THE UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

FINAL EXAMINATION

CHEMISTRY 353

April 26th, 2008 Time: 3 Hours

PLEASE WRITE YOUR **NAME, STUDENT I.D. NUMBER** ON THE **COMPUTER ANSWER SHEET** AND THE **BOOKLET** FOR THE WRITTEN ANSWER QUESTIONS.

READ THE INSTRUCTIONS CAREFULLY

The examination consists of Parts 1 - 10, each of which should be attempted. Note that some Parts provide you with a choice of questions, *e.g.* answer 5 out of 6. These will be graded in order the answers appear until the required number have been completed, ***regardless*** of whether they are right or wrong.

Parts 1 - 7 will be computer graded, and only Parts 8, 9 and 10 are to be answered in the booklet. Parts 1 - 7 consist of a series of multiple choice questions numbered 1 - 59 which are to be answered on your computer answer sheet. Indicate your answer by blackening out the appropriate space, A, B, C, D or E on the answer sheet. Use a pencil only and ***not ink***. In some cases it is required that you indicate ***multiple*** items for a complete and/or correct answer by blackening out more than one space. In some other cases more than five options are available and some of these also require more than one space to be blackened out. For an example, an option specified as AB requires that you blacken out ***both*** space A and space B. Part marks may be awarded in some of the questions. Incorrect answers must be erased ***cleanly***.

A periodic table with atomic numbers and atomic weights and tables of spectroscopic data are provided at the end of the examination paper.

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

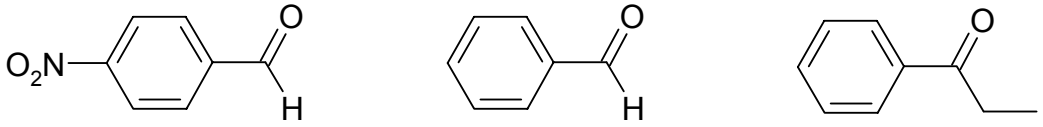
12% PART 1: RELATIVE PROPERTIES

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

Arrange the items in questions **1-10** in **DECREASING ORDER** (*i.e.* greatest, most etc. first) with respect to the indicated property. Use the following code to indicate your answers:

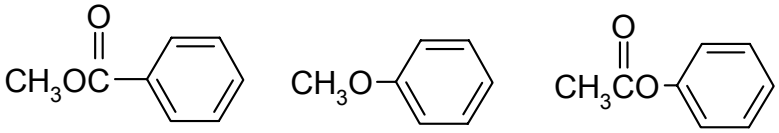
A	**i > ii > iii**	**D**	**ii > iii > i**
B	**i > iii > ii**	**E**	**iii > i > ii**
C	**ii > i > iii**	**AB**	**iii > ii > i**

1. The relative reactivity towards lithium aluminium hydride of each of the following:



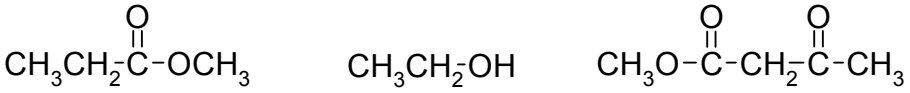
i **ii** **iii**

2. The relative reactivity towards HNO_3 / H_2SO_4 of each of the following:



i **ii** **iii**

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



i **ii** **iii**

4. The relative reactivity of each of the following towards 1-pentene:

HI HBr CH_3O^-

i **ii** **iii**

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

CH_2=CH-CH_3 CH_2=CH-O-CH_3 CH_2=CH-CCl_3

i **ii** **iii**

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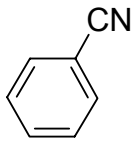
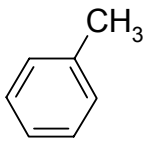
Use the following code to indicate your answers:

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

6. The % of the ***para*** product produced by the reaction of HNO_3/H_2SO_4 with each of the following:



i



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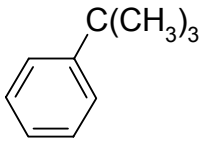
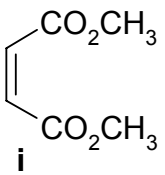
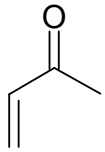


iii

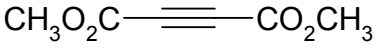
7. The number isomeric products from the reaction of each the following with 1-methyl-1,3-cyclopentadiene



i



ii



iii

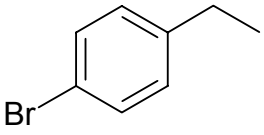
8. The number of enolisable hydrogens in each of the following:

i 3-pentanone **ii** propanal **iii** ethyl ethanoate

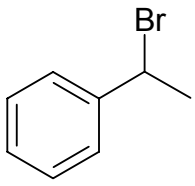
9. The relative reactivity of the following towards propanal in dry THF:

CH_3MgBr	CH_3Li	CH_3SH
i	**ii**	**iii**

10. The relative yields of the following products for the reaction of ethylbenzene with Br_2 / uv light:



i



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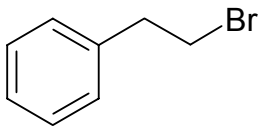

iii

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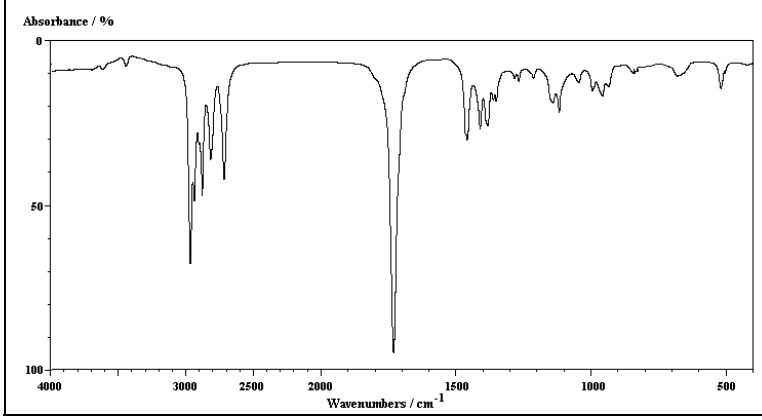
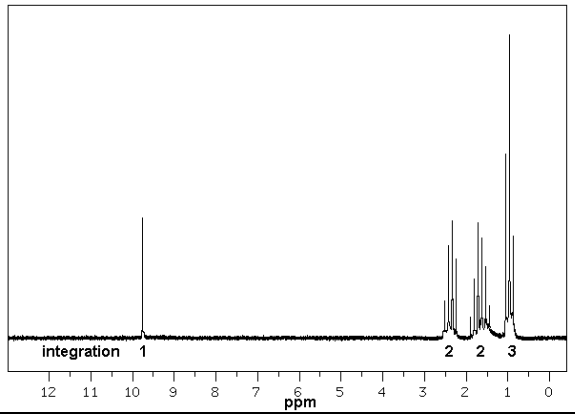
9% PART 2: LABORATORY

ANSWER ANY SIX (6) OF THE QUESTIONS 11-18.

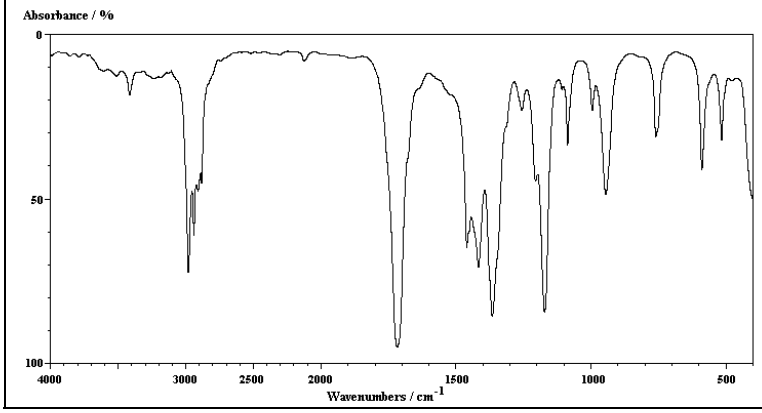
The IR and H-nmr of seven compounds **A-AC** are provided. For each of the questions **11-18**, select **ONE** of the compounds **A-AC** that best matches the chemical test result data given.

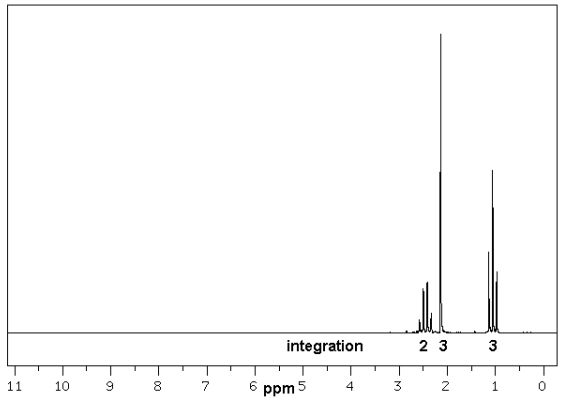
A



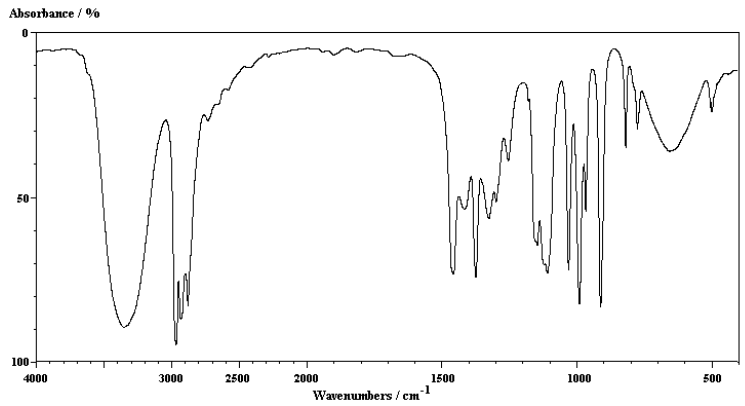


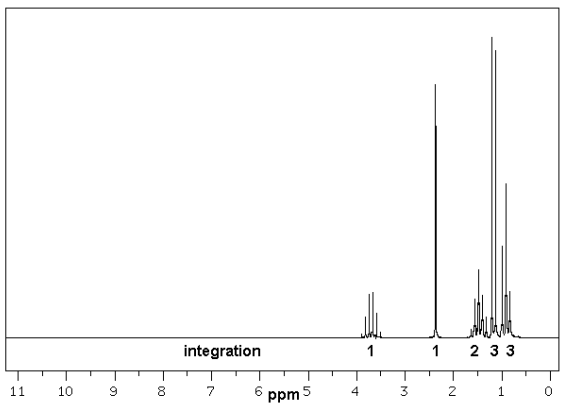
B





C





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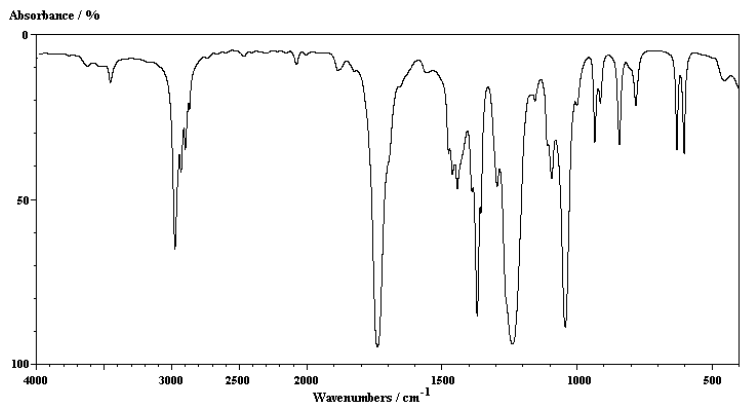
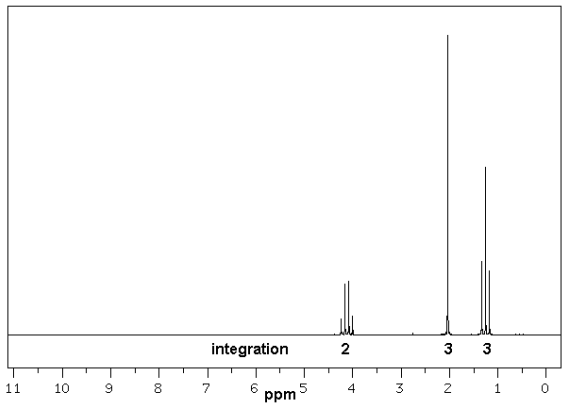
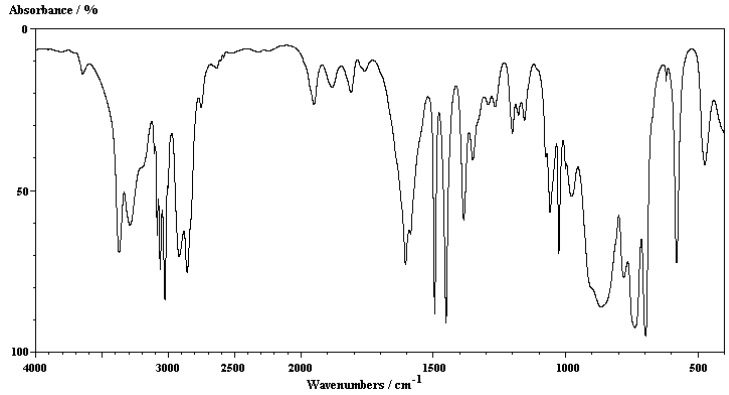
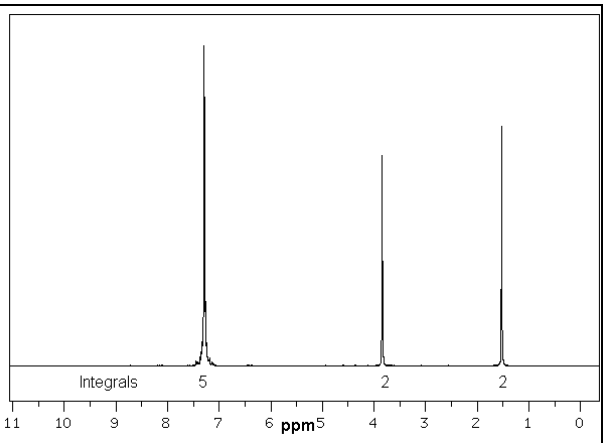
D



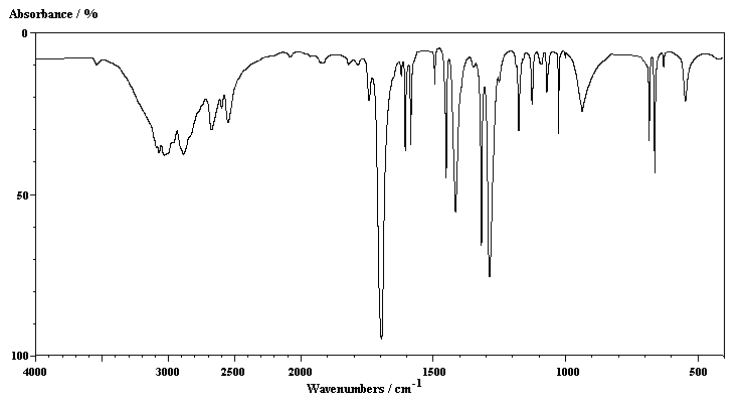


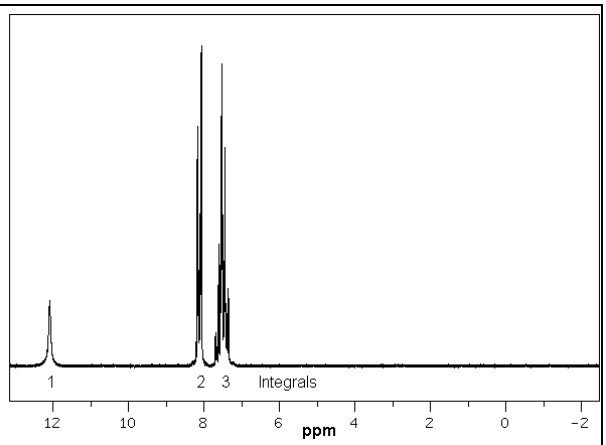
E





AB





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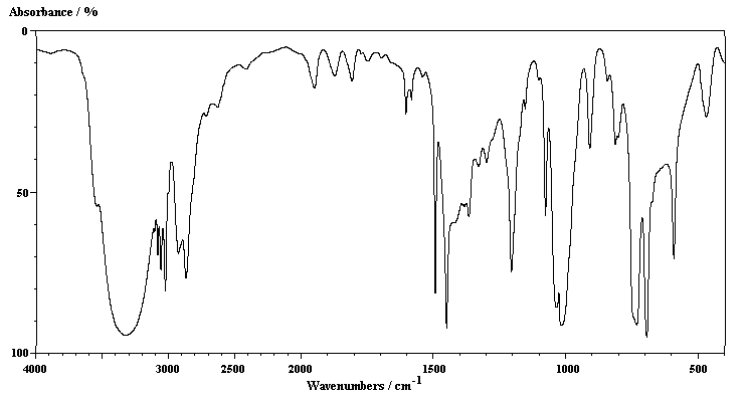
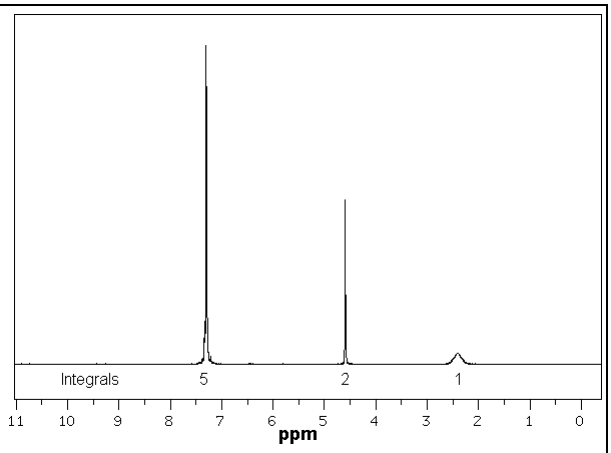
AC





For each of the questions **11-18**, select **ONE** of the compounds **A-AC** that best matches the chemical test result data given.

11. A compound that dissolves in 10% aq. HCl.

12. A compound that will give an orange precipitate when reacted with 2,4-dinitrophenylhydrazine *and* an orange solution with acidic sodium dichromate.

13. A compound that will give an orange precipitate when reacted with 2,4-dinitrophenylhydrazine *and* a green solution with acidic sodium dichromate.

14. A compound that reacts when heated with conc. H_2SO_4 to give a product that reacts with bromine in chloroform to give a colourless solution.

15. A compound that contains a carbonyl group, but gives no precipitate when reacted with 2,4-dinitrophenylhydrazine and does gives no colour when tested with indicator paper.

16. A compound that will react very rapidly in the Lucas test.

17. A compound that will react at a moderate rate in the Lucas test.

18. A compound that dissolves in 5% aq. NaOH and turns indicator paper red.

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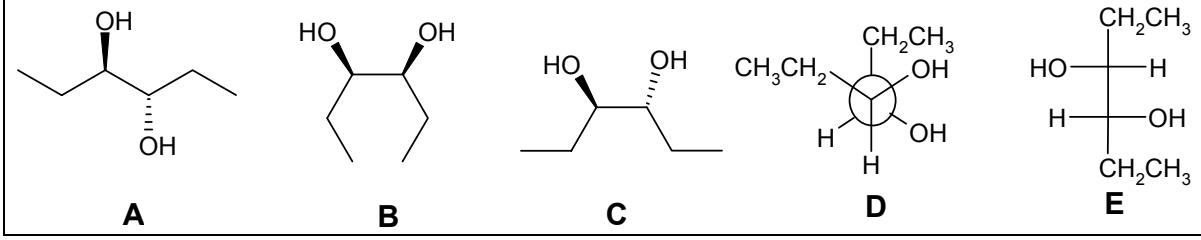
10 % PART 3: STRUCTURE AND PROPERTIES

ANSWER ANY TEN (10) OF THE QUESTIONS 19-30.

In some cases more than one answer may be correct and all compounds that apply must be selected for full credit.

SET 1:



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

Answer questions 19-22 by selecting the compounds from SET 1 above.

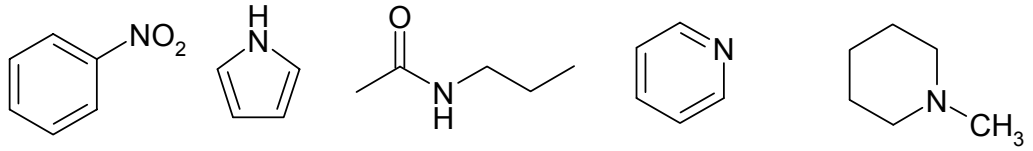
19. Select **ALL** the meso compounds

20. Select **ANY TWO** compounds that are a pair of diastereomers

21. Select **ALL** the structures that represent the product from the reaction of *cis*-3-hexene with CH_3CO_3H followed by treatment with aq. H_2SO_4.

22. Select **ALL** the structures that represent the product from the reaction of *trans*-hex-3-ene with $KMnO_4$ / aq. NaOH / 0 ^oC.

SET 2:



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

Answer questions 23-26 by selecting the compounds from SET 2 above.

23. Select **ALL** the compounds that are amines.

24. Select **ALL** the compounds in which the nitrogen atoms are sp^3 hybridized.

25. Select **ALL** the compounds that are aromatic.

26. Select the compound that has the most basic nitrogen.

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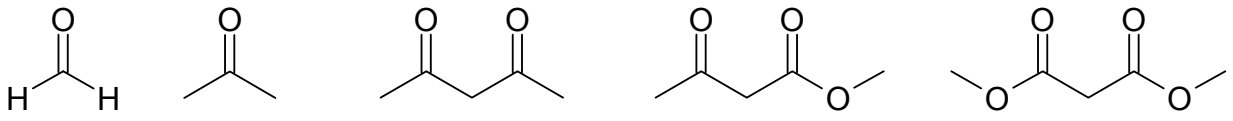
SET 3:



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

Answer questions 27-30 by selecting the compounds from SET 3 above.

27. Select the compound that has the most acidic hydrogen.

28. Select the compound that has the most enolisable hydrogens.

29. Select **ALL** the compounds would react with excess CH_3MgBr to give 2,4-dimethylpentan-2,4-diol after a normal dilute acid work-up.

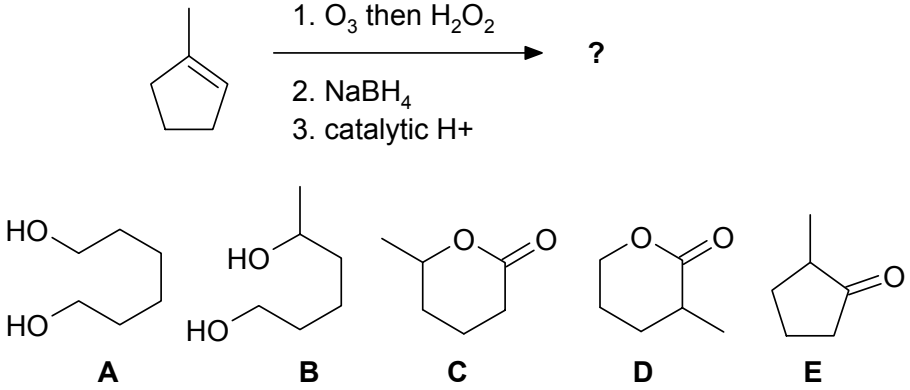
30. Select **ALL** the active methylene compounds.

9% PART 4: PRODUCTS OF SYNTHESIS

ANSWER ANY SIX (6) OF QUESTIONS 31-37.

For each of the questions **31-37** identify the **major product** obtained from each of the reaction sequences shown by selecting from the list of possible products provided.

31.



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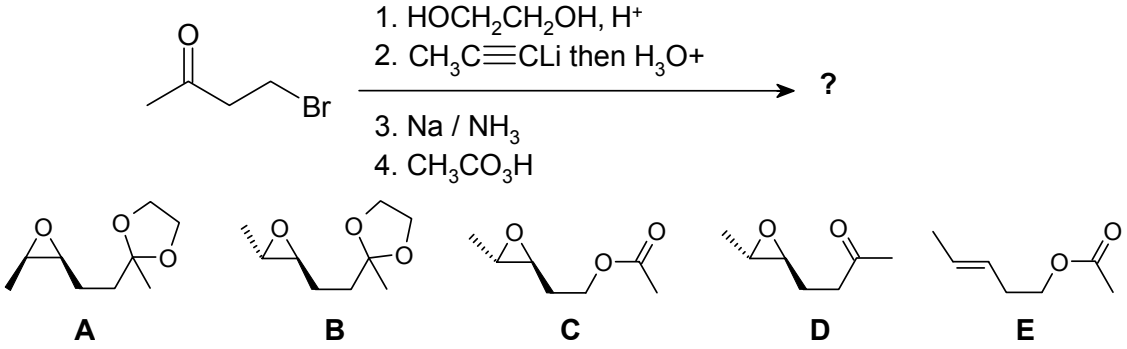

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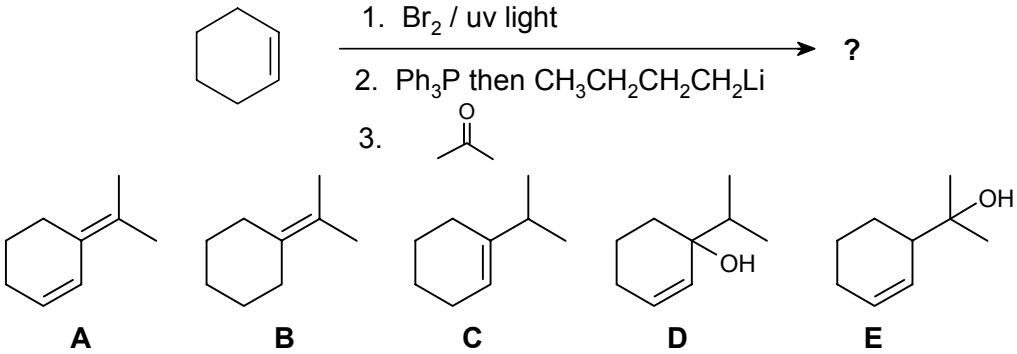

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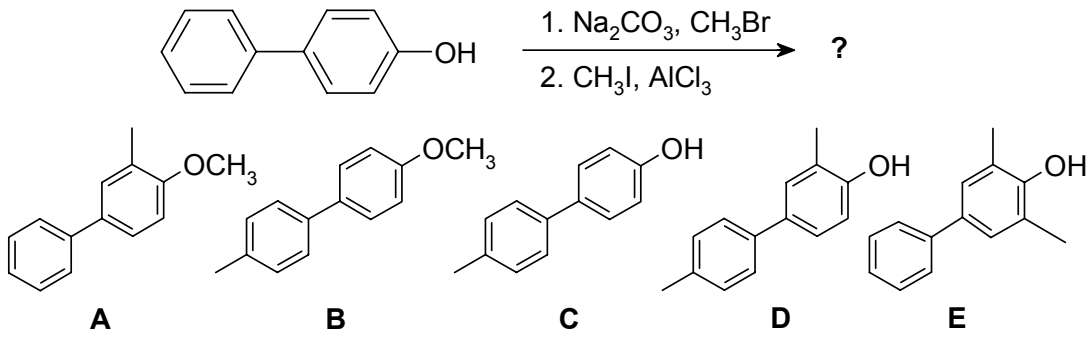
34.



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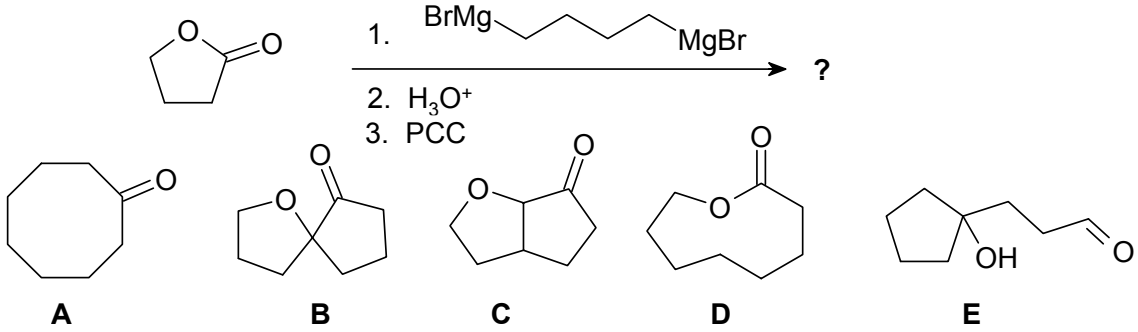

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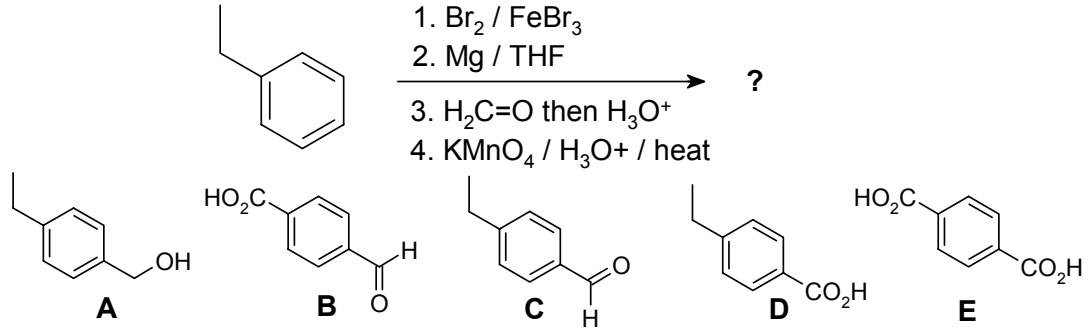
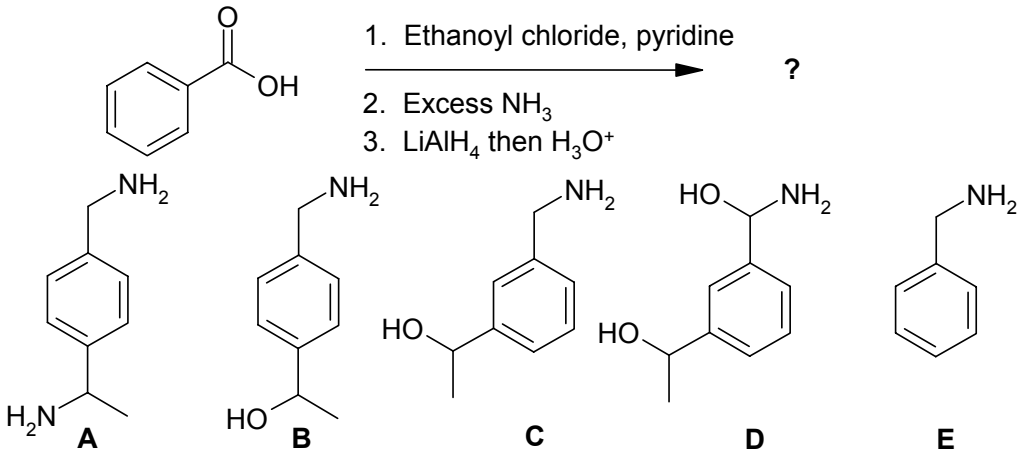


37.



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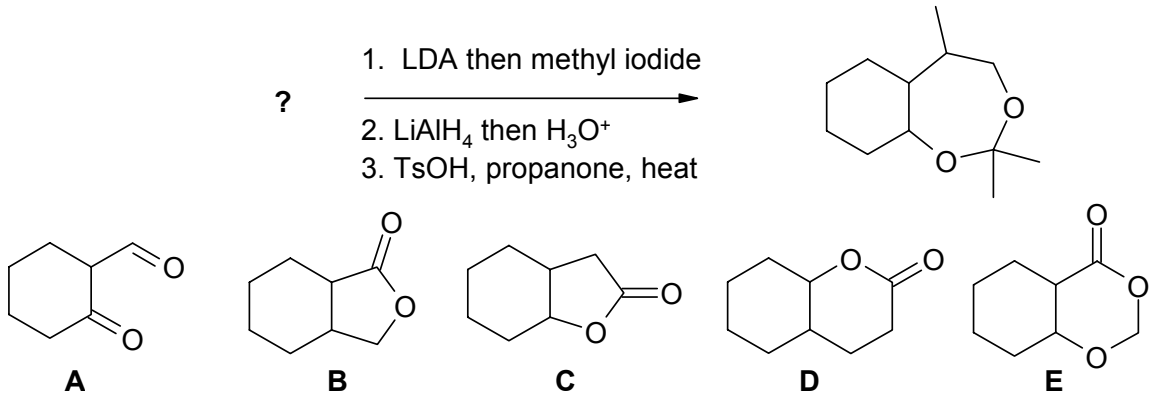
9% PART 5: STARTING MATERIALS FOR SYNTHESIS

ANSWER ANY SIX (6) OF QUESTIONS 38-44.

For each of the questions **38-44**, choose the starting material from the selection provided that gives the product indicated via the transformations shown.

38.



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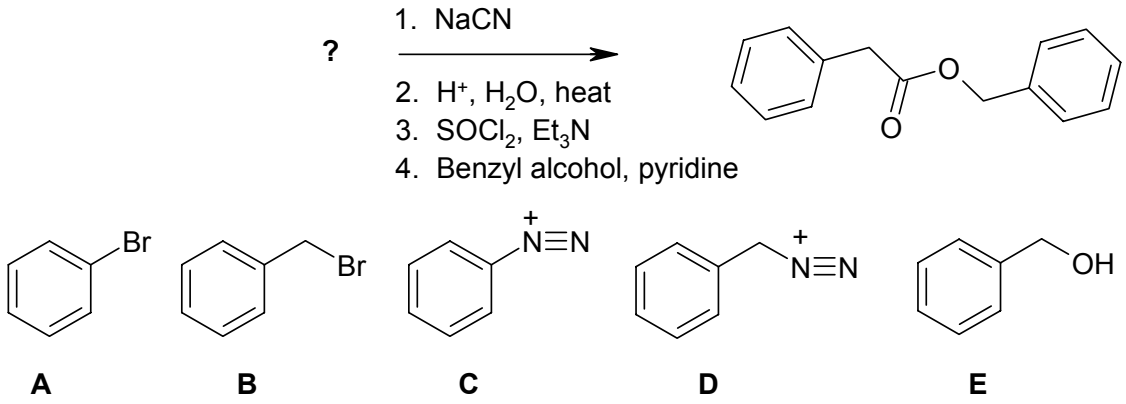
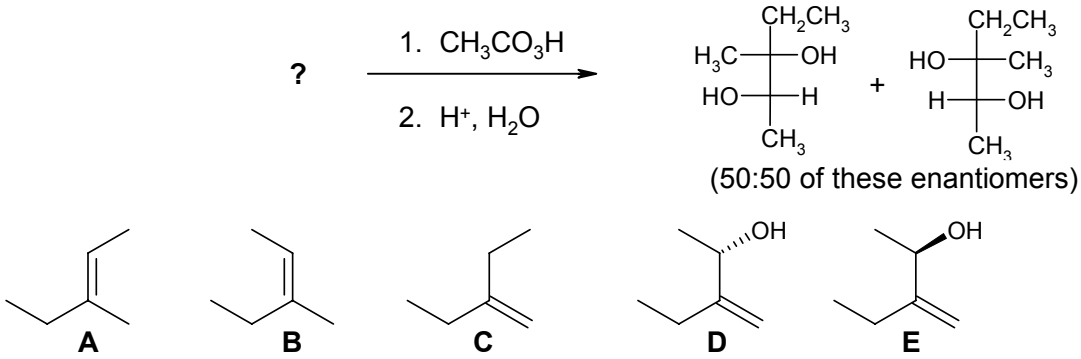


40.



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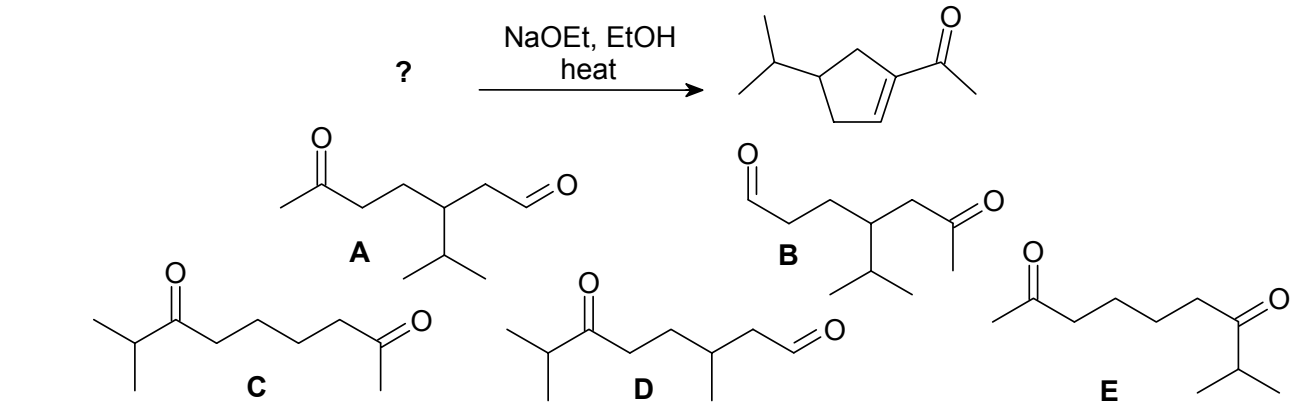
41.



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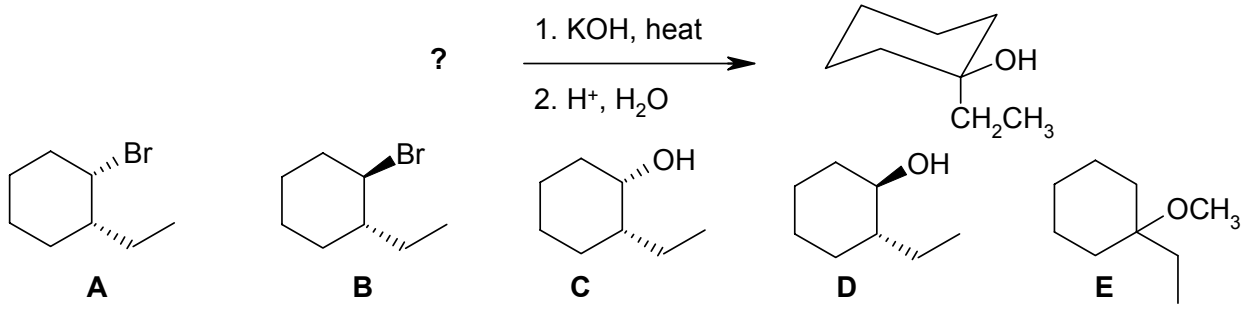
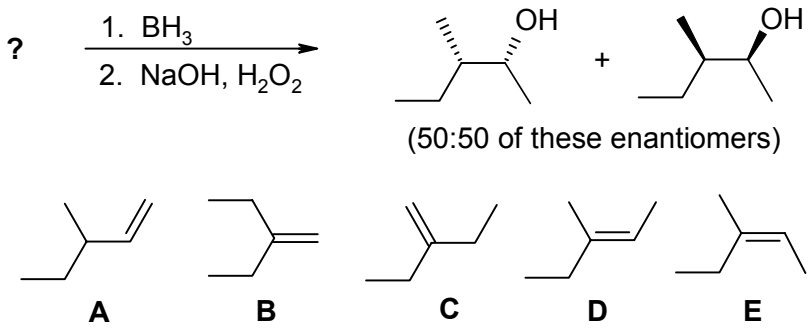


43.



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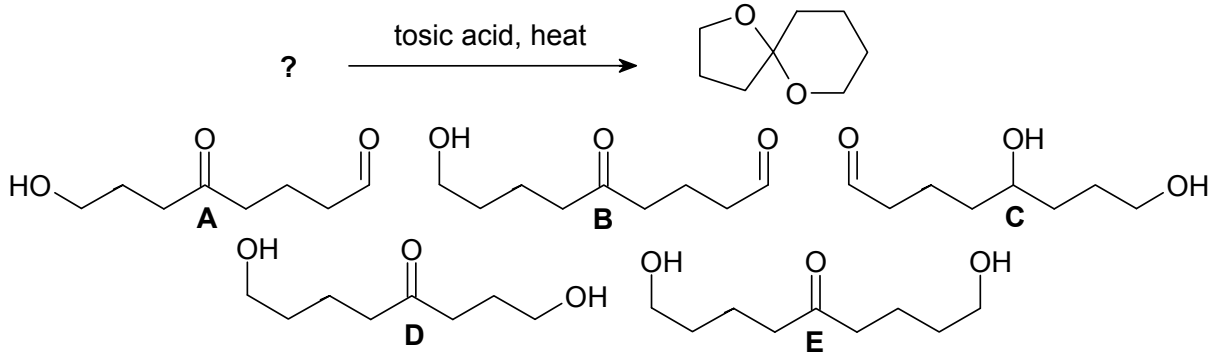

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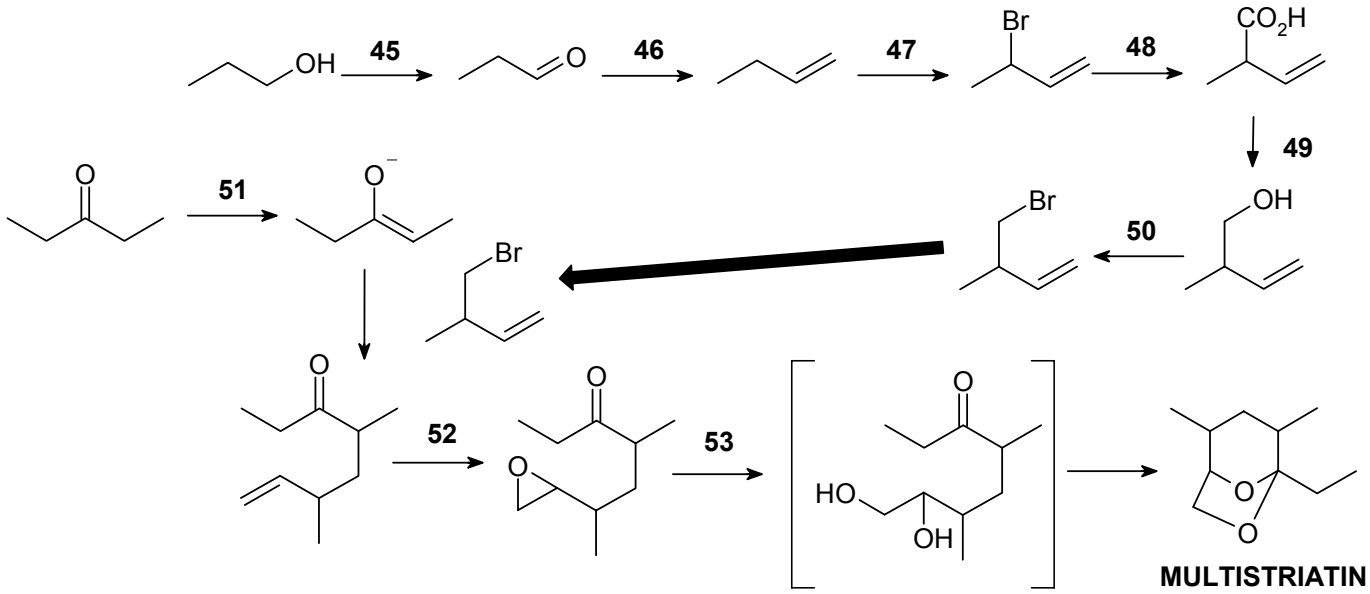
9% PART 6: REAGENTS FOR SYNTHESIS

ANSWER ALL OF THE QUESTIONS 45-53

The following reaction scheme shows a potential synthesis of **MULTISTRIATIN**, an aggregation pheromone of the European Elm Beetle (*scolytus multistriatus*), the vector for Dutch Elm Disease.

From the list of reagents provided in the table below, select the best reagent combination to carry out each of the reactions required at each numbered step.



A. $NaBH_4$ / THF then H_3O^+	**AE**. NaOEt / EtOH
B. $LiAlH_4$ / THF then H_3O^+	**BC**. H_3O^+ / heat
C. CH_3CO_3H	**BD**. aq. NaOH / heat
D. Pyridinium chlorochromate	**BE**. NaBr / DMSO
E. H_2CrO_3	**CD**. PBr_3 / pyridine
AB. Mg / THF then CO_2 then H_3O^+	**CE**. HBr / dark / N_2
AC. $Ph_3P{=}CH_2$	**DE**. HBr / light
AD. LDA / THF	**ABC**. Br_2 / hv

CONTINUED -->

9% **PART 7: EXPLANATION OF PHENOMENA**

ANSWER ALL OF THE QUESTIONS 54 - 59.

CHOOSE THE SINGLE EXPLANATION THAT BEST RATIONALISES THE PHENOMENON INDICATED.

54. Cyclopentadiene has a pKa = 15, whereas cyclopentane has a pKa > 50. This is because:

A. Cyclopentadiene is particularly unstable.

B. Cyclopentane contains no lone pairs.

C. Cyclopentadiene is a 4π anti-aromatic compound.

D. Cyclopentadiene is a 4π non-aromatic compound.

E. Cyclopentadiene has a 6π aromatic conjugate base.

55. The α-hydrogens of esters typically have a pKa = 25, whereas for ketones pKa = 20. This is because:

A. There is no resonance stabilisation of the enolates of esters

B. The inductive effect of the oxygen in the ester destabilises the ester enolate

C. The electron donating alkoxy group in esters destabilises the enolate

D. The electron donating alkoxy group in esters stabilises the enolate

E. The resonance stabilisation of the enolate is better in esters than in ketones

56. The reaction of a Grignard reagent with a carboxylic acid does not give a secondary alcohol. This is because:

A. Grignard reagents only react with the aldehydes, ketones, esters and epoxides.

B. The carboxylic acid is too sterically hindered to react.

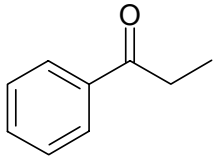
C. The carboxylic acid is not electrophilic enough to react.

D. The Grignard reagent is a base, so an acid-base reaction occurs.

E. Carboxylic acids are reduced to primary alcohols.

CONTINUED -->

57. When 1-phenylpropyne reacts with H_2O / $HgSO_4$ / H_2SO_4, the major product is propiophenone shown below. This is because:



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

B. Carbonyl groups are electron withdrawing groups due to resonance.

C. Phenyl groups can stabilise positive charge by resonance.

D. The reaction is controlled by steric factors.

E. The oxygen adds to the more substituted end.

58. When methyl benzoate is nitrated with HNO_3 / H_2SO_4, the *meta* product is the major product. This is because:

A. The $–CO_2CH_3$ group is a *meta* director.

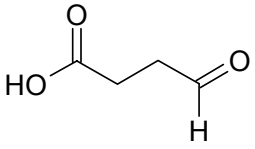
B. The $–OCH_3$ is a *meta* director.

C. The $–NO_2$ group is deactivating and a *meta* director.

D. Nitration usually occurs at the *meta* position.

E. Statistically, the *meta* position is preferred over the *para* position.

59. A chemist attempted to reduce the compound shown below with $NaBH_4$, but could not isolate the desired product 4-hydroxybutanoic acid. This is because:



A. $NaBH_4$ reduced both the carboxylic acid and the aldehyde.

B. $NaBH_4$ is not reactive enough to reduce the carboxylic acid or the aldehyde..

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

D. An intermediate was formed that reacted to give a cyclic ester.

E. An intermediate was formed that reacted to give a aldol reaction.

CONTINUED -->

10% PART 8: MECHANISM

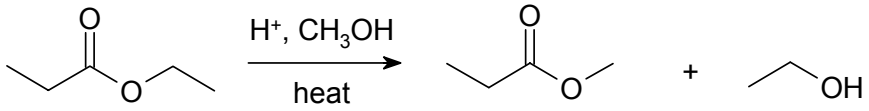
WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED.

ANSWER TWO (2) QUESTIONS, ONE FROM PART A AND ONE FROM PART B.

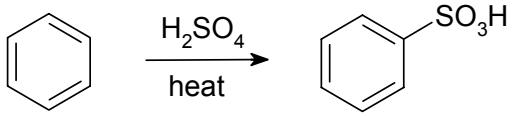
NO REAGENTS OTHER THAN THOSE ALREADY SHOWN IN EACH QUESTION ARE REQUIRED.

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

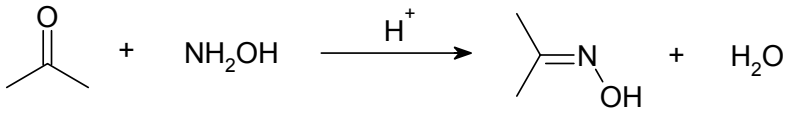
i



ii

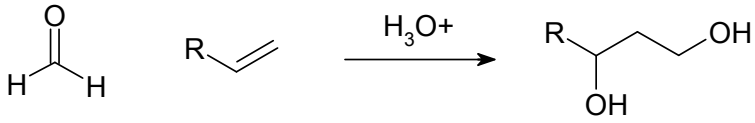


iii

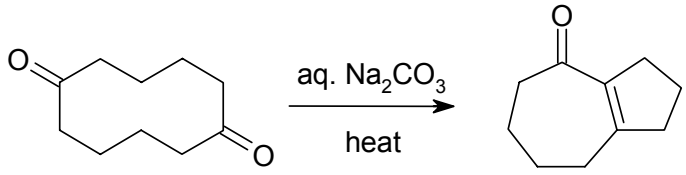


(5%) PART B: Use a curly arrow mechanism to answer ONE of the following:

i. When methanal and a substituted alkene are combined with an aqueous acid catalyst, the 1,3-diol product shown to the right is formed. **Propose a mechanism for this reaction.** (FYI:it's a Prins reaction).



ii. Provide a detailed mechanism showing the steps involved in the following reaction that involves the reaction of a cyclic diketone to give a bicyclic enone.



96% yield

CONTINUED -->

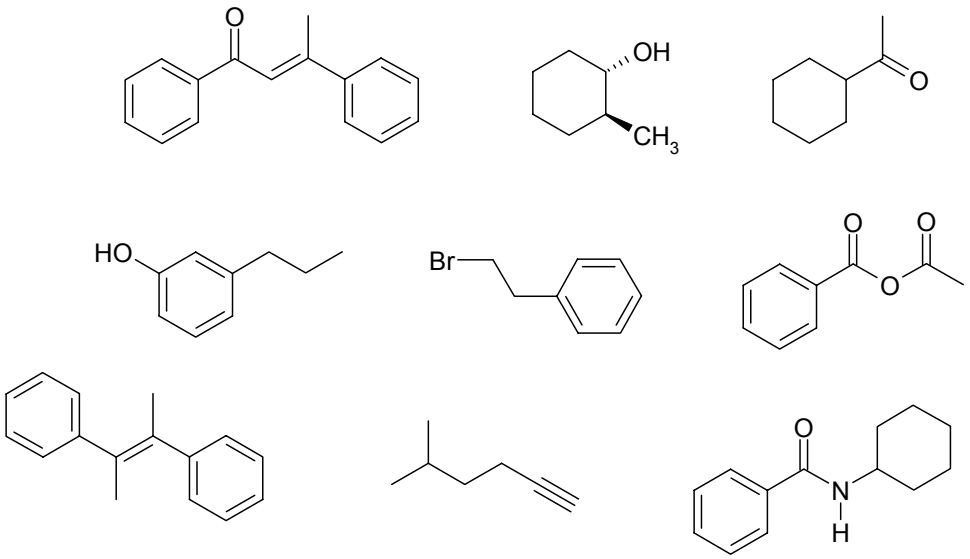
12% PART 9: TOTAL SYNTHESIS

WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED

Design an efficient synthesis for any **THREE (3)** of the following target molecules using any of the starting materials and reagents given in the accompanying list.

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

SHOW YOUR ANSWER AS A STEPWISE REACTION SCHEME SHOWING THE REAGENT REQUIRED FOR EACH STEP AND THE SYNTHETIC INTERMEDIATE FORMED FROM EACH REACTION.



Permitted organic starting materials*

- any organic compounds with no more than FOUR carbons
- benzene

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

You can use any solvents or other reagents for the reactions provided that they do not contribute carbon atoms to the target.

CONTINUED -->

11% PART 10: STRUCTURE DETERMINATION

WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED

When compound **A** (mass spectrum shown below) is treated with magnesium in diethyl ether, followed by addition of carbon dioxide and an acid work-up, **B** is the product. **B** was then reacted with thionyl chloride / Et_3N to give **C**. Compound **C** was then heated with toluene (methylbenzene) in the presence of aluminum trichloride to give **D** as the major product. The 13C-NMR of **D** was found to have six peaks at 196, 143, 135, 130, 129 and 22 ppm, while the 1H-NMR of **D** had three sets of peaks at 7.69 (doublet), 7.26 (doublet) and 2.42 (singlet) ppm, which integrated in a 2:2:3 ratio, respectively.

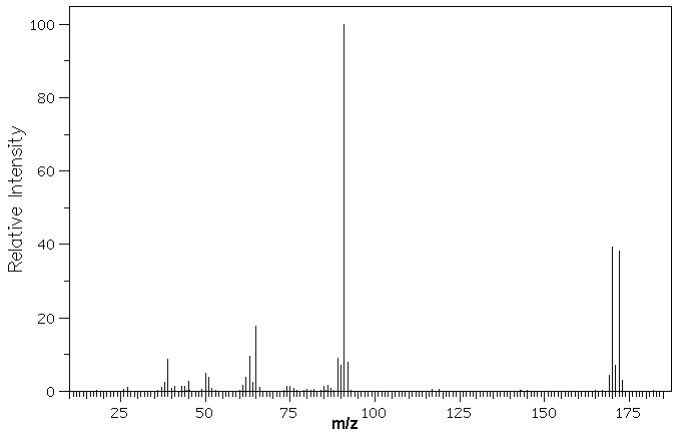
When **D** is reacted with peroxyethanoic acid, compound **E** was obtained as the major product.

When **D** was heated with HNO_3 / H_2SO_4, the major product was found to be **F** where dinitration had occurred.

In contrast, careful treatment of **E** with HNO_3 / H_2SO_4 / heat resulted in **G** as the major product due to mononitration.

Refluxing **E** in aqueous acid resulted in recovery of compound **B** and a new compound **H**. **H** was found to be soluble in dilute aqueous NaOH but not in aqueous $NaHCO_3$.

Identify the compounds **A**, **B**, **C**, **D**, **E**, **F**, **G** and **H** (structures are sufficient)



Mass spectrum of **A**

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

IRH / AC W2008

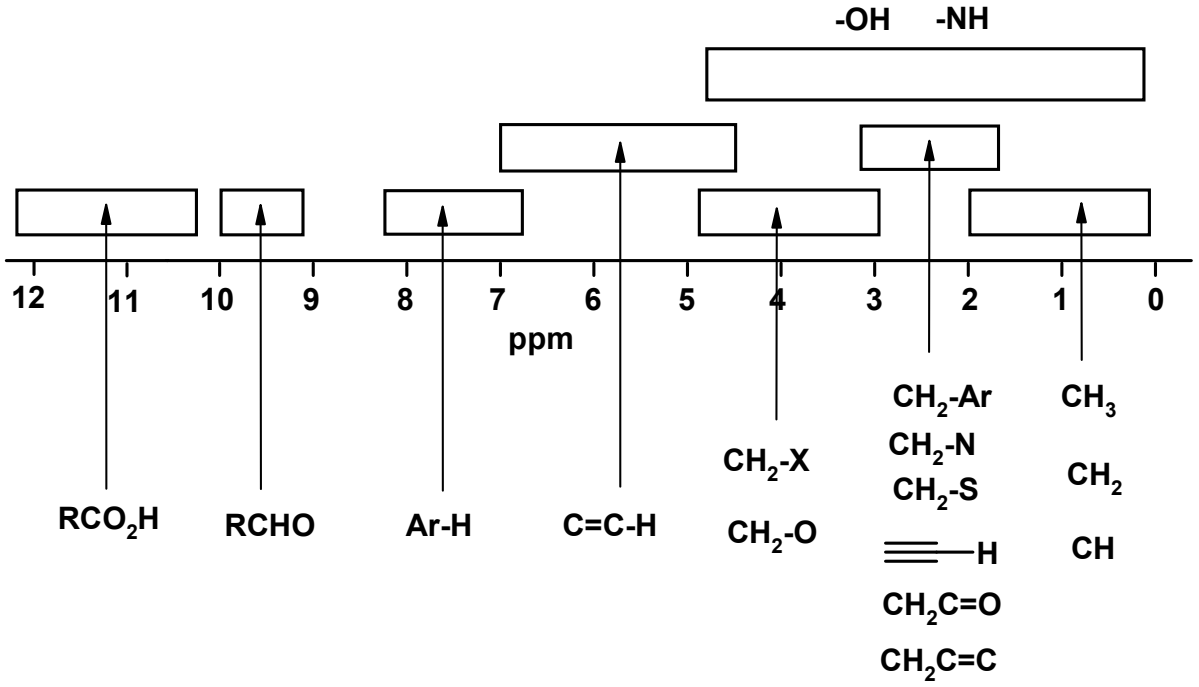
PERIODIC TABLE

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)							

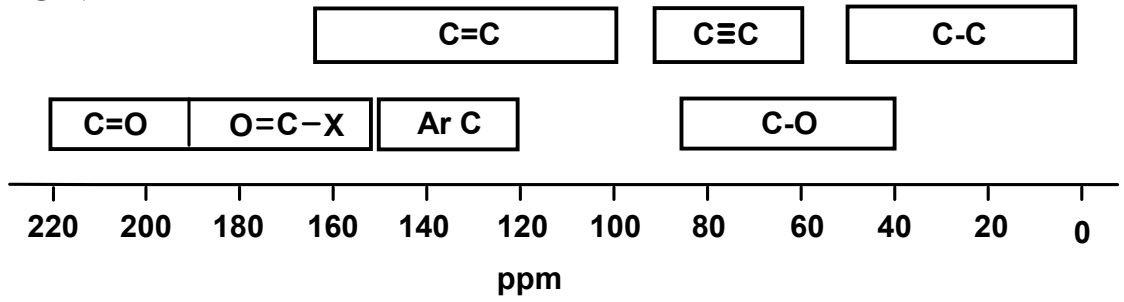
Lanthanides *	58 **Ce** 140.1	59 **Pr** 140.9	60 **Nd** 144.2	61 **Pm** (145)	62 **Sm** 150.4	63 **Eu** 152.0	64 **Gd** 157.3	65 **Tb** 158.9	66 **Dy** 162.5	67 **Ho** 164.9	68 **Er** 167.3	69 **Tm** 168.9	70 **Yb** 173.0	71 **Lu** 175.0
Actinides **	90 **Th** 232.0	91 **Pa** 231.0	92 **U** 238.0	93 **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)

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

^{1}H NMR



^{13}C NMR



A Correlation Table of Infra-Red Group Absorption Frequencies

	TYPE OF VIBRATION		FREQUENCY (cm^{-1})	WAVELENGTH (μ)	INTENSITY
C–H	Alkanes	(stretch)	3000-2850	3.33-3.51	s
	$-CH_3$	(bend)	1450 and 1375	6.90 and 7.27	m
	$-CH_2-$(bend)	1465	6.83	m	
	Alkenes	(stretch)	3100-3000	3.23-3.33	m
		(bend)	1700-1000	5.88-10.0	s
	Aromatics	(stretch)	3150-3050	3.17-3.28	s
		(out-of-plane bend)	1000-700	10.0-14.3	s
	Alkyne	(stretch)	ca. 3300	ca.3.03	s
	Aldehyde		2900-2800	3.45-3.57	w
			2800-2700	3.57-3.70	w
C–C	Alkane	not interpretatively useful			
C=C	Alkene		1680-1600	5.95-6.25	m-w
	Aromatic		1600-1400	6.25-7.14	m-w
C≡C	Alkyne		2250-2100	4.44-4.76	m-w
C=O	Aldehyde		1740-1720	5.75-5.81	s
	Ketone		1725-1705	5.80-5.87	s
	Carboxylic acid		1725-1700	5.80-5.88	s
	Ester		1750-1730	5.71-5.78	s
	Amide		1700-1640	5.88-6.10	s
	Anhydride		ca. 1810	ca. 5.52	s
			ca. 1760	ca. 5.68	s
C–O	Alcohols, Ethers, Esters, Carboxylic acids		1300-1000	7.69-10.0	s
O–H	Alcohols, Phenols				
	Free		3650-3600	2.74-2.78	m
	H-Bonded		3400-3200	2.94-3.12	m
	Carboxylic acids*		3300-2500	3.03-4.00	m
N–H	Primary and secondary amines		ca. 3500	ca. 2.86	m
C≡N	Nitriles		2260-2240	4.42-4.46	m
N=O	Nitro ($R-NO_2$)		1600-1500	6.25-6.67	s
			1400-1300	7.14-7.69	s
C–X	Fluoride		1400-1000	7.14-10.0	s
	Chloride		800-600	12.5-16.7	s
	Bromide, Iodide		<600	>16.7	s

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