

**THE UNIVERSITY OF CALGARY**  
**FACULTY OF SCIENCE**  
**FINAL EXAMINATION**  
**CHEMISTRY 353**

April 25<sup>th</sup>, 2000

Time: 3 Hours

PLEASE WRITE YOUR **NAME, STUDENT I.D. NUMBER** AND SECTION NUMBER (01 for MWF lectures and 02 for TR lectures) 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. Parts 1 - 7 will be computer graded, and only Parts 8, 9 and 10 are to be answered in the booklet. A periodic table with atomic numbers and atomic weights, and tables of spectroscopic data are appended to the end of the exam.

Parts 1 - 7 consist of a series of multiple choice questions numbered 1 - 51 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**.

Molecular models are permitted during the exam; calculators are also permitted, **but NOT programmable calculators**.

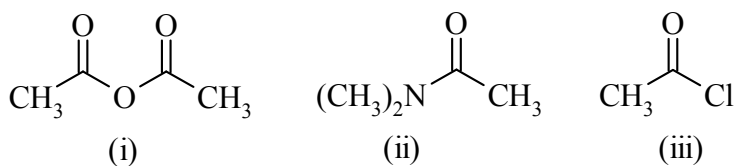
Value**PART 1: RELATIVE PROPERTIES****9% ANSWER ANY SIX (6) OF QUESTIONS 1-10.**

Arrange the items in Questions 1-10 in **DECREASING ORDER** (i.e. greatest, most etc. first) with respect to the indicated property.

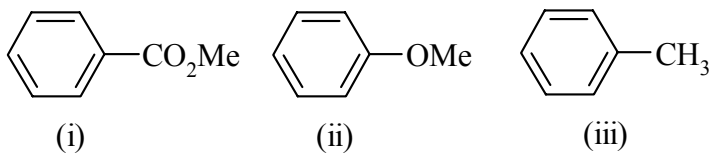
Use the following code to indicate your answers.

- |    |                           |     |                           |
|----|---------------------------|-----|---------------------------|
| A. | <b>i &gt; ii &gt; iii</b> | D.  | <b>ii &gt; iii &gt; i</b> |
| B. | <b>i &gt; iii &gt; ii</b> | E.  | <b>iii &gt; i &gt; ii</b> |
| C. | <b>ii &gt; i &gt; iii</b> | AB. | <b>iii &gt; ii &gt; i</b> |

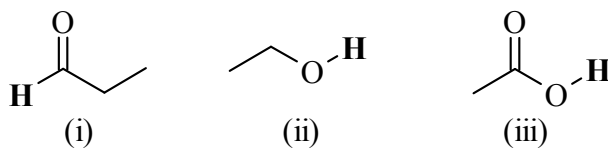
1. The relative rate of hydrolysis using dilute aq. HCl of the following:



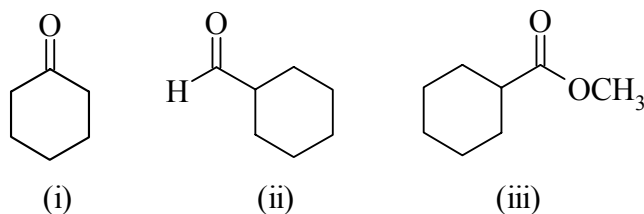
2. The relative rate of reaction of ethanoyl chloride / AlCl<sub>3</sub> with each of the following



3. The relative acidity of the indicated **H** in each of the following:



4. The relative reactivity towards NaBH<sub>4</sub> /EtOH of each of the following:

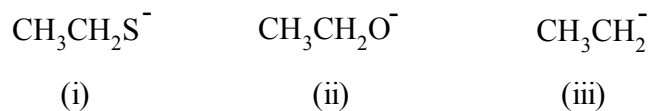


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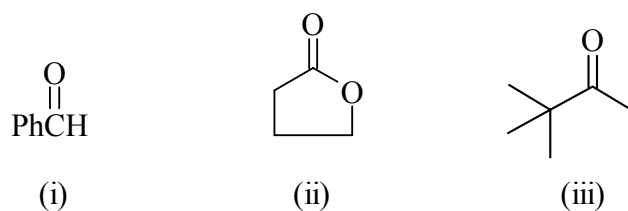
Use the following code to indicate your answers.

- |    |                           |     |                           |
|----|---------------------------|-----|---------------------------|
| A. | <b>i &gt; ii &gt; iii</b> | D.  | <b>ii &gt; iii &gt; i</b> |
| B. | <b>i &gt; iii &gt; ii</b> | E.  | <b>iii &gt; i &gt; ii</b> |
| C. | <b>ii &gt; i &gt; iii</b> | AB. | <b>iii &gt; ii &gt; i</b> |

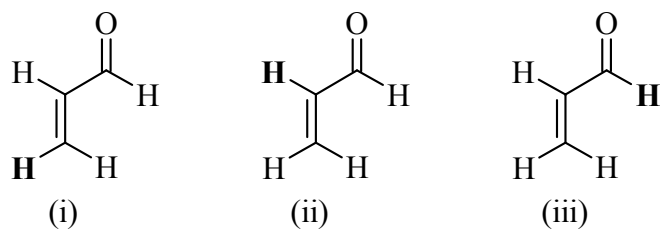
5. The relative basicity of the following:



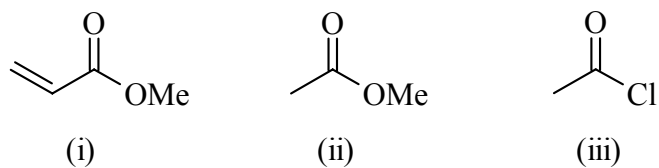
6. The number of enolizable protons in each of the following:



7. The H-nmr chemical shifts,  $\delta$ , in ppm for the **H** atom indicated in each of the following:



8. The stretching frequency in  $\text{cm}^{-1}$  of the C=O stretches in each of the following:



Value

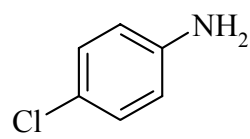
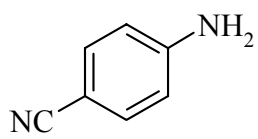
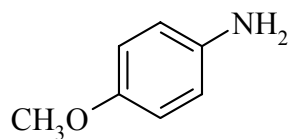
Use the following code to indicate your answers.

- |    |                           |     |                           |
|----|---------------------------|-----|---------------------------|
| A. | <b>i &gt; ii &gt; iii</b> | D.  | <b>ii &gt; iii &gt; i</b> |
| B. | <b>i &gt; iii &gt; ii</b> | E.  | <b>iii &gt; i &gt; ii</b> |
| C. | <b>ii &gt; i &gt; iii</b> | AB. | <b>iii &gt; ii &gt; i</b> |

9. The relative yield of the following products from the reaction of phenyl ethanoate with  $\text{HNO}_3 / \text{H}_2\text{SO}_4 / \text{heat}$ :

- (i) 2-nitrophenyl ethanoate
- (ii) 3-nitrophenyl ethanoate
- (iii) 4-nitrophenyl ethanoate

10. The relative basicity of the following:

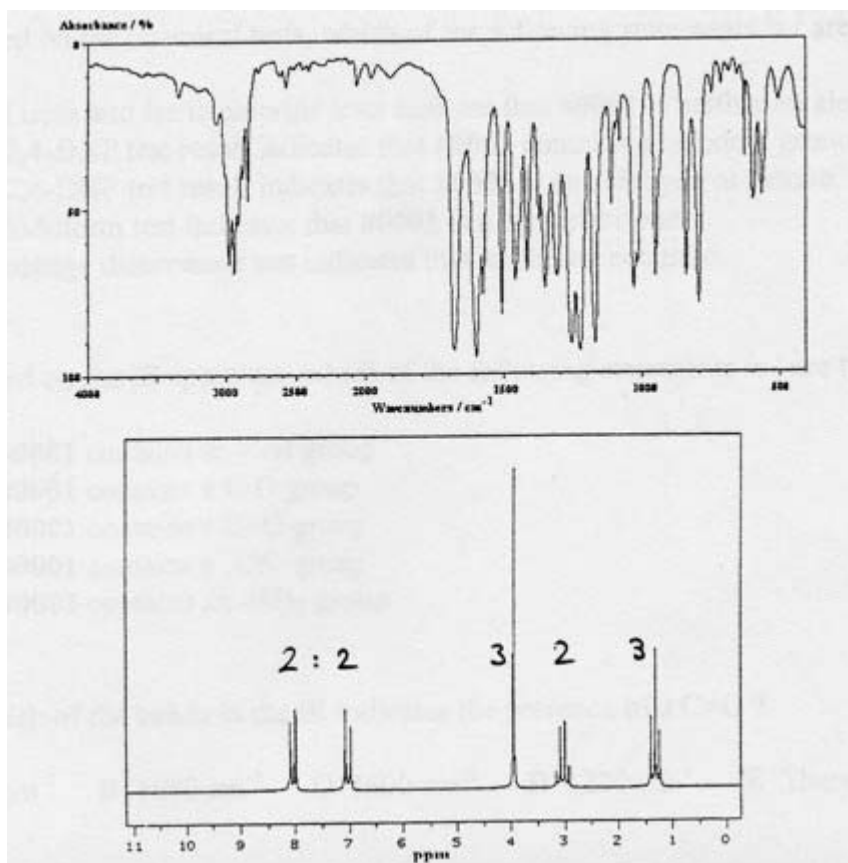


Value

**PART 2: LABORATORY****9% ANSWER ALL OF THE QUESTIONS 11-19.**

The following questions are based on the experiments you have done this semester. Some answers **MAY** require that you fill in **MORE** than one option.

Sue Dent here at the U of C, had unknown **#0001**, which was a colourless, white crystalline solid. She measured the melting point to be 28 °C and a boiling point of 260 °C (uncorrected). IR and H-NMR spectra of **#0001** are shown below. Sue also carried out a series of chemical tests on **#0001**. The results of these tests are also shown below.



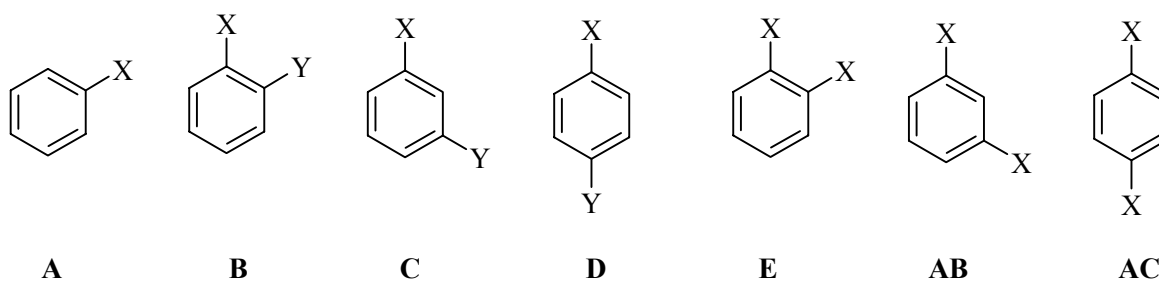
Chemical Test	Observations for #0001
Water solubility	Insoluble
5% NaHCO <sub>3</sub>	Insoluble
5% NaOH	Insoluble
5% HCl	Insoluble
Lucas	Clear solution obtained
2,4-Dinitrophenylhydrazine	Red-orange precipitate formed
Iodoform	Yellow solution formed
Ferric Chloride	No reaction
Dichromate	Orange solution obtained
Bromine in chloroform	Brown solution obtained

Value

11. The corrected melting point for the unknown #0001 should be approximately :
- A < 26 °C      B 26 °C      C 28 °C      D 30 °C      E >30 °C
12. The corrected boiling point for the unknown #0001 should be approximately :
- A 255 °C      B 260 °C      C 265 °C      D 270 °C      E 275 °C
13. Based on the chemical tests, which of the following statements is / are true ?
- A. The Lucas and ferric chloride tests indicate that #0001 is neither an alcohol nor a phenol  
 B. The 2,4-DNP test result indicates that #0001 contains a carbonyl group.  
 C. The 2,4-DNP test result indicates that #0001 is an aldehyde or ketone.  
 D. The iodoform test indicates that #0001 is a methyl ketone.  
 E. The orange dichromate test indicates that oxidation occurred.
14. Based on the IR spectrum, which of the following statements is / are true ?
- A. #0001 contains an -OH group  
 B. #0001 contains a C-O group  
 C. #0001 contains a C=O group  
 D. #0001 contains a -CN group  
 E. #0001 contains an -NH<sub>2</sub> group
15. Which of the bands in the IR indicates the presence of a C=O ?
- A 3000 cm<sup>-1</sup>      B 1680 cm<sup>-1</sup>      C 1600 cm<sup>-1</sup>      D 1220 cm<sup>-1</sup>      E There is no C=O !
16. Which of the following H (indicated by the arrow) best describes the peaks at 3.0ppm in the H-NMR spectrum ?
- |  |   |   |  |  |  |
|--|---|---|--|--|--|
| $\begin{array}{c} \text{-CH}_2\text{-} \\ \uparrow \\ \text{A} \end{array}$      | $\begin{array}{c} \text{-CH}_2\text{CH}_3 \\ \uparrow \\ \text{B} \end{array}$              | $\begin{array}{c} \text{-CH}_2\text{CH}_3 \\ \uparrow \\ \text{C} \end{array}$              | $\begin{array}{c} \text{-CH}_2\text{CH}_2\text{CH}_3 \\ \uparrow \\ \text{D} \end{array}$          | $\begin{array}{c} \text{-CH}_2\text{CH}_2\text{CH}_3 \\ \uparrow \\ \text{E} \end{array}$          | $\begin{array}{c} \text{-OCH}_2\text{CH}_3 \\ \uparrow \\ \text{AB} \end{array}$ |
| $\begin{array}{c} \text{-OCH}_2\text{CH}_3 \\ \uparrow \\ \text{AC} \end{array}$ | $\begin{array}{c} \text{-OCH}_2\text{CH}_2\text{CH}_3 \\ \uparrow \\ \text{AD} \end{array}$ | $\begin{array}{c} \text{-OCH}_2\text{CH}_2\text{CH}_3 \\ \uparrow \\ \text{AE} \end{array}$ | $\begin{array}{c} \text{O} \\    \\ \text{-CCH}_2\text{CH}_3 \\ \uparrow \\ \text{BC} \end{array}$ | $\begin{array}{c} \text{O} \\    \\ \text{-CCH}_2\text{CH}_3 \\ \uparrow \\ \text{BD} \end{array}$ |  |

Value

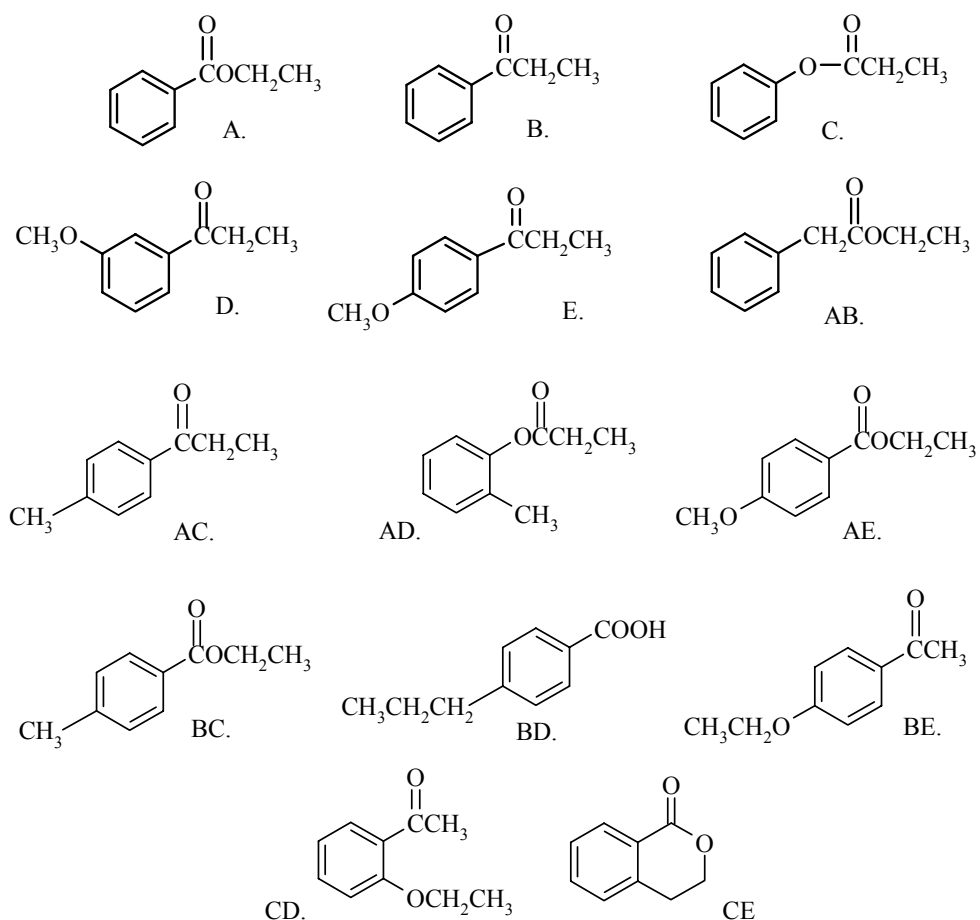
17. Which of the following partial structures best rationalise the peaks at 7 to 8 ppm in the H-NMR spectrum ?



18. Based on all the available data, which of the following functional groups could be present in #0001:

A. Aromatic    B. Carboxylic acid    C. Ester    D. Ether    E. Ketone

19. Which of the following compounds is #0001 ?

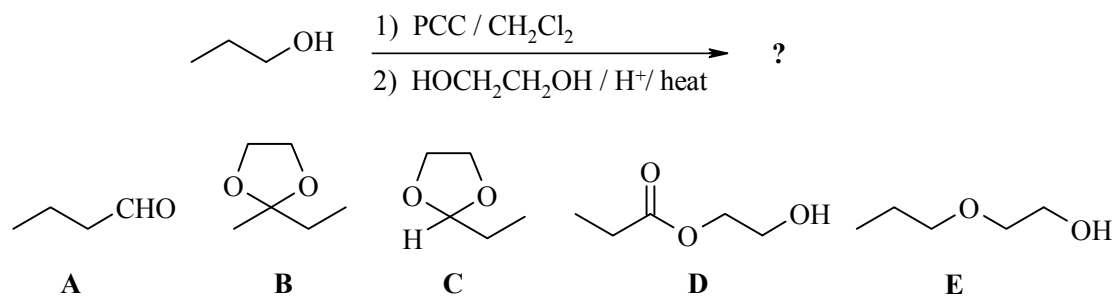




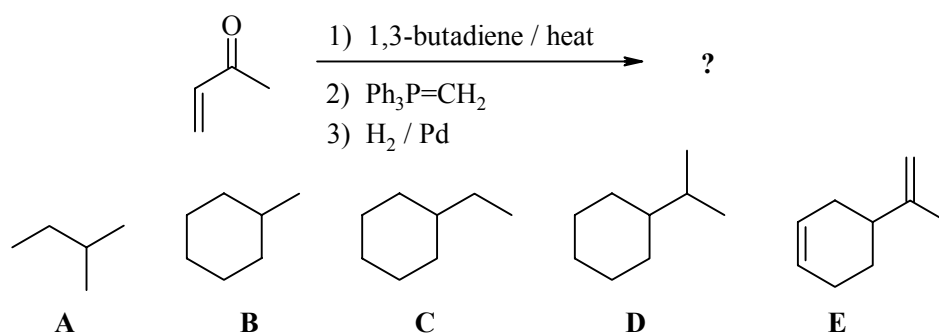


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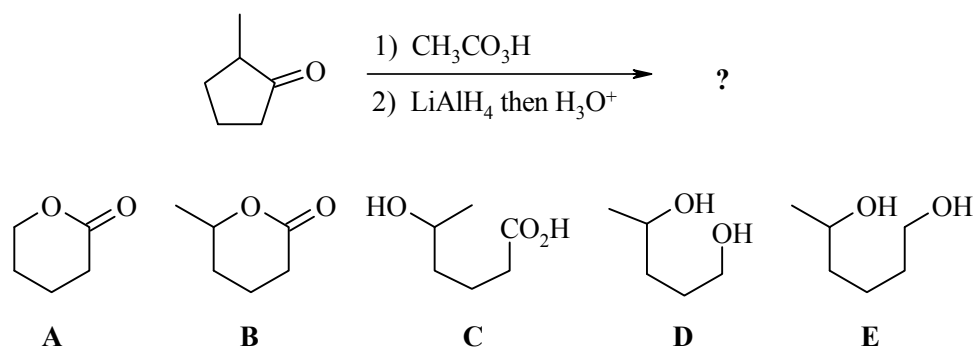
23.



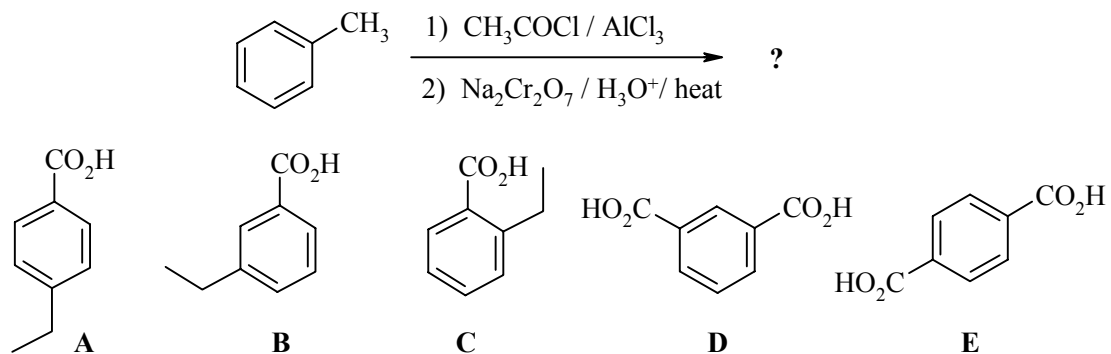
24.



25.



26.

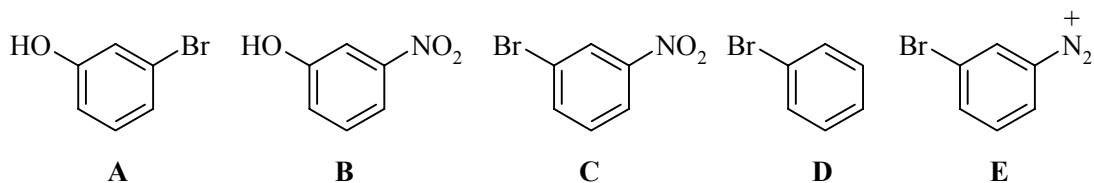
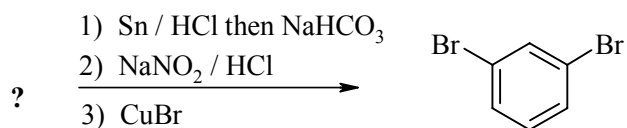


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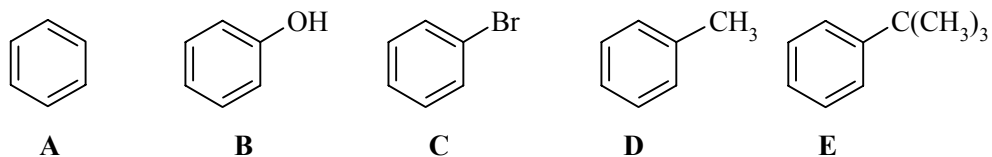
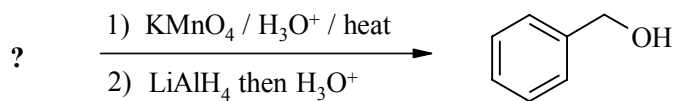
**PART 4: STARTING MATERIALS FOR SYNTHESIS****10% ANSWER ANY FIVE (5) OF QUESTIONS 27-33.**

For each of the questions 27-33, choose the starting material from the selection provided that gives the product indicated via the transformations shown.

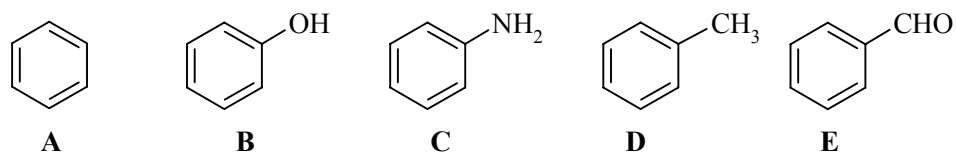
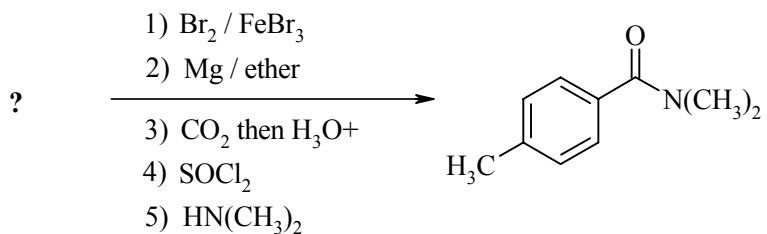
27.



28.

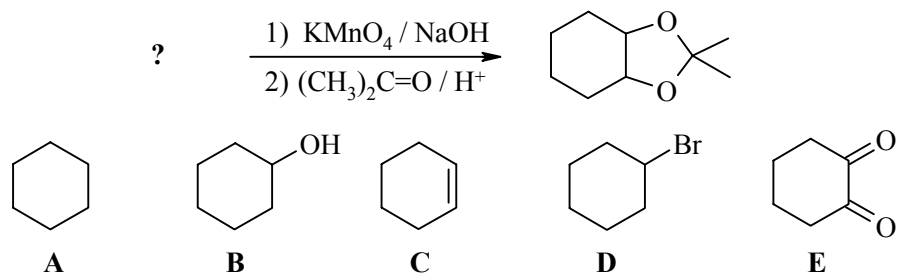


29.

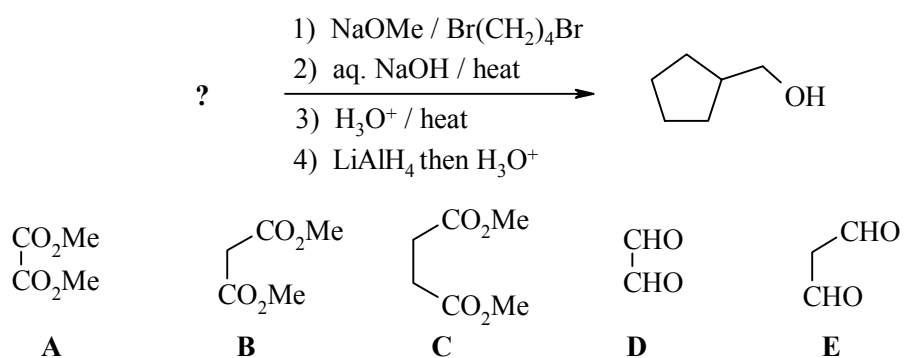


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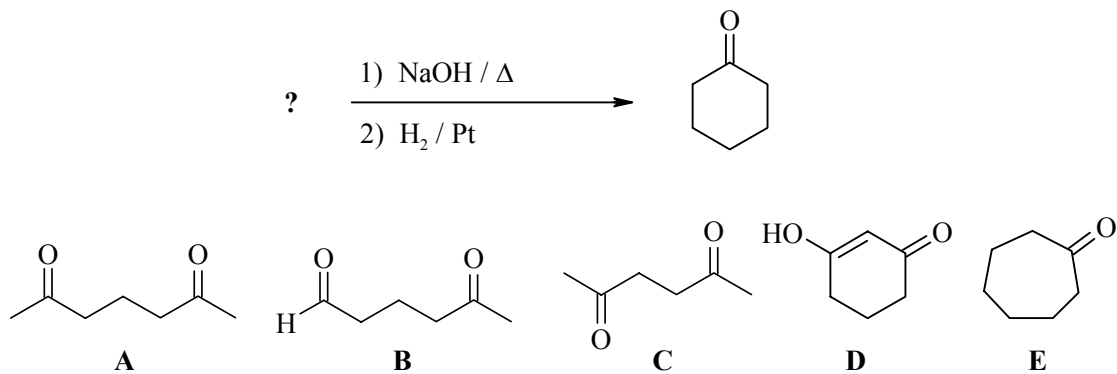
30.



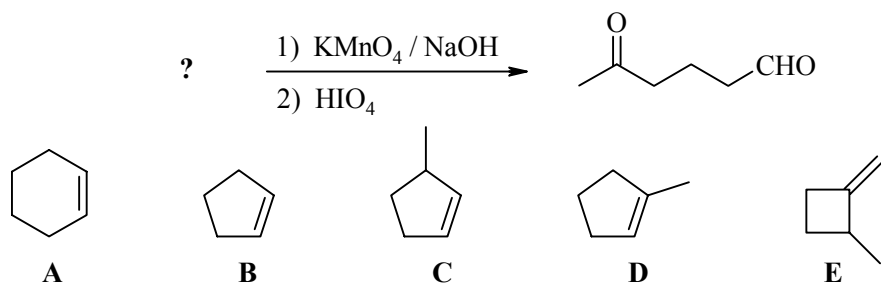
31.



32.

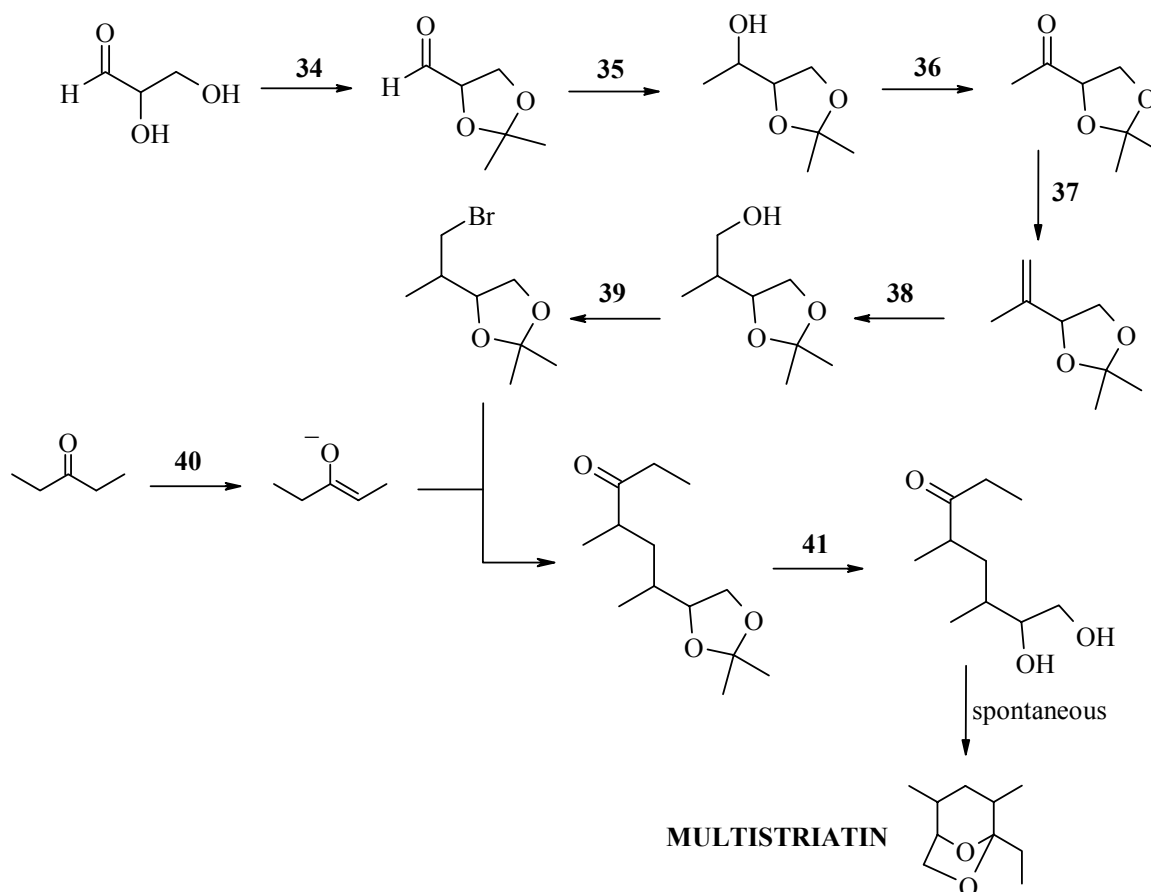


33.



Value**PART 5: REAGENTS FOR SYNTHESIS****8% ANSWER ALL OF THE QUESTIONS 34 - 41**

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.

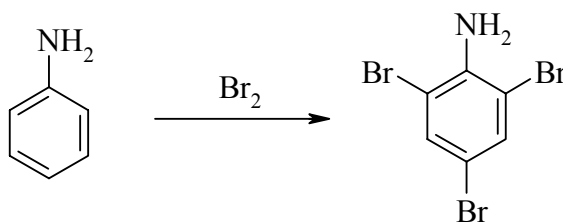


A. $\text{LiAlH}_4$ then $\text{H}_3\text{O}^+$	AE. $(\text{CH}_3)_2\text{C}=\text{O} / \text{H}^+ / \text{heat}$
B. $\text{MeMgBr}$ then $\text{H}_3\text{O}^+$	BC. $\text{H}_3\text{O}^+$
C. $\text{PBr}_3, \text{Et}_3\text{N}$	BD. $\text{BH}_3$ then $\text{NaOH} / \text{H}_2\text{O}_2$
D. $\text{Br}_2 / \text{CHCl}_3$	BE. $\text{Ph}_3\text{PCH}_2$
E. $\text{HBr}$	CD. $\text{NaOEt} / \text{EtOH}$
AB. $\text{PCC}$	CE. $\text{Li NiPr}_2 / \text{THF}$
AC. $\text{MCPBA}$	DE. $\text{NaOH} / \text{H}_2\text{O}$
AD. $\text{Na}_2\text{Cr}_2\text{O}_7 / \text{aq. H}_2\text{SO}_4$	

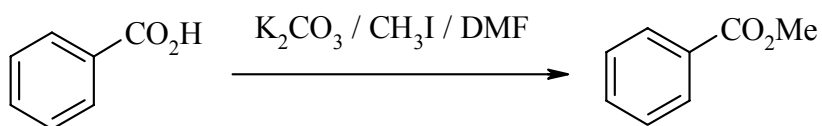
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**PART 6: MECHANISMS****8% ANSWER ANY FOUR (4) OF QUESTIONS 42 - 46**For each of the questions 42 - 46, select the single mechanistic term that **BEST** describes the reaction shown:

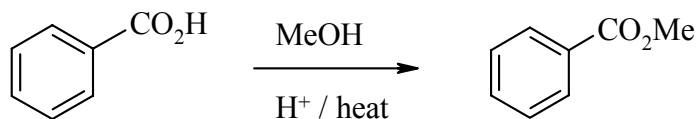
42.



43.



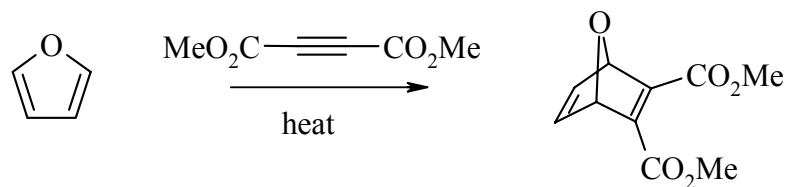
44.



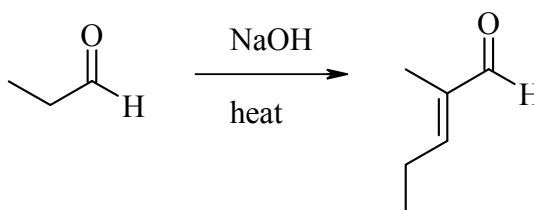
A.	$S_N1$	AE.	Markovnikov addition
B.	$S_N2$	BC.	Anti-Markovnikov addition
C.	Wittig Reaction	BD.	Electrophilic aromatic substitution
D.	Williamson ether synthesis	BE.	Nucleophilic aromatic substitution
E.	Fischer Esterification	CD.	Nucleophilic addition
AB.	Friedel-Crafts reaction	CE.	Nucleophilic acyl substitution
AC.	Diels-Alder reaction	DE.	Aldol condensation
AD.	Conjugate addition	ABC.	Claisen condensation

Value

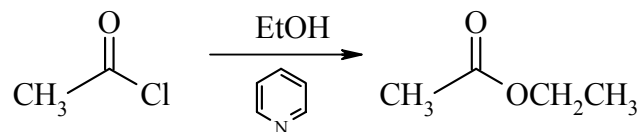
45.



46.



47.



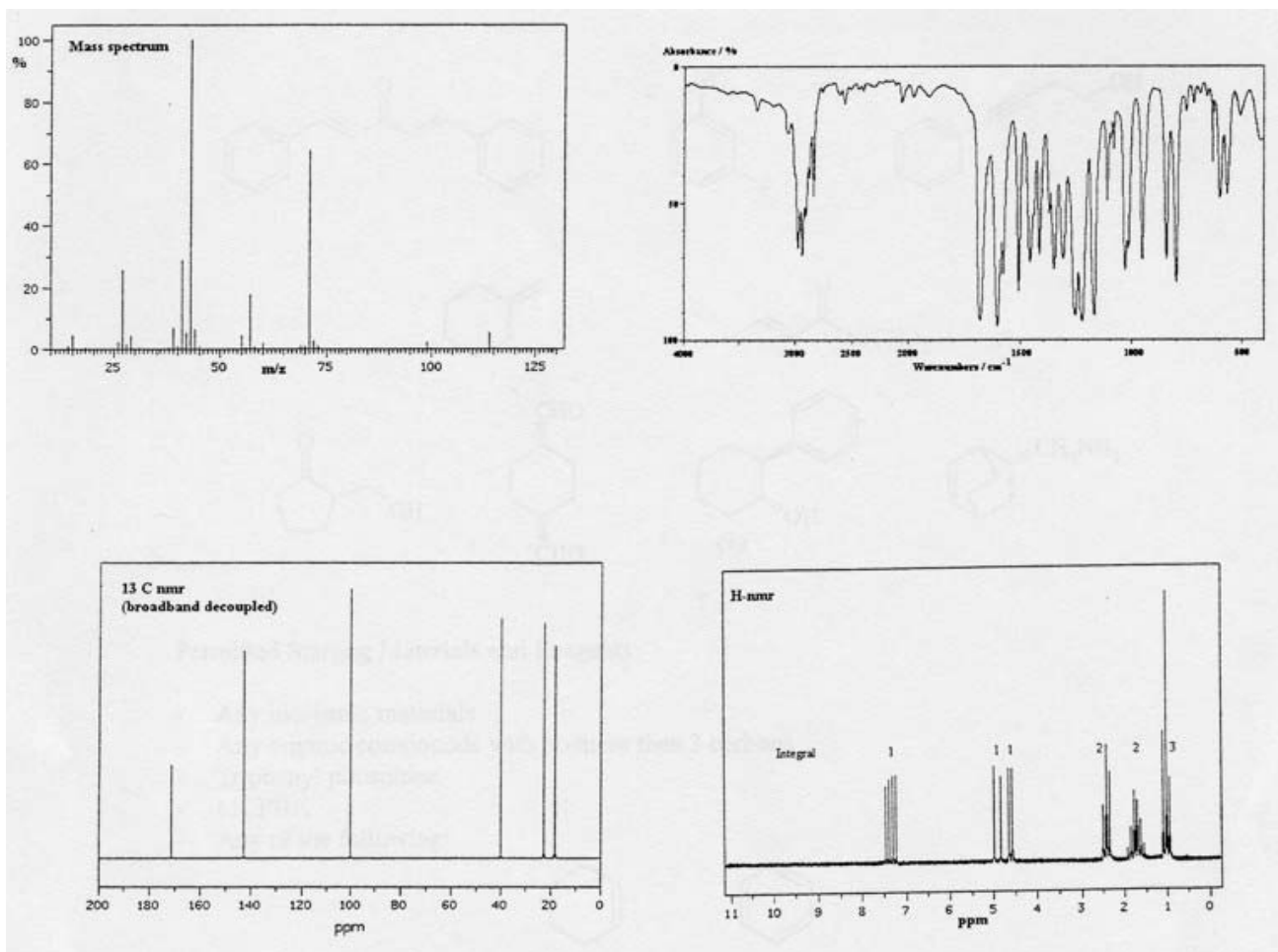
- |     |                            |      |                                     |
|-----|----------------------------|------|-------------------------------------|
| A.  | $\text{S}_{\text{N}}1$     | AE.  | Markovnikov addition                |
| B.  | $\text{S}_{\text{N}}2$     | BC.  | Anti-Markovnikov addition           |
| C.  | Wittig Reaction            | BD.  | Electrophilic aromatic substitution |
| D.  | Williamson ether synthesis | BE.  | Nucleophilic aromatic substitution  |
| E.  | Fischer Esterification     | CD.  | Nucleophilic addition               |
| AB. | Friedel-Crafts reaction    | CE.  | Nucleophilic acyl substitution      |
| AC. | Diels-Alder reaction       | DE.  | Aldol condensation                  |
| AD. | Conjugate addition         | ABC. | Claisen condensation                |

Value**PART 7: EXPLANATION OF PHENOMENA****8% ANSWER ALL OF THE QUESTIONS 48 - 51.**Choose the **SINGLE** explanation that **BEST** describes the phenomenon indicated.

48. Cyclopentadiene has a  $pK_a = 15$ , whereas cyclopentane has a  $pK_a > 50$ . This is because:
- A. Cyclopentadiene is particularly unstable.
  - B. Cyclopentane contains no lone pairs.
  - C. Cyclopentadiene has a  $6\pi$  aromatic conjugate base.
  - D. C-H bonds are not very polar.
  - E. Cyclopentadiene is a  $4\pi$  non-aromatic compound.
49. When methylbenzene is reacted with n-propyl chloride /  $AlCl_3$ , the major product is p-isopropylmethylbenzene. This is because:
- A. This is a Friedel-Crafts alkylation reaction.
  - B. This is a Friedel-Crafts acylation reaction.
  - C.  $AlCl_3$  is a Lewis acid.
  - D. The n-propyl chloride eliminates to propene which then reacts with the aromatic.
  - E. The reaction proceeds via a  $1^\circ$  cationic system that rearranges to a more stable  $2^\circ$  cation.
50. When methyl benzoate is brominated with  $Br_2 / FeBr_3$ , the *meta* product is the major product. This is because:
- A. The  $-CO_2CH_3$  group is a *meta* director.
  - B. The  $-COCH_3$  is a *meta* director.
  - C. The  $-Br$  group is deactivating and a *meta* director.
  - D. Bromination usually occurs at the *meta* position.
  - E. Statistically, the *meta* position is preferred over the *para* position.
51. The reaction of  $EtMgBr$  with a carboxylic acid does not give an alcohol because:
- A. Grignard reagents only react with aldehydes, ketones and esters.
  - 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 proton abstraction gives an unreactive alkane.
  - E. Carboxylic acids are reduced to primary alcohols.

Value**PART 8: SPECTROSCOPY****12% WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED.****Show your workings as PARTIAL marks will be given.**

The elemental analysis of an unknown molecule was found to be 63.16 % C and 8.77 % H (by weight). From this data and the spectral data provided below, identify the structure of the unknown molecule.

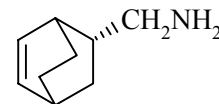
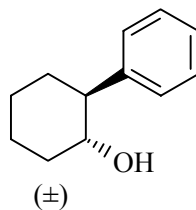
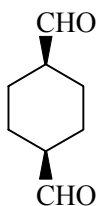
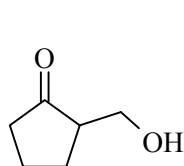
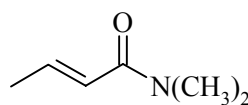
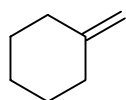
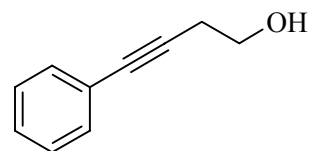
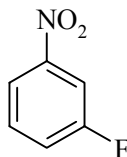
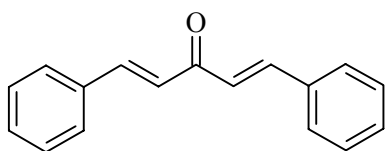


H-NMR L to R : doublet of doublets, doublet, doublet, triplet, sextet, triplet



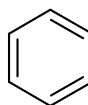
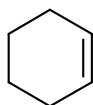
Value**PART 9: TOTAL SYNTHESIS****WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED**

**12%** 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. Show the product of each step and clearly identify the reagents.

**DO NOT SHOW MECHANISMS.**

Permitted Starting Materials and Reagents

- Any inorganic materials
- Any organic compounds with no more than 3 carbons
- Triphenyl phosphine
- MCPBA
- Any of the following:



Value**PART 10: STRUCTURE DETERMINATION****12% WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED**

Compound **A**,  $C_8H_{12}$ , was treated with  $O_3$  followed by  $H_2O_2$  work-up to form a single compound **B**,  $C_4H_6O_3$ . Subsequently, **B** was heated in EtOH with an acid catalyst and **C**,  $C_{10}H_{20}O_4$  was obtained. **C** was also prepared in a separate reaction sequence using ethyl ethanoate and NaOEt to prepare **D**,  $C_6H_{10}O_3$ , which gave **C** when heated in EtOH with an acid catalyst. **D** could also be converted into **B** by heating with aq. NaOH. On further heating of **B** with  $H_3O^+$ , a gas was released and the only organic compound obtained was propanone.

**C** was then reacted with excess phenyl magnesium bromide followed by the usual acid work-up to yield **E**,  $C_{20}H_{26}O_3$ . **E** was then heated with  $H_3O^+$  to provide **F**,  $C_{16}H_{16}O_2$  which was easily dehydrated to give **G**,  $C_{16}H_{14}O$ . **G** was also obtained by the reaction of propanone with diphenyl ketone (also known as benzophenone) in hot ethanolic NaOH.

All the compounds **A-G** were achiral.

What are **A - G** ?

Draw the curly arrow mechanism for **EITHER**

- the preparation of **D** from ethyl ethanoate, **OR**,
- the conversion of **D**, via **B**, to propanone

**THE END**