E. It is more favorable to form a new C-O bond, rather than a C-C bond.
AB. Benzoic acid will lose CO_2 under these reaction conditions.

31. Two aromatic esters are shown below. Which of the following statements about the reaction of X and Y with ethanoyl chloride / $AlCl_3$ / heat best describes what happens ?

X

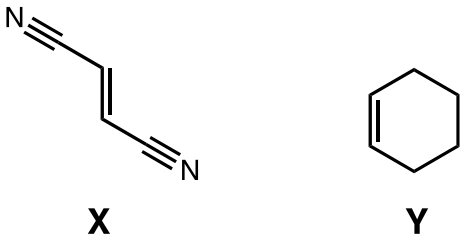


Y



A. Both **X** and **Y** react readily because esters are electron donating groups
B. Neither **X** or **Y** react because esters are electron withdrawing groups
C. Only **X** reacts because the substituent is an electron donating group
D. Only **Y** reacts because the substituent is an electron donating group
E. Both react but **Y** reacts more rapidly than **X** because **Y** is more electron donating
AB. Both react but **X** reacts more rapidly than **Y** because **X** is more electron donating

32. Which of the dienophiles shown, **X** or **Y**, is more reactive towards 1,3-cyclopentadiene?



X **Y**

A. **Y** because it is locked in the 's-cis' conformation.

B. **Y** because alkyl substituents are electron donating groups.

C. **Y** because **X** is a triene, and trienes do not participate in Diels-Alder.

D. **X** because the substituents are trans-substituted on the dienophile.

E. **X** because the dienophile is the electrophilic component of the reaction.

AB. X because the dienophile is the nucleophilic component of the reaction.

33. Which of the nitrogen-containing molecules below, **X** or **Y**, is the most ***basic*** ?

X **Y**

A. **Y** because the lone pair in **X** is necessary to fulfil the Huckel rule for **X**.

B. **Y** because the lone pair is in a pure 'p' orbital.

C. **Y** because the nitrogen atom is sp^3 hybridized.

D. **X** because the ring is aromatic.

E. **X** because the lone pair is necessary to fulfil the Huckel rule for **X**.

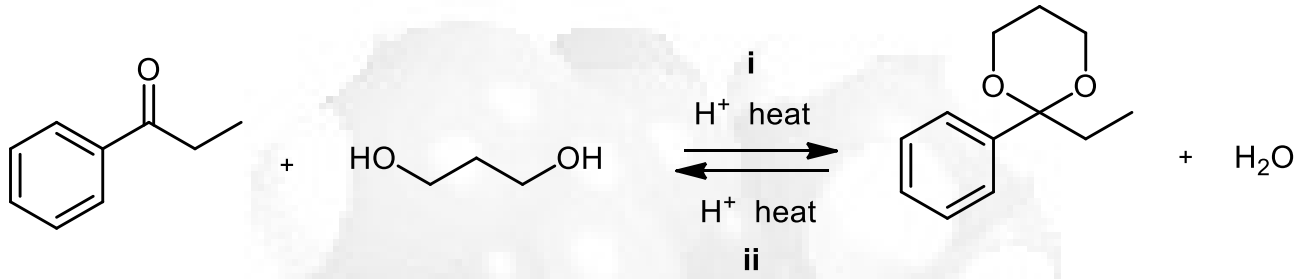
AB. X because the nitrogen atom is sp^2 hybridized.

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:

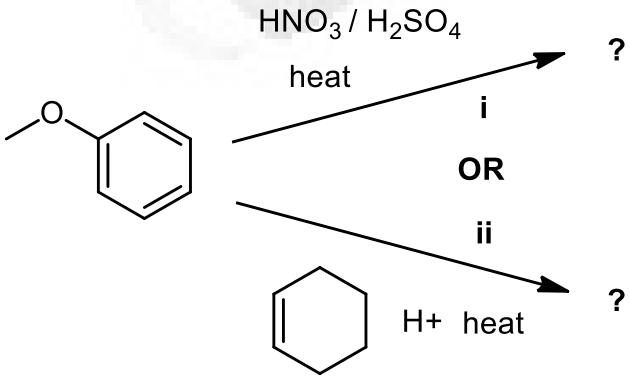
Draw the curly arrow mechanism for EITHER the reaction (i) from left to right OR (ii) from right to left of the following transformation:



AND

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

i. Predict the product and provide a mechanism for EITHER of the reactions shown below:



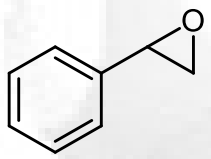
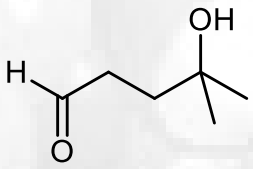
10% PART 7: TOTAL SYNTHESIS

WRITE YOUR ANSWERS IN THE BLUE ANSWER BOOKLET PROVIDED.

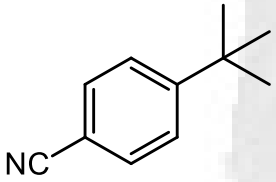
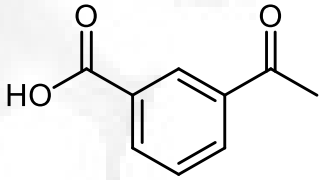
Design an efficient synthesis from the starting materials in the list below for TWO (2) of the following target molecules. Choose ONE target from each of the sections A and B.

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.

A  **OR** 

AND

B  **OR** 

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
- 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_4H_8) is a common petrochemical building block, with more than 10 million tons produced *annually*.

Reaction of **A** with 9-BBN, followed by treatment with basic hydrogen peroxide produced compound **B**. **B** has the following spectral data: IR absorption 3350 cm^{-1}; H NMR/ppm 3.39 (2H, doublet), 2.07 (1H, broad singlet, D2O exchangeable), 1.75 (1H, multiplet), 0.92 (6H, doublet). Compound **B** is reacted with $SOCl_2$ / Et_3N to yield compound **C**.

Compound **A** can also be made from the reaction of the Wittig reagent $Ph_3P{=}CH_2$ with a carbonyl compound. If that same carbonyl compound is reacted with the Grignard reagent CH_3MgBr, compound **D**, an isomer of **B**, is produced after an acidic aqueous work-up.

Methoxybenzene (also known as anisole) can be reacted with either compound **C** along with $AlCl_3$, or compound **D** along with H_2SO_4, to produce **E**, which has the molecular formula of $C_{11}H_{16}O$, and which displays *only* 7 signals in its 13C NMR spectrum.

(10%) Identify the compounds **A** to **E** (drawn structures are sufficient).

(3%) **Briefly** explain how / why both **C** and **D** lead to product **E** using the given conditions.

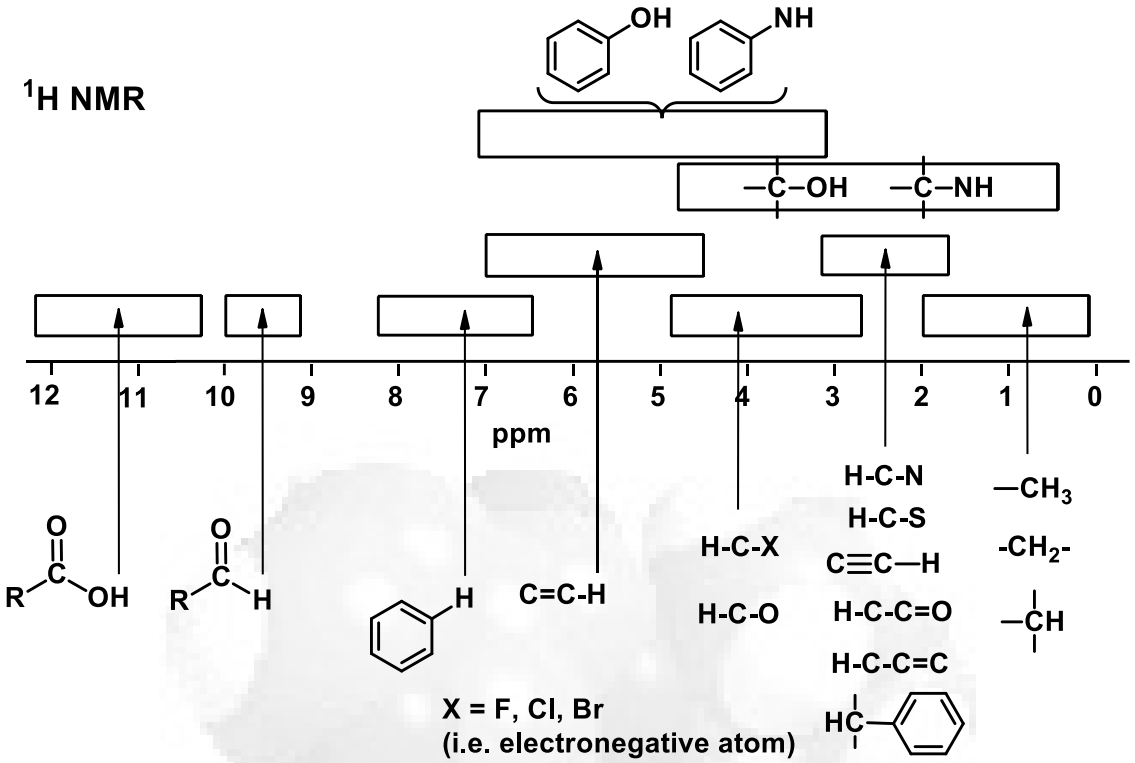
*****THE END*****

PERIODIC TABLE

1 1A												13 3A	14 4A	15 5A	16 6A	17 7A	18 8A
1 **H** 1.008	**2** 2A																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)

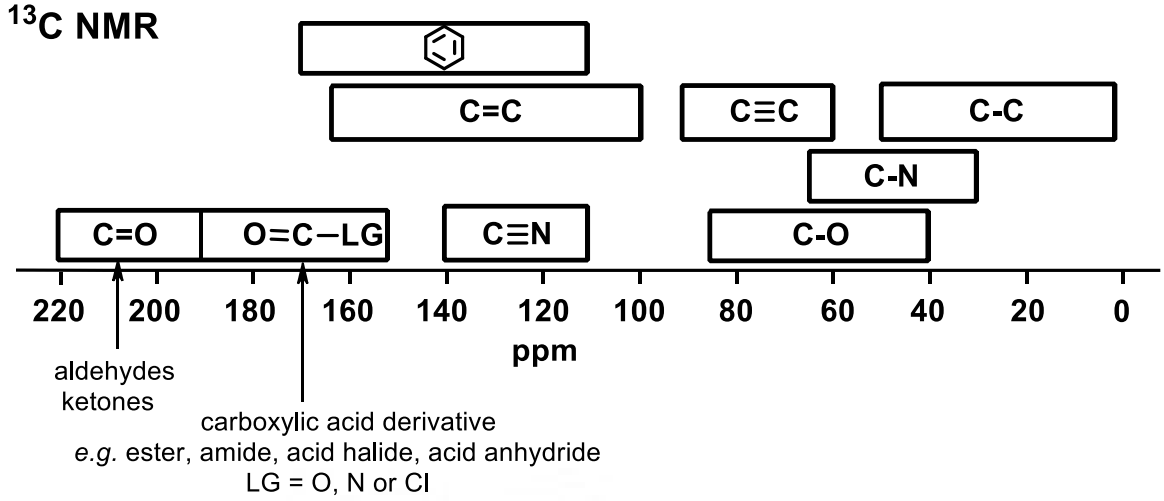
SPECTROSCOPIC TABLES



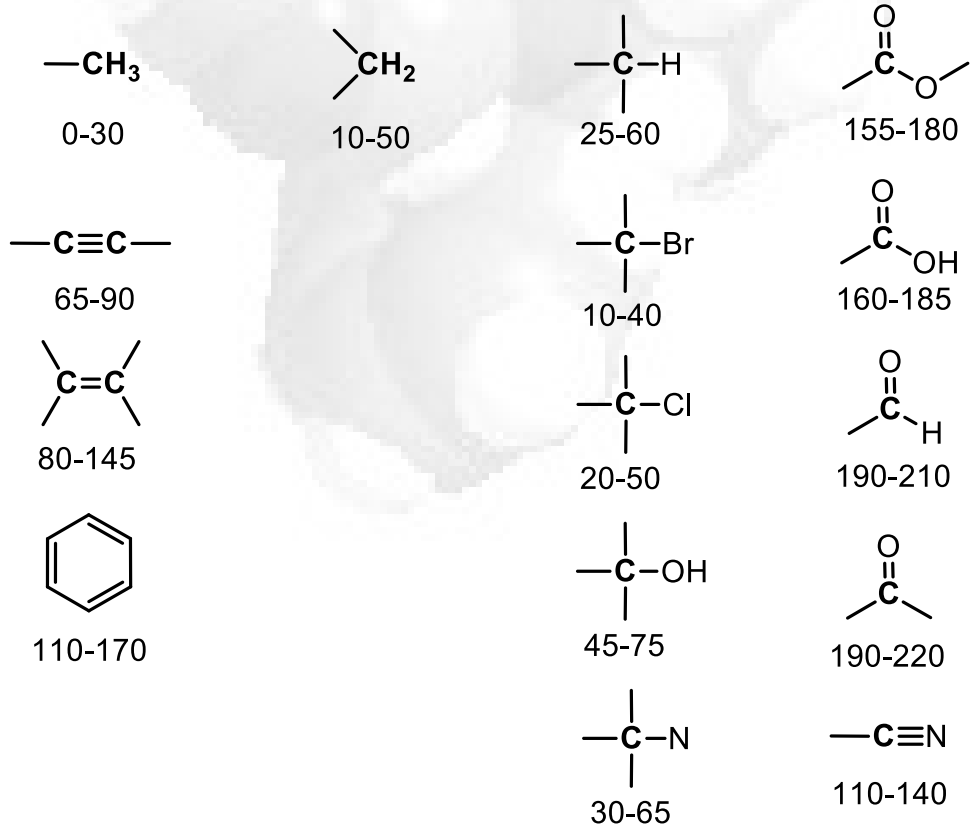
^{1}H NMR CHARACTERISTIC CHEMICAL SHIFTS / ppm

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.