

THE UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

FINAL EXAMINATION

CHEMISTRY 353

April 19th, 2005

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 - 58 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.**

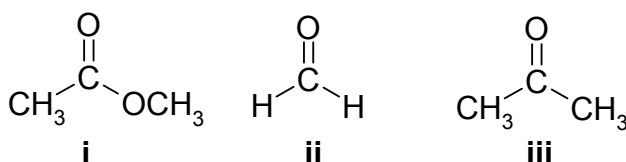
12% **PART 1: RELATIVE PROPERTIES**

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

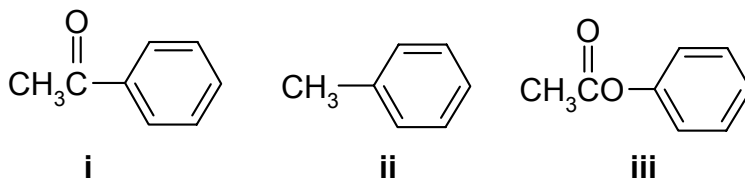
Arrange the items in questions 1-10 in **DECREASING ORDER** (*i.e.* greatest, most etc. first) with respect to the indicated property. Use the following code to indicate your answers:

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

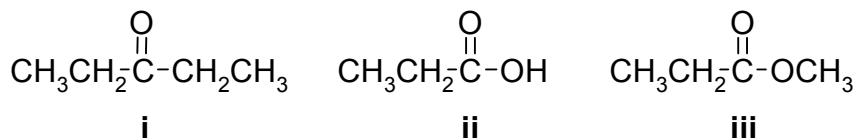
1. The relative reactivity towards  $\text{CH}_3\text{MgI}$  in diethyl ether of each of the following:



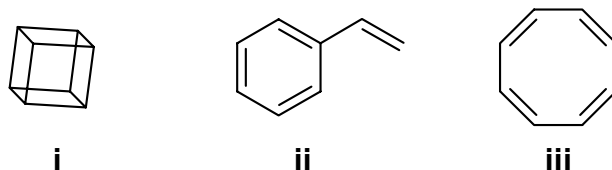
2. The relative rate of reaction towards  $\text{HNO}_3 / \text{H}_2\text{SO}_4$  of each of the following:



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



4. The relative stability of the following isomers:



5. The relative reactivity towards aq. sulfuric acid of each of the following :

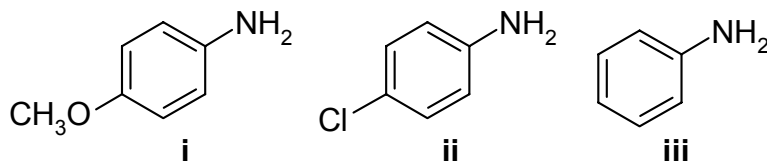


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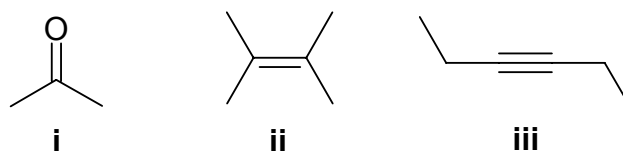
Use the following code to indicate your answers:

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

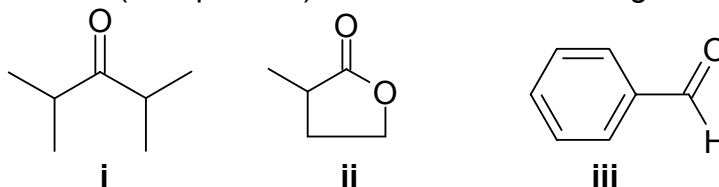
6. The relative basicity of each of the following:



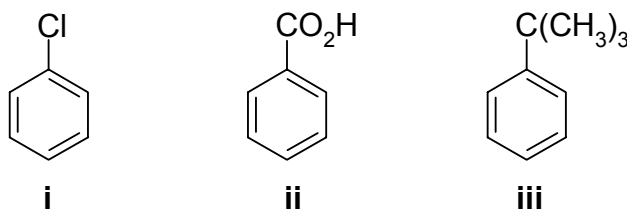
7. The relative reactivity towards reaction with  $H_2$  / Pt of each of the following:



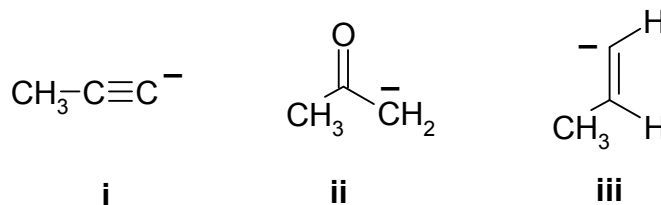
8. The number of enolizable (or  $\alpha$ -protons) in each of the following:



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



10. The relative stability of the following carbanions :

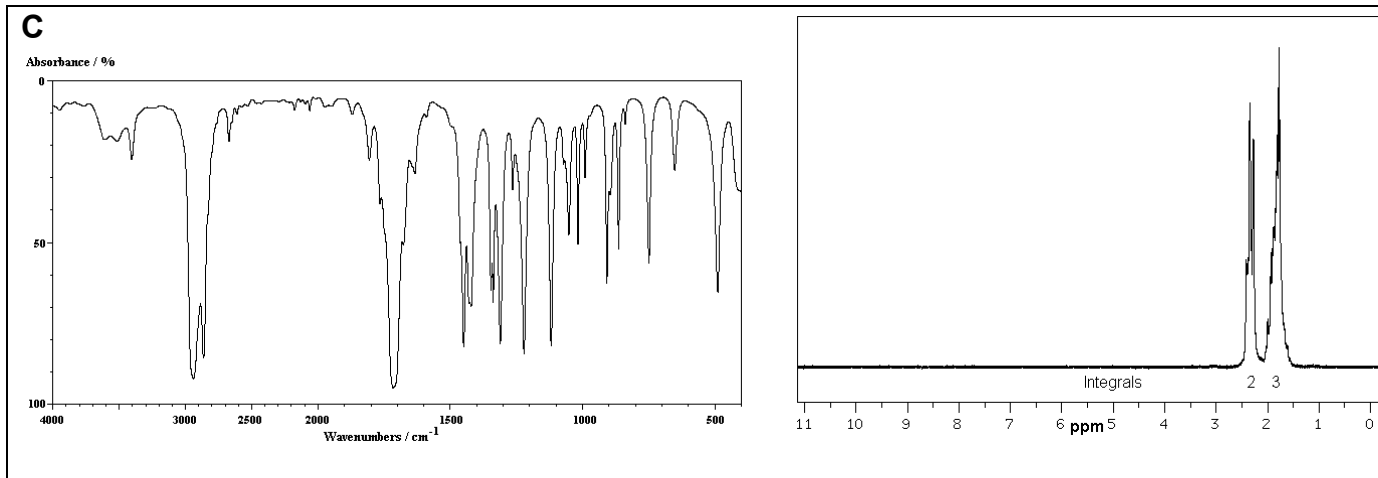
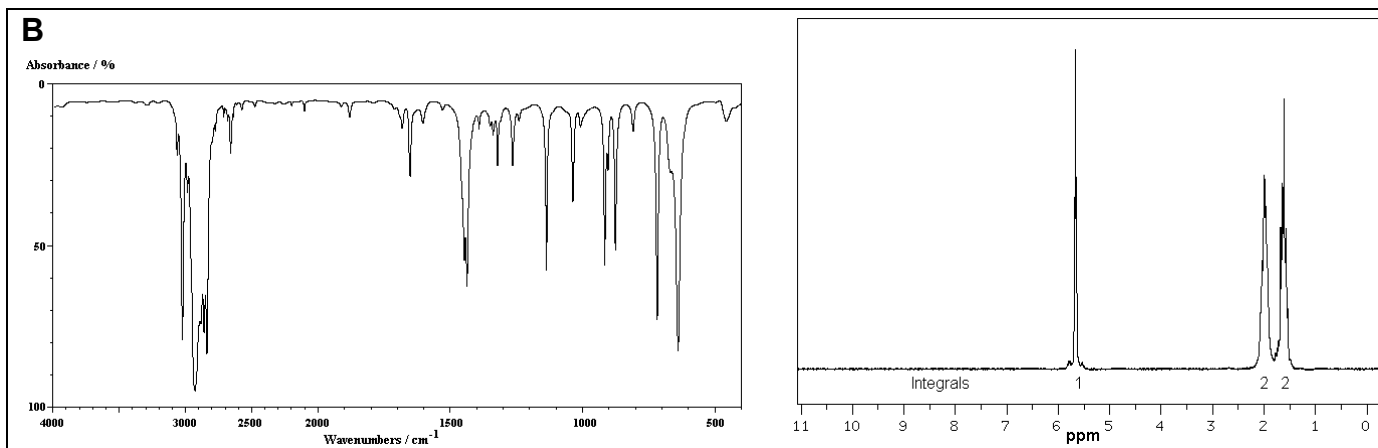
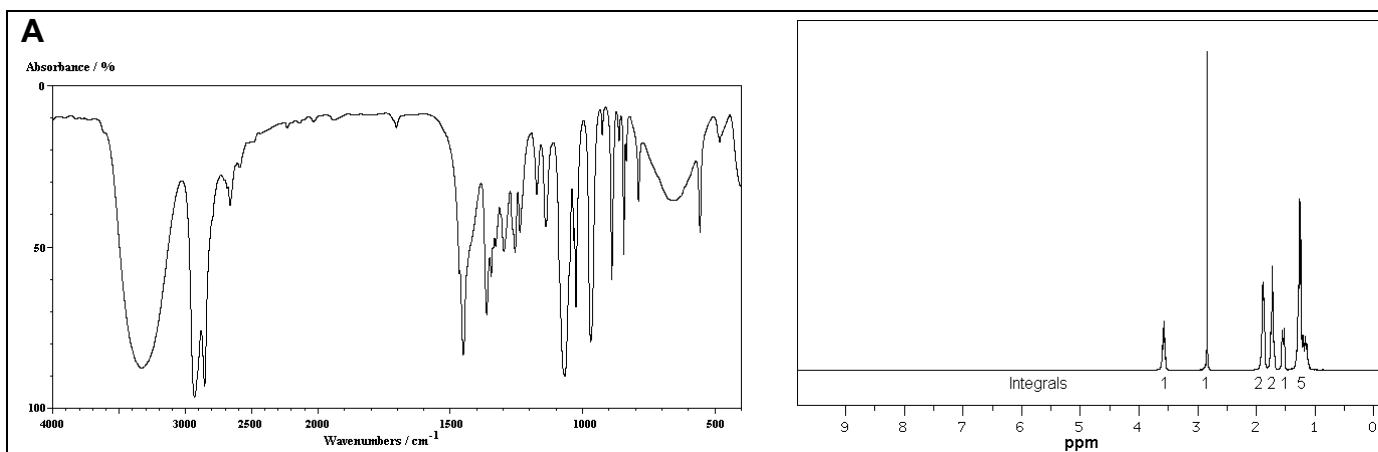


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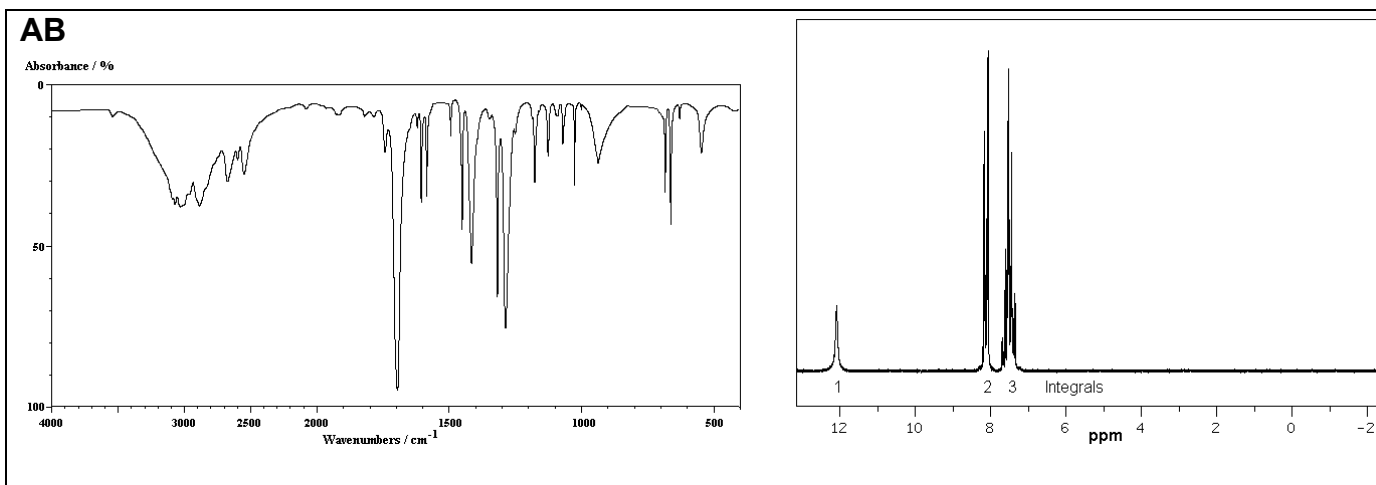
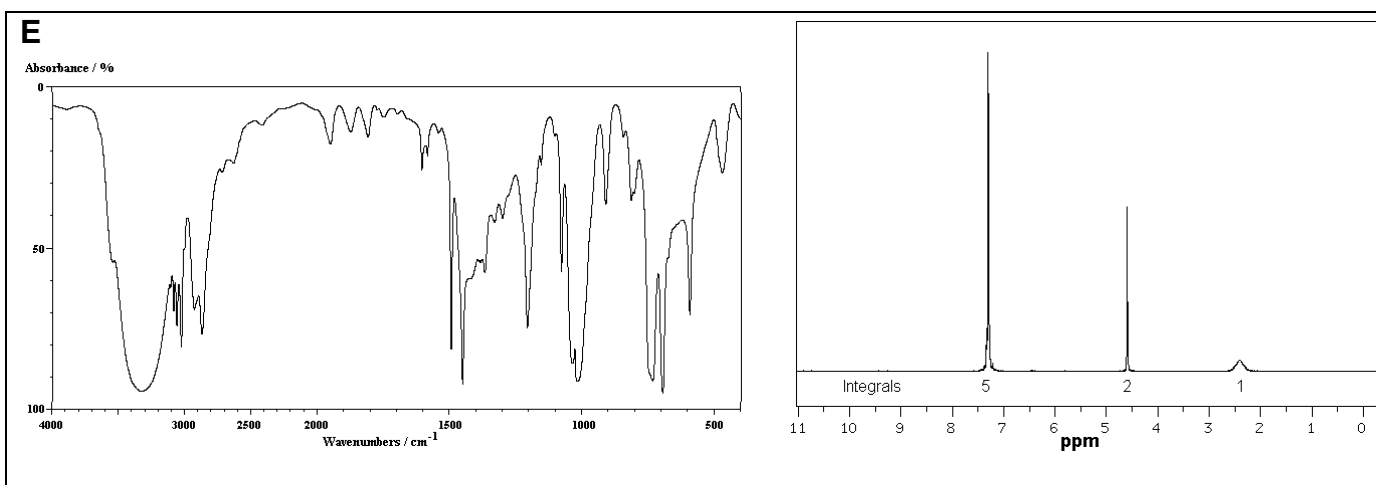
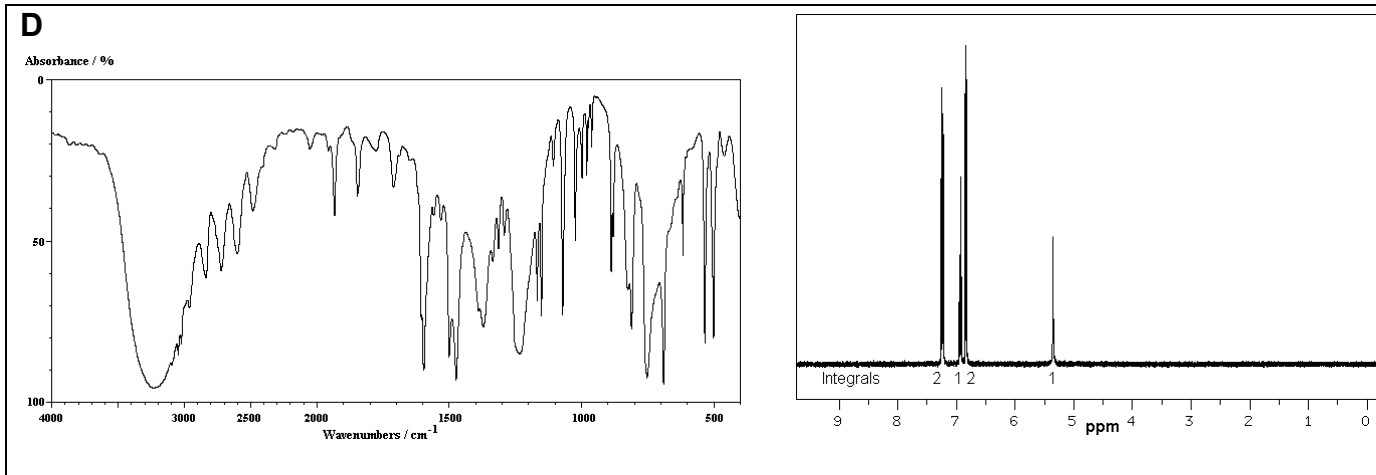
9% **PART 2: LABORATORY**

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

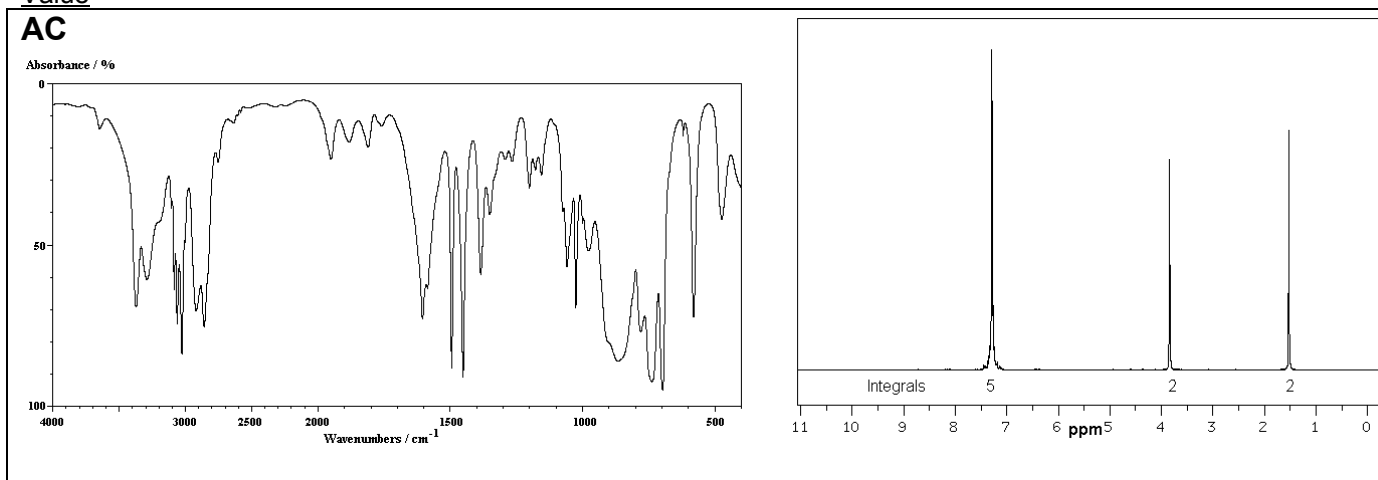
The IR and H-nmr of seven compounds **A-AC** are provided. For each of the questions **11-18**, select one of the compounds **A-AC** that best matches the functional group test results given.



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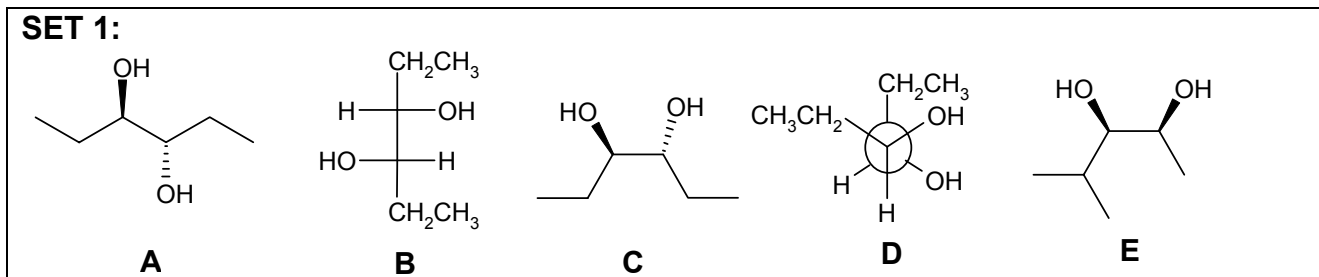
For each of the questions **11-18**, select one of the compounds **A-AC** that best matches the functional group test results given.

11. A compound that will react very rapidly in the Lucas test.
12. A compound that will give an orange precipitate when reacted with 2,4-dinitrophenylhydrazine *and* an orange solution with dichromate.
13. A compound that will give a violet coloured solution with aqueous ferric chloride.
14. A compound that reacts when heated with conc. H<sub>2</sub>SO<sub>4</sub> 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.
16. A compound that will react with bromine in chloroform to give a colourless solution.
17. A compound that dissolves in 10% aq. HCl.
18. A compound that dissolves in 5% aq. NaOH but not in 5% aq. NaHCO<sub>3</sub>.

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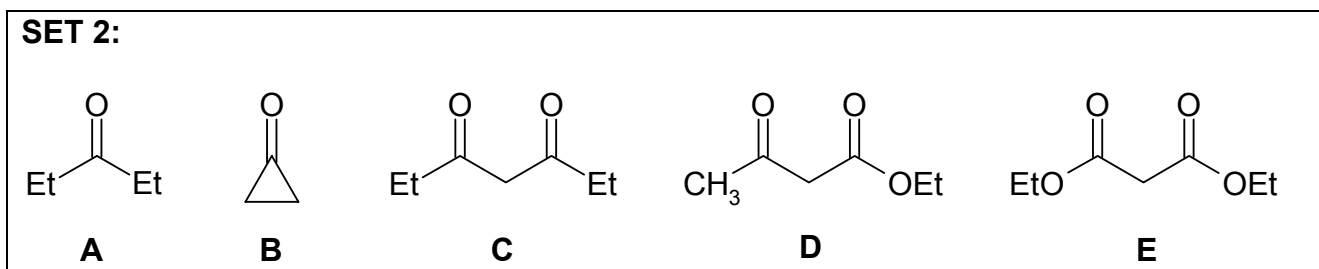
**ANSWER ANY TEN (10) OF THE QUESTIONS 19-29.**

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



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

19. Select all the meso compounds
20. Select two compounds that are a pair of enantiomers
21. Select two compounds that are a pair of diastereomers
22. Select a compound with an (S,S) configuration

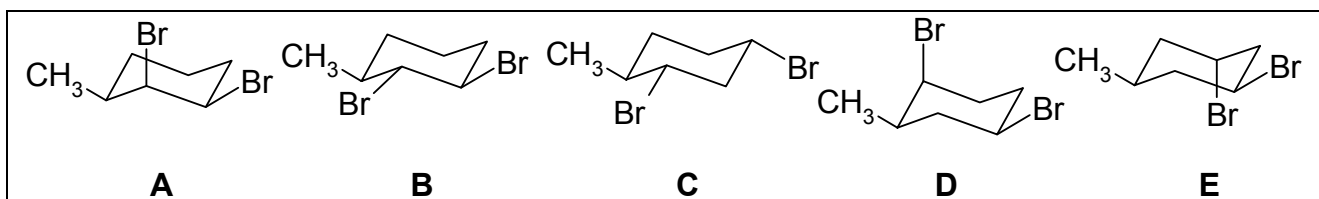


Answer questions **23-26** by selecting the compounds from **SET 2** above.

23. Which compound most readily forms a hydrate in water ?
24. Which compound has the most acidic hydrogen?
25. Select all the compounds that are **not** reduced by  $\text{NaBH}_4$  ?
26. Select all the  $\beta$ -ketoesters

**CONTINUED -->**

**SET 3**



Answer questions **27-29** by selecting the compounds from **SET 3** above.

27. Select all the cis-dibromides?
28. Which structure(s) could be made by reaction of 3-methylcyclohexene with Br<sub>2</sub>?
29. Select all the structures with two equatorial bromine atoms

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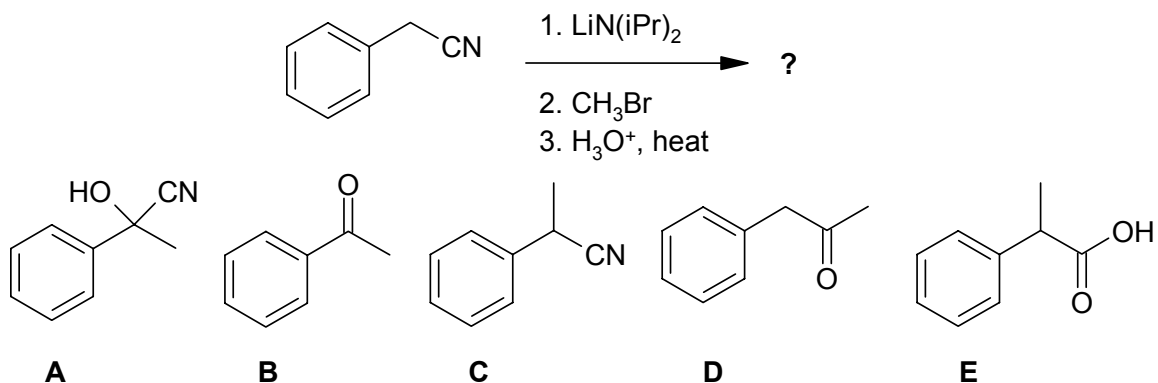


9% **PART 4: PRODUCTS OF SYNTHESIS**

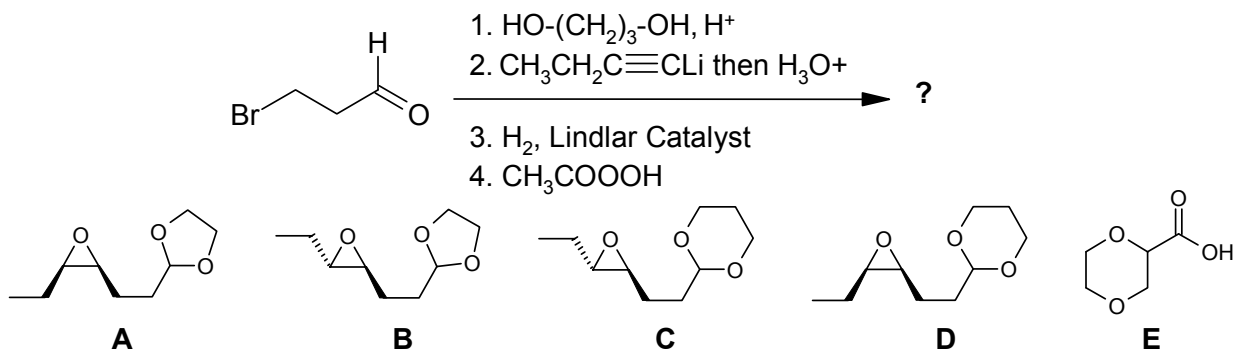
**ANSWER ANY SIX (6) OF QUESTIONS 30-36.**

For each of the questions **30-36** identify the **major product** obtained from each of the reaction sequences shown by selecting from the list of possible products provided.

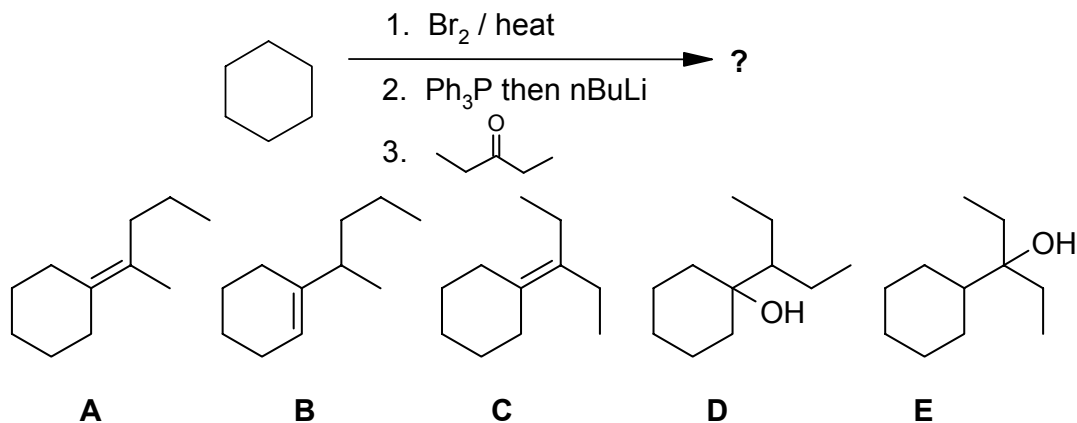
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31.

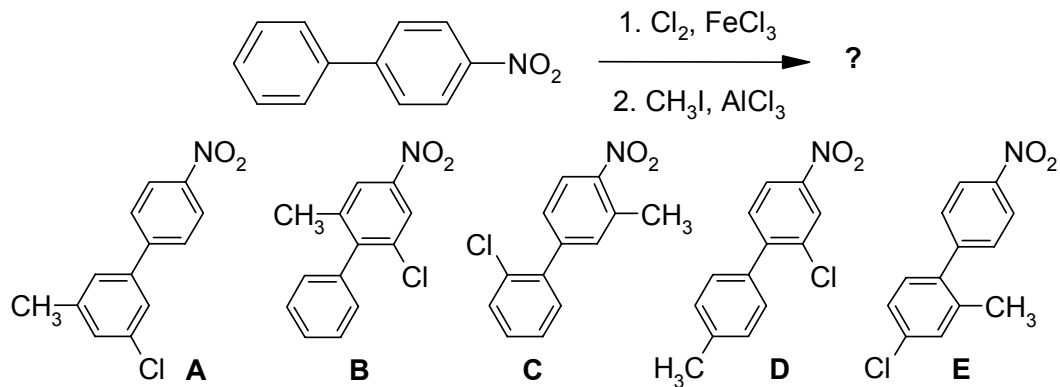


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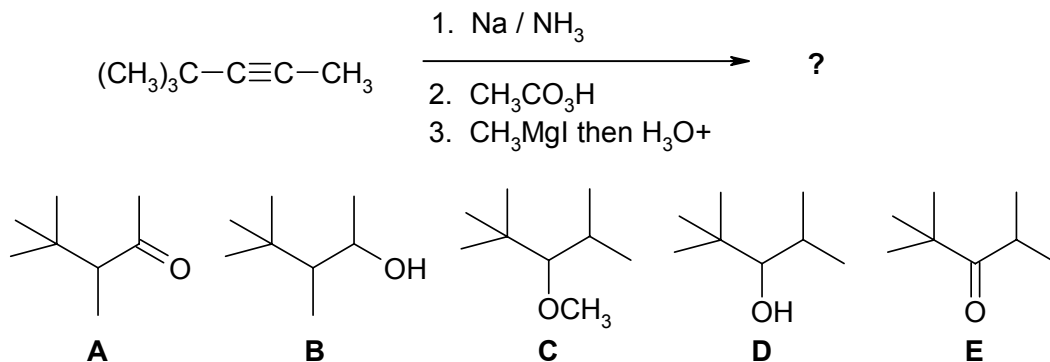


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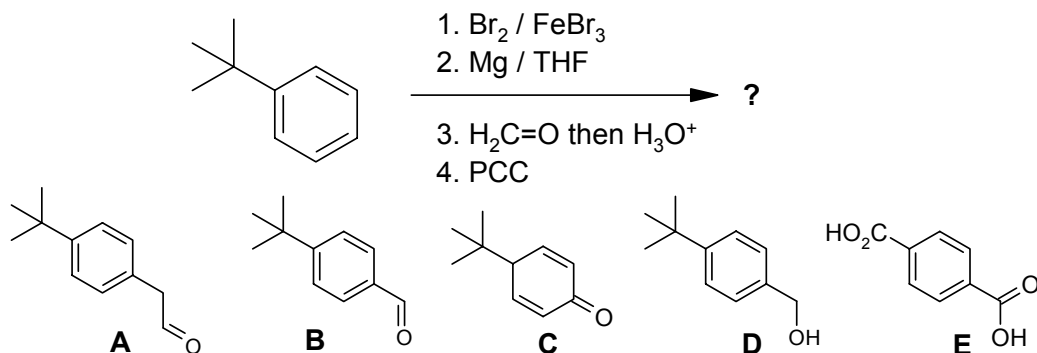
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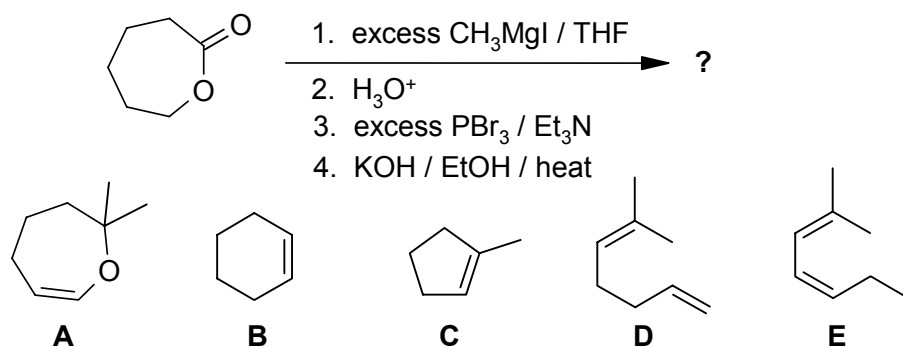
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35.



36.



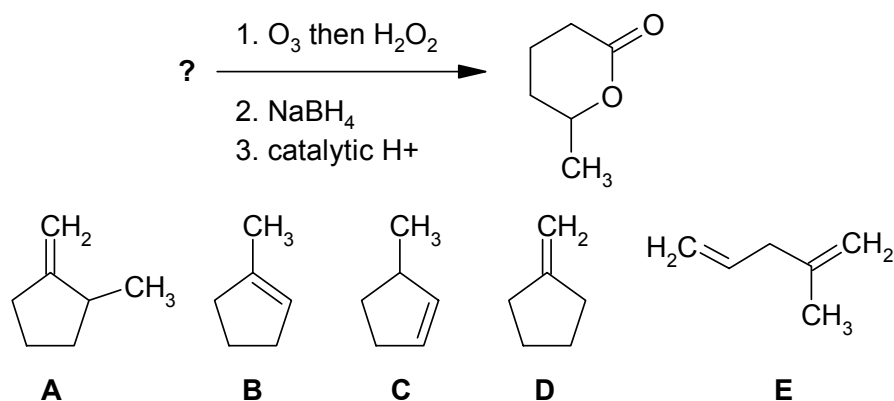
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**9% PART 5: STARTING MATERIALS FOR SYNTHESIS**

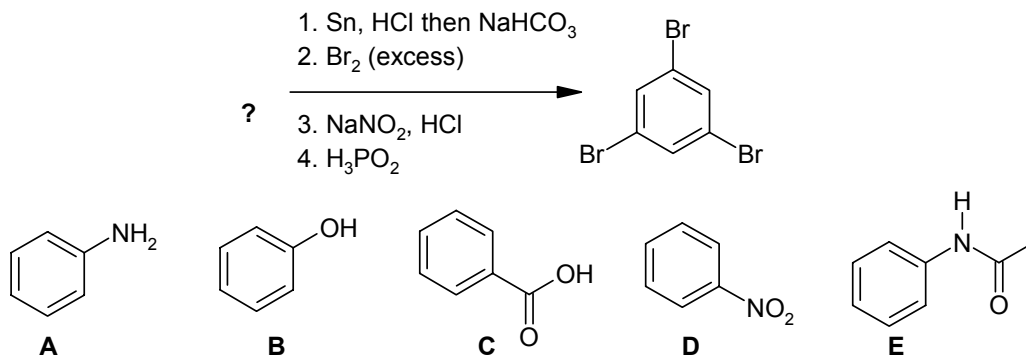
**ANSWER ANY SIX (6) OF QUESTIONS 37-43.**

For each of the questions **37-43**, choose the starting material from the selection provided that gives the product indicated via the transformations shown.

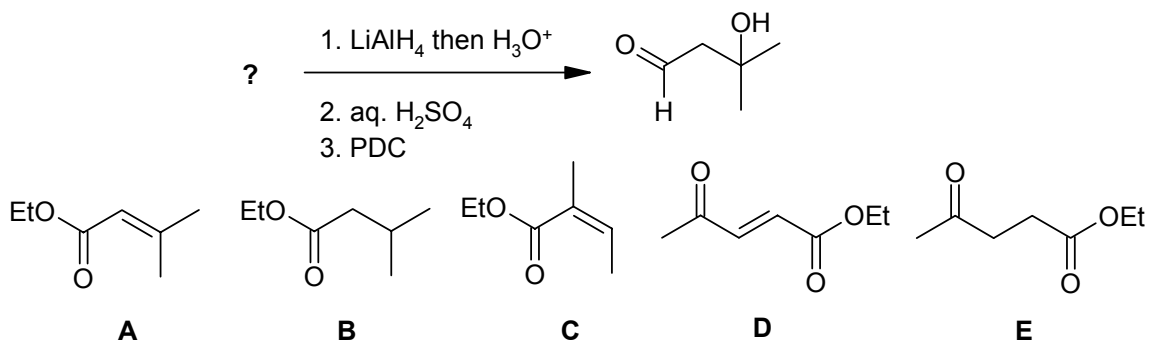
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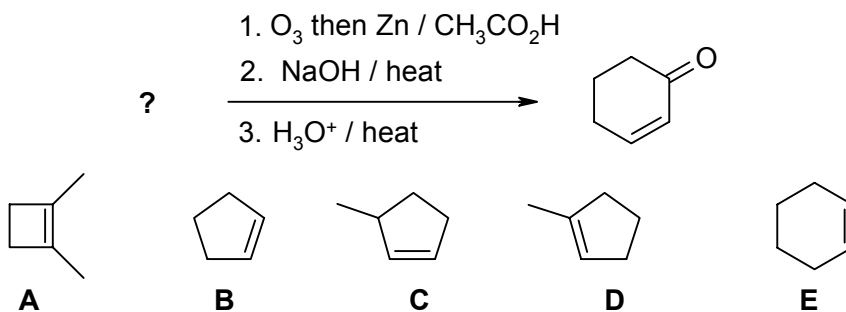


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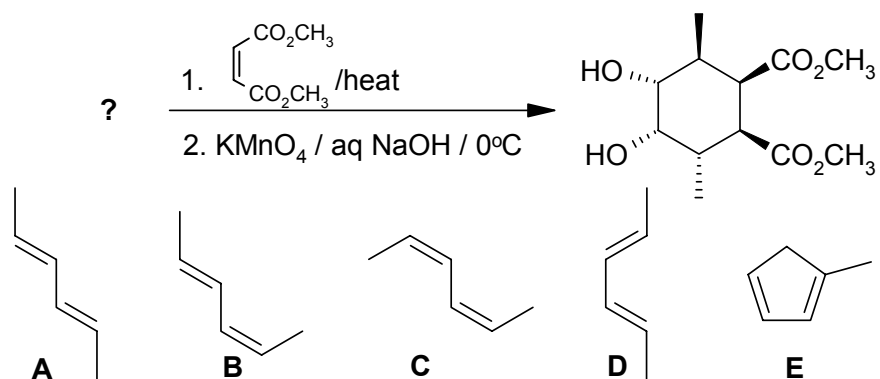


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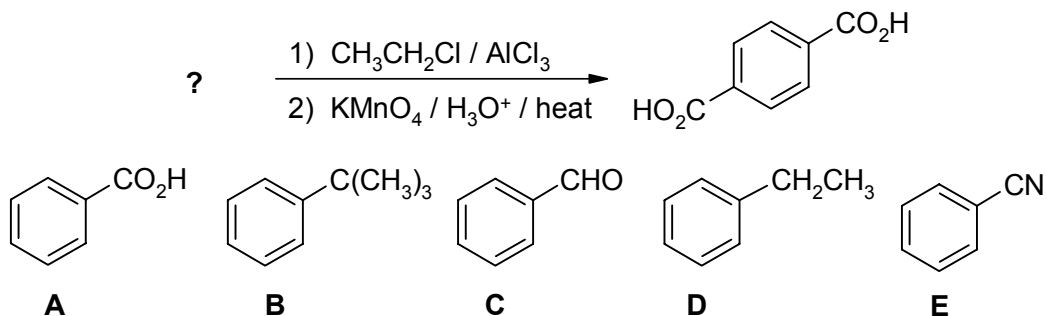
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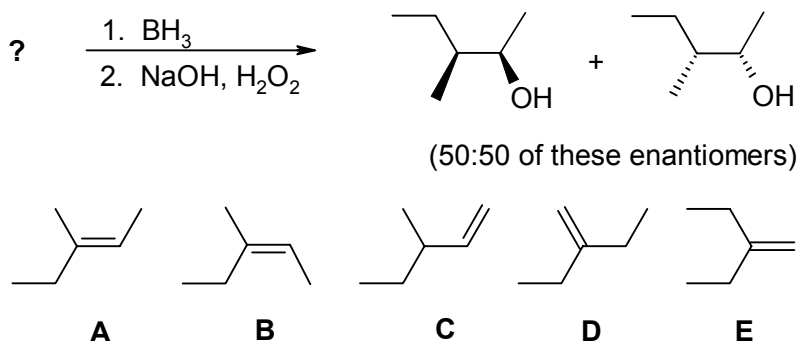
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42.



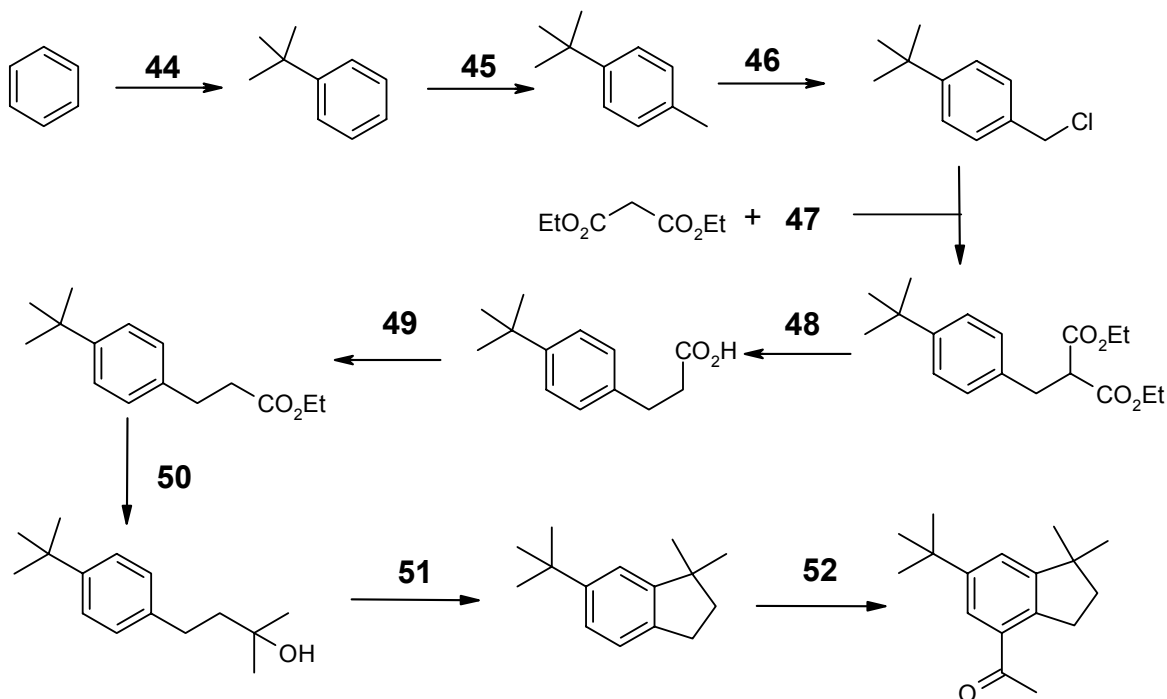
43.



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**9% PART 6: REAGENTS FOR SYNTHESIS****ANSWER ALL OF THE QUESTIONS 44 - 52**

The following reaction scheme shows a possible synthesis of **CELESTOLIDE**, a modern musk or perfume. 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 (assume heat can be used as and if required).



- |  |   |
|--|---|
| <b>A.</b> KOH / H <sub>2</sub> O   | <b>BD.</b> excess CH <sub>3</sub> MgI then H <sub>3</sub> O <sup>+</sup>          |
| <b>B.</b> NaOEt / EtOH   | <b>BE.</b> conc. HCl  |
| <b>C.</b> CH <sub>3</sub> ONa / CH <sub>3</sub> OH                       | <b>CD.</b> NCS or Cl <sub>2</sub>   |
| <b>D.</b> CH <sub>3</sub> CH <sub>2</sub> OH / H <sup>+</sup>            | <b>CE.</b> LiAlH <sub>4</sub> then H <sub>3</sub> O <sup>+</sup>                  |
| <b>E.</b> CH <sub>3</sub> OH / H <sup>+</sup>                            | <b>DE.</b> NaBH <sub>4</sub>  |
| <b>AB.</b> Excess CH <sub>3</sub> I                                      | <b>ABC.</b> Ph <sub>3</sub> P=CH <sub>2</sub>                                     |
| <b>AC.</b> conc. H <sub>2</sub> SO <sub>4</sub>                          | <b>ABD.</b> tBuOH / H <sup>+</sup>  |
| <b>AD.</b> BH <sub>3</sub> then aq. NaOH / H <sub>2</sub> O <sub>2</sub> | <b>ABE.</b> tBuCl / KOH   |
| <b>AE.</b> CH <sub>3</sub> Cl / AlCl <sub>3</sub>                        | <b>ACD.</b> H <sub>2</sub> O / HgSO <sub>4</sub> / H <sub>2</sub> SO <sub>4</sub> |
| <b>BC.</b> CH <sub>3</sub> COCl / AlCl <sub>3</sub>                      |   |

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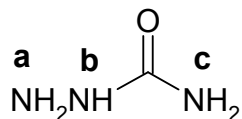
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**9% PART 7: EXPLANATION OF PHENOMENA****ANSWER ALL OF THE QUESTIONS 53 - 58.****CHOOSE THE SINGLE EXPLANATION THAT BEST RATIONALISES THE PHENOMENON INDICATED.**

53. When methylcyclohexene is reacted with borane in THF then aq. NaOH/ H<sub>2</sub>O<sub>2</sub> the major product of the reaction is 2-methylcyclohexanol. THIS IS BECAUSE:
- A. The reaction proceeds via the most stable carbocation.
  - B. The reaction proceeds via the most stable carboanion.
  - C. The reaction proceeds via the most stable radical.
  - D. Boron is less electronegative than H so the boron is the electrophile.
  - E. Boron is more electronegative than H so the boron is the nucleophile.
54. Primary amides undergo acid catalysed hydrolysis much more slowly than esters. THIS IS BECAUSE:
- A. RNH<sub>2</sub> is a better leaving group than ROH **AND** N is less electron donating than O.
  - B. RNH<sub>2</sub> is a better leaving group than ROH **AND** O is less electron donating than N.
  - C. ROH is a better leaving group than RNH<sub>2</sub> **AND** N is less electron donating than O.
  - D. ROH is a better leaving group than RNH<sub>2</sub> **AND** O is less electron donating than N.
  - E. Water is a weak nucleophile.
55. When 2-butyne reacts with excess HBr (dark, inert atmosphere) the major product is 2,2-dibromobutane. THIS IS BECAUSE:
- A. alkyl groups are weak electron donors.
  - B. bromine atoms can stabilise +ve charge by inductive effects.
  - C. bromine atoms can stabilise +ve charge by resonance effects.
  - D. the reaction is controlled by steric factors.
  - E. the reaction is controlled by radical stability.

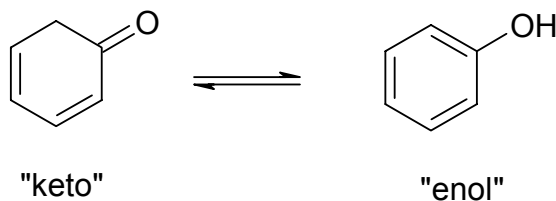
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56. Semicarbazoles react with aldehydes and ketones to give semicarbazones where one of the N atoms acts as nucleophile. WHICH NITROGEN, N, REACTS AND WHY ?



- A. N **a** because it is least sterically hindered on the N atoms  
B. N **a** because both N **b** and N **c** are involved in resonance with the carbonyl group  
C. N **b** because it is bonded to the most electron withdrawing groups  
D. N **c** because it is sterically unhindered  
E. N **c** because it is  $\text{sp}^3$  hybridised

57. An example of a keto-enol tautomerism is shown below. WHICH SIDE OF THE EQUILIBRIUM IS FAVOURED AND WHY ?



- A. The enol because they are generally more stable than the keto tautomers  
B. The enol because cyclic enols are generally more stable than the keto tautomers  
C. The enol because it has higher resonance energy  
D. The keto because they are generally more stable than the enol tautomers  
E. The keto because they are generally more nucleophilic

58. Carboxylic acids and alcohols are both acidic systems. WHICH ONE IS MORE ACIDIC AND WHY ?

- A. The acid because it has a lower pKa  
B. The acid because the carbonyl group is polarised  
C. The acid because the conjugate base is resonance stabilised  
D. The alcohol because the conjugate base is quite basic  
E. The alcohol because the conjugate base is resonance stabilised

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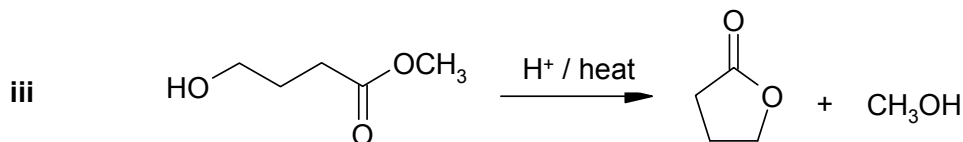
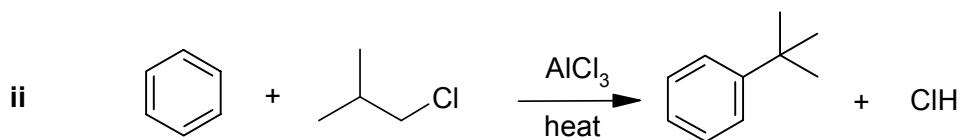
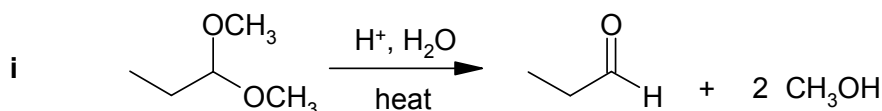
10% **PART 8: MECHANISM**

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

WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED.

NO REAGENTS OTHER THAN THOSE ALREADY SHOWN ARE REQUIRED FOR THESE QUESTIONS.

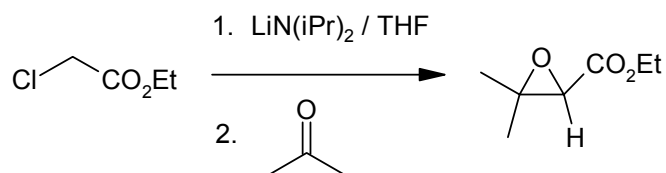
(4) **PART A: Use a curly arrow mechanism to explain ONE of the following transformations :**



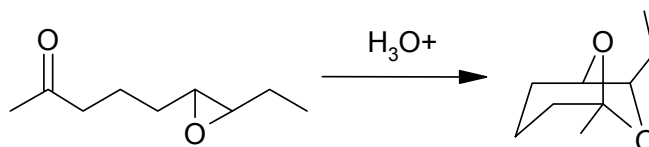
(6) **PART B : Use a curly arrow mechanism to answer ONE of the following :**

i. When an  $\alpha$ -halo ester is reacted with a strong base, then an aldehyde or ketone is added, an  $\alpha,\beta$ -epoxy ester is obtained, see right. **Propose a mechanism for this reaction**

(FYI : it's a Darzen's condensation).



ii. **Provide a detailed mechanism** showing the steps for the final part of the synthesis of BREVICOMIN, a pheromone of the Western Pine Beetle:



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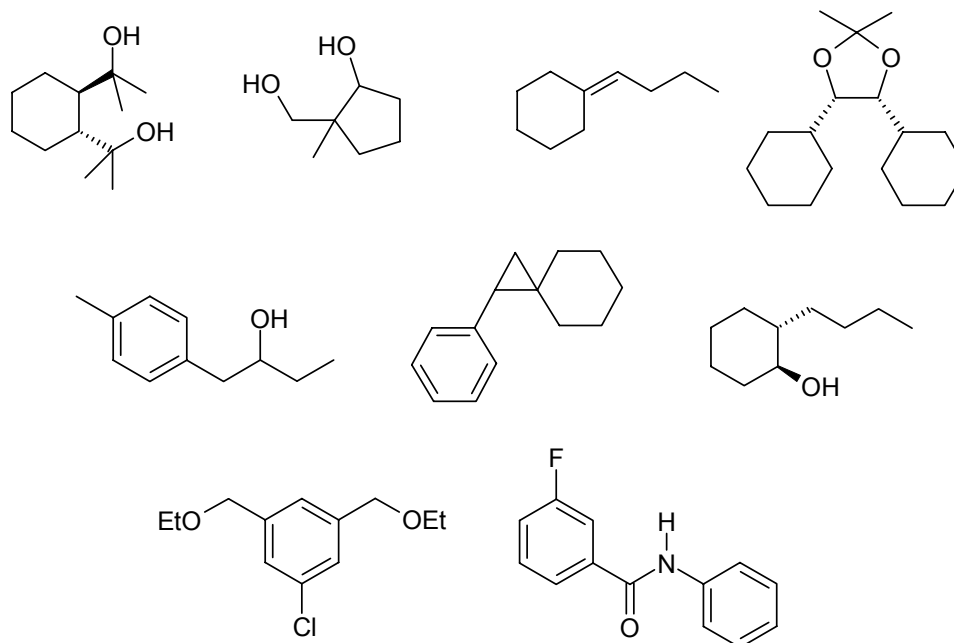


12% **PART 9: TOTAL SYNTHESIS**

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

**DO NOT SHOW MECHANISMS**



**Permitted Starting Materials and Reagents\***

- Any inorganic materials
- Any organic compounds with no more than FOUR carbons
- triphenyl phosphine
- Either of the following:



\* any materials that contribute carbon atoms to the target must come from this allowed list.

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**11% PART 10: STRUCTURE DETERMINATION**

**WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED**

Compound **A** was found to have elemental analysis for C, H, N that showed 47.35% C and 10.60% H, strong IR absorptions at 3350 (broad) and 1063  $\text{cm}^{-1}$  and  $^{13}\text{C}$  nmr spectra peaks at 62 and 34 ppm. When **A** was reacted with  $\text{K}_2\text{Cr}_2\text{O}_7$  in aq. sulfuric acid, **B** was obtained, IR absorptions 3000 (broad) and two bands near 1710  $\text{cm}^{-1}$ . **B** was then heated in ethanol with an acid catalyst to give **C** as a sweet smelling liquid. **C** was found to have  $^1\text{H}$  nmr spectra peaks at 4.2 (2H, quartet), 3.4 (1H, singlet) and 1.4 ppm (3H, triplet) IR absorptions at 1730  $\text{cm}^{-1}$  (strong).

Compound, **D**,  $\text{C}_5\text{H}_8$ , was found to have major IR absorptions at 3086 and 1598  $\text{cm}^{-1}$  and had 5 peaks in the  $^{13}\text{C}$  nmr spectra (142, 140, 117, 114, and 18 ppm). When **D** was reacted with bromine at 40°C, two isomeric products were obtained, the major product was **E**,  $\text{C}_5\text{H}_8\text{Br}_2$ . Subsequent reaction of **E** with  $\text{H}_2 / \text{Pd}$  gave **F**,  $\text{C}_5\text{H}_{10}\text{Br}_2$

**C** was treated with one equivalent of sodium ethoxide in ethanol to which **F** was then added. The reaction was refluxed for an hour then a second equivalent of sodium ethoxide was added and the reflux was continued. After cooling and neutralising the reaction and a normal work-up, **G** was obtained as the major product,  $\text{C}_{12}\text{H}_{20}\text{O}_4$ , **G** was then heated with aq. NaOH, during the reaction a gas was evolved and 3-methylcyclopentanecarboxylic acid was isolated as the major product.

Only **F** and **G** are chiral.

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

**(1.5)** Show the mechanism of how **E** is formed from **D**

**THE END**