

THE UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

FINAL EXAMINATION

CHEMISTRY 353

April 23rd, 2004

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**.

**PART 1: RELATIVE PROPERTIES**

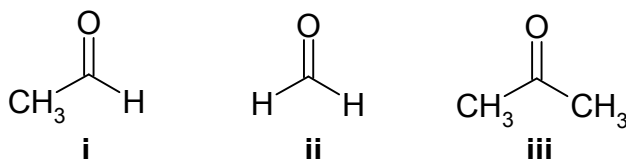
**9% ANSWER ANY SIX (6) OF QUESTIONS 1-10.**

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

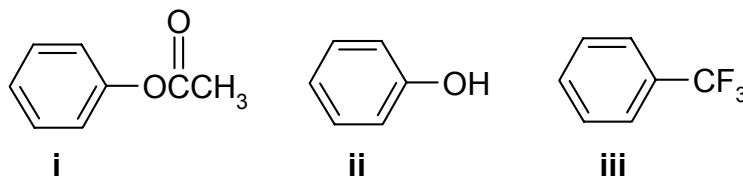
Use the following code to indicate your answers:

<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>

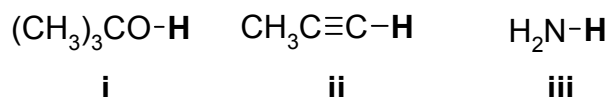
1. The relative reactivity towards  $\text{LiAlH}_4$  in diethyl ether of each of the following:



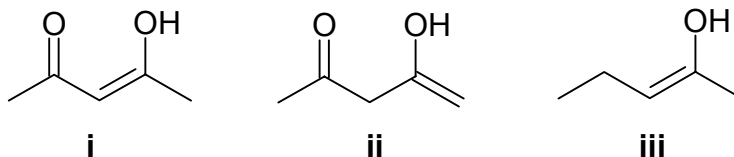
2. The relative rate of reaction towards  $\text{Br}_2 / \text{FeBr}_3$  of each of the following:



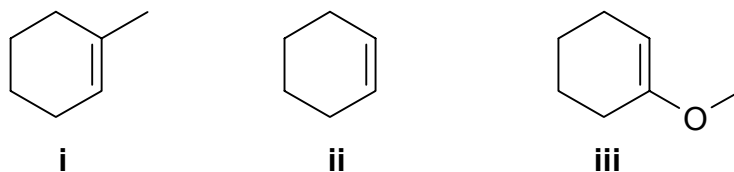
3. The relative acidity of the indicated **H** in each of the following:



4. The relative stability of the following enols:



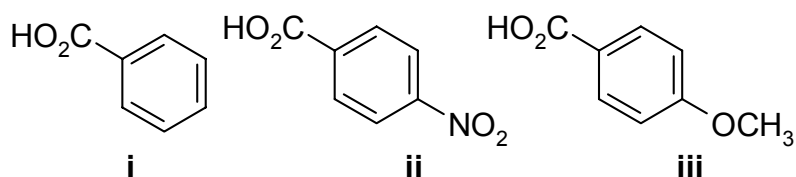
5. The relative reactivity of each of the following towards reaction with  $\text{HBr}$  :



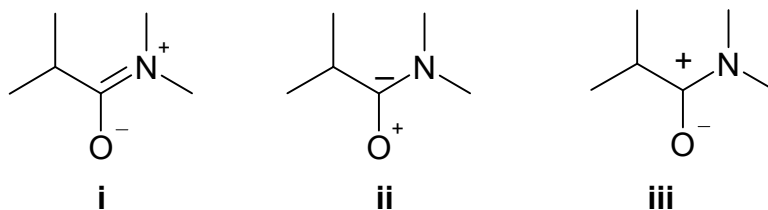
Use the following code to indicate your answers:

<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>

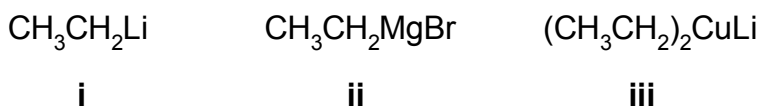
6. The relative acidity of each of the following :



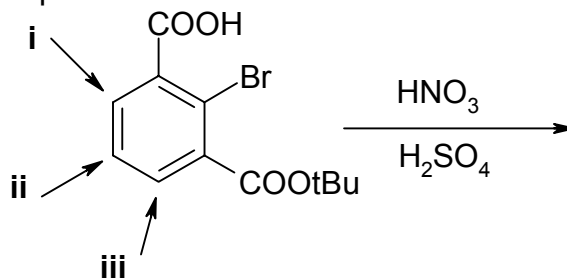
7. The relative importance of the following resonance contributors:



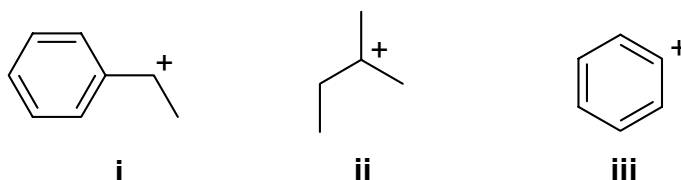
8. The relative reactivity of the following towards reaction with 2-propanone :



9. The relative yields of the products from the nitration reaction of the following with  $\text{HNO}_3$  /  $\text{H}_2\text{SO}_4$  at each of the positions indicated:



10. The relative stability of the following carbocations :



Value

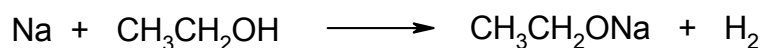
**PART 2: LABORATORY****10% ANSWER ALL TEN (10) OF THE FOLLOWING TRUE / FALSE QUESTIONS 11-20.**

**Questions 11-20** are based on the laboratory component of Chem 353. In each case decide whether the statements are true or false. If the statement is true select "**A**", if it is "false" then select "**B**"

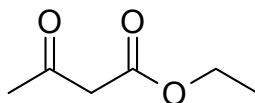
**Questions 11-16** are from the barbiturate synthesis experiment.

11. Diethyl malonate has a pKa = 23.

12. The balanced equation for the reaction of sodium with ethanol is :



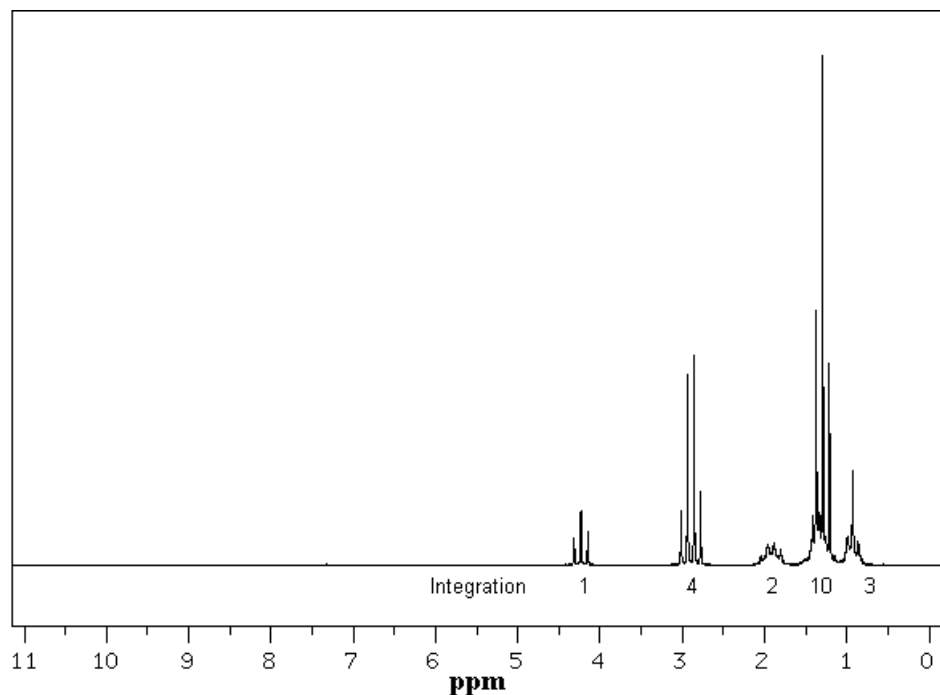
13. Diethyl malonate has the structure shown below :



14. Potassium iodide acts as a catalyst because it reacts with the diethyl malonate to create a better leaving group.

15. Ethoxide is chosen as the base rather than methoxide because it is a stronger base.

16. The H-nmr spectra shown below is that of diethyl n-butylmalonate :



**Questions 17-20** are from the identification of unknowns experiment :

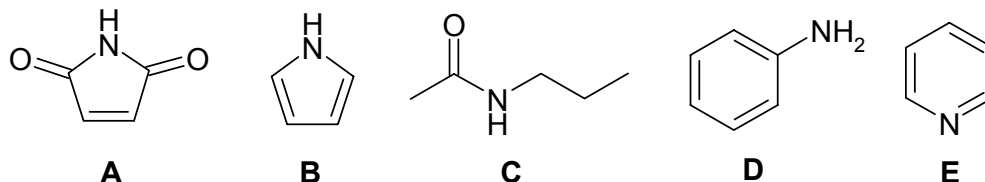
17. 2,4-dinitrophenylhydrazine reacts with the carbonyl group in aldehydes, ketones, carboxylic acids and esters to give a yellow to red precipitate.
18. The iodoform test is used to detect the presence of methyl ketones.
19. Phenols can be detected using the Lucas test, *i.e.* the reaction with HCl / ZnCl<sub>2</sub>, by the formation of a secondary clear layer of the aryl chloride.
20. Tollen's reagent using silver (I) reacts with aldehydes to form silver (0) which often forms on the sides of the test tube in a silver mirror.

**PART 3: STRUCTURE AND PROPERTIES**

**10 % ANSWER ALL of the questions 21-30.**

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

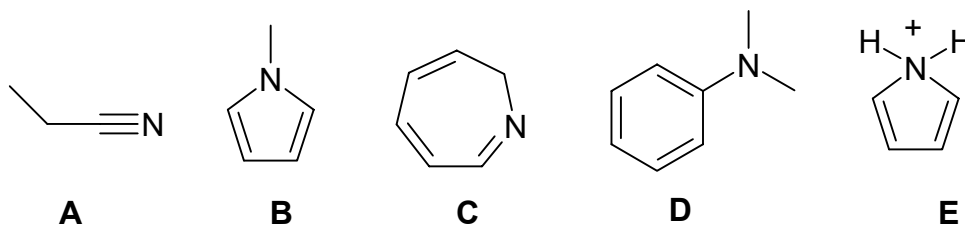
**SET 1:**



**Answer questions 21-24 by selecting the compounds from SET 1 above.**

21. Which compound(s) is (are) amides?
22. In which compound(s) is (are) the nitrogen  $sp^2$  hybridized?
23. Which compound(s) is (are) aromatic?
24. Which compound has the most acidic hydrogen?

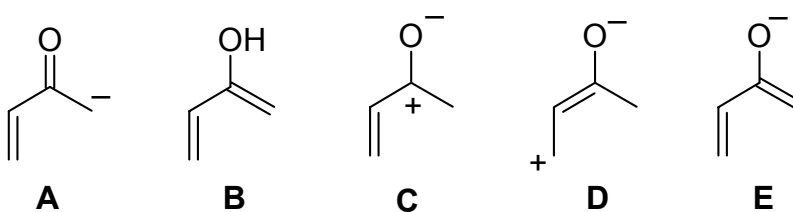
**SET 2:**



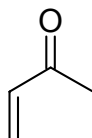
**Answer questions 25-27 by selecting the compounds from SET 2 above.**

25. In which compound(s) is (are) the nitrogen  $sp^2$  hybridized?
26. Which compound(s) is (are) aromatic?
27. Which compound has the most acidic hydrogen?

**SET 3**



**Answer questions 28-30 by selecting the compounds from SET 3 above**



2-but-3-enone

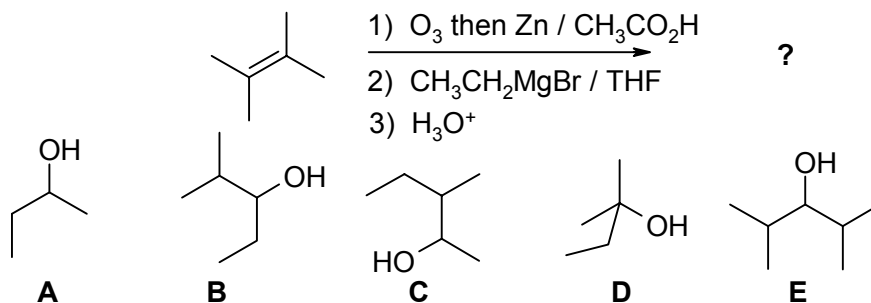
28. Which structure(s) is (are) resonance contributors of 2-but-3-enone?
29. Which structure(s) is (are) tautomers of 2-but-3-enone?
30. Which structure(s) is (are) represent the enolate 2-but-3-enone?

**PART 4: PRODUCTS OF SYNTHESIS**

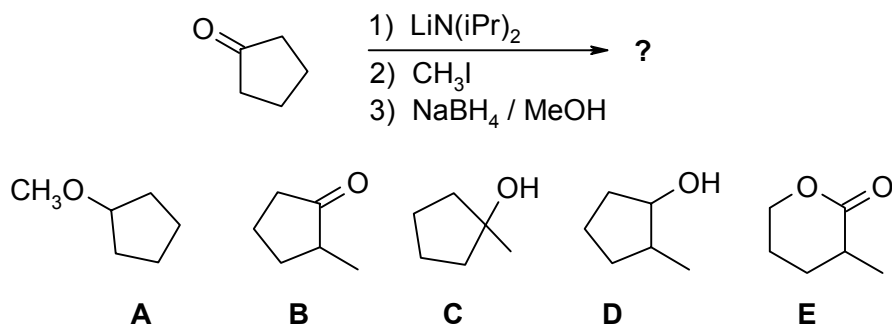
**10% ANSWER ANY FIVE (5) OF QUESTIONS 31-37.**

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.

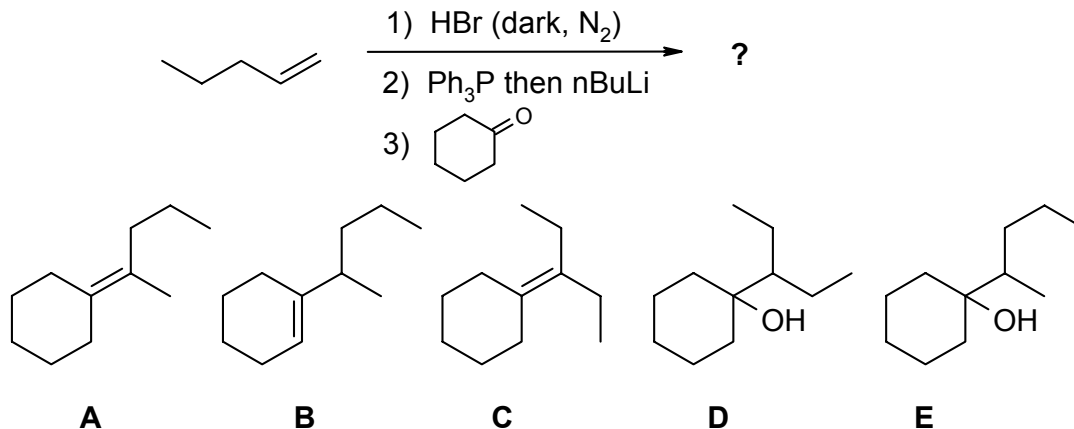
31.



32.

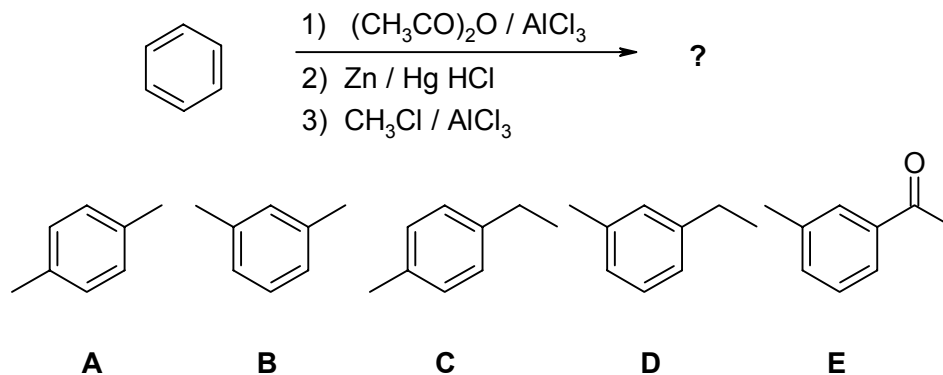


33.

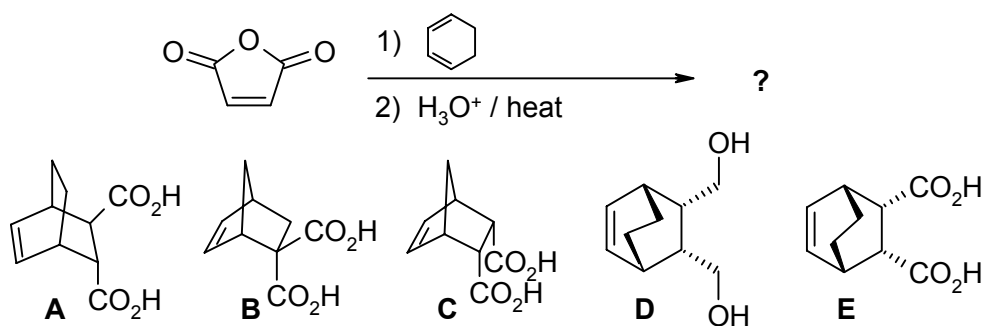




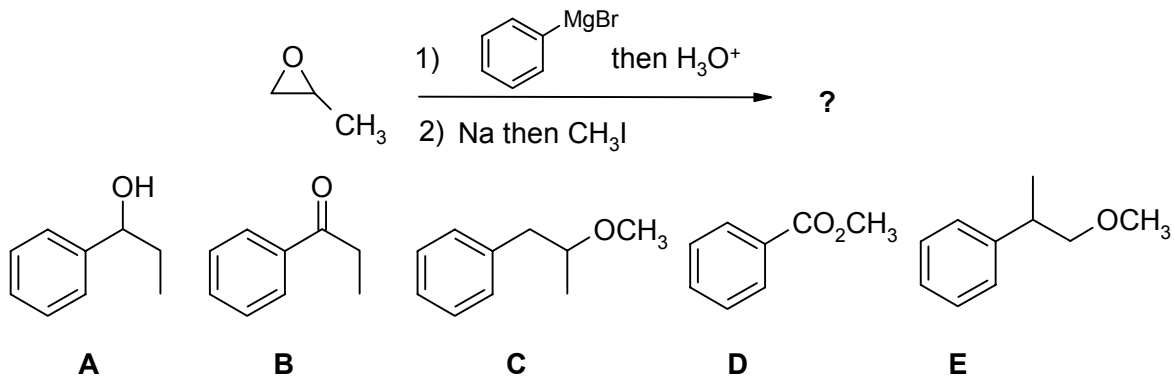
34.



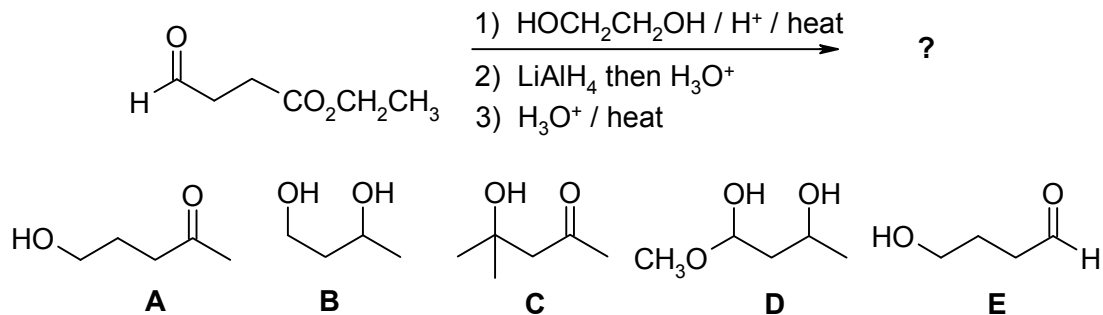
35.



36.



37.

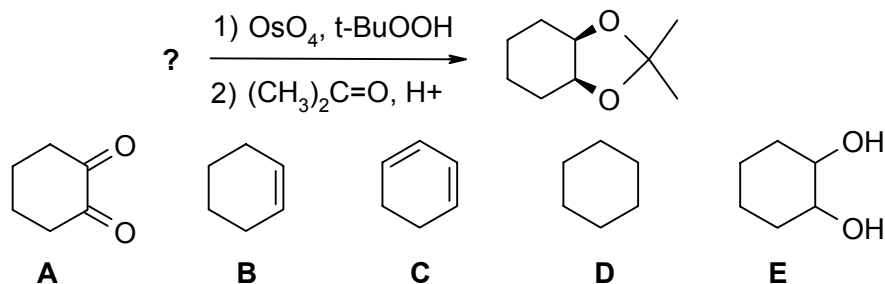


**PART 5: STARTING MATERIALS FOR SYNTHESIS**

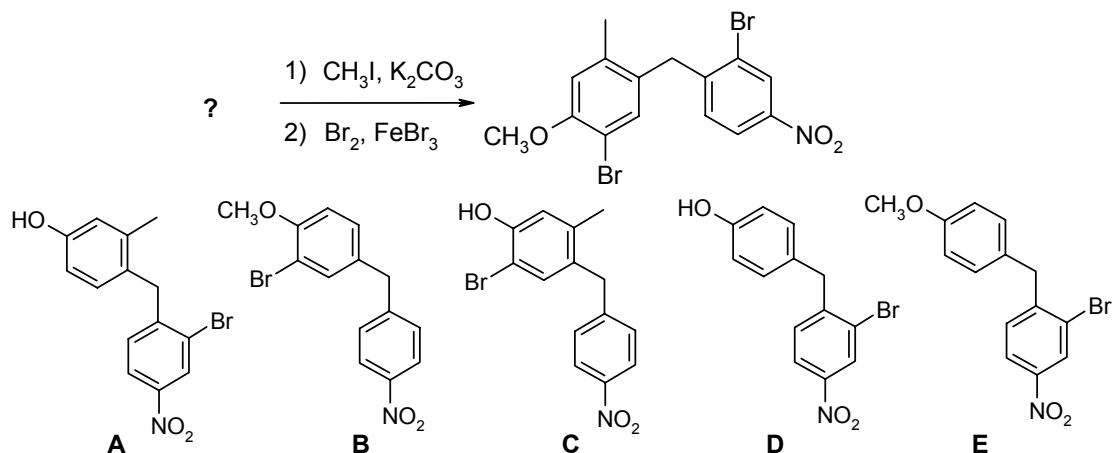
**10% ANSWER ANY FIVE (5) OF QUESTIONS 38-44.**

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

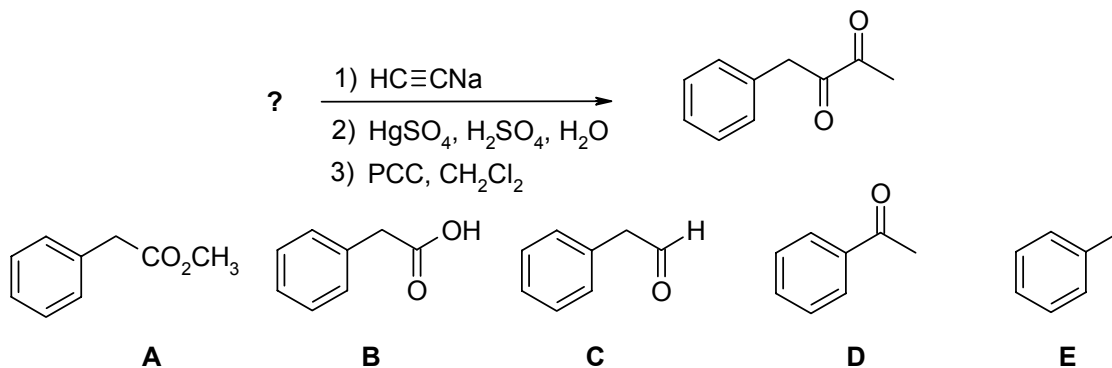
38.



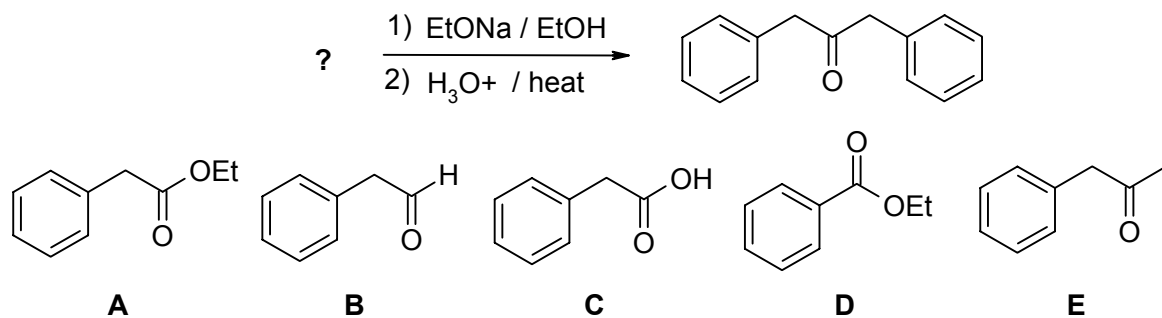
39.



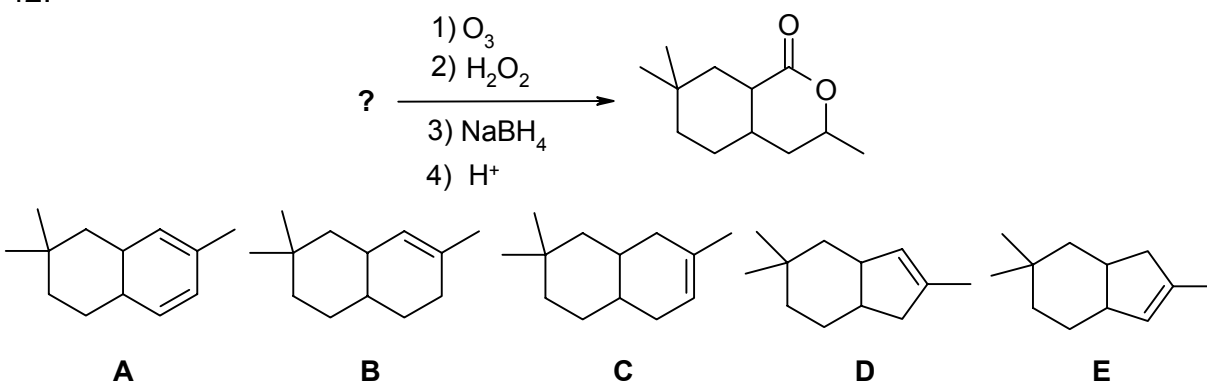
40.



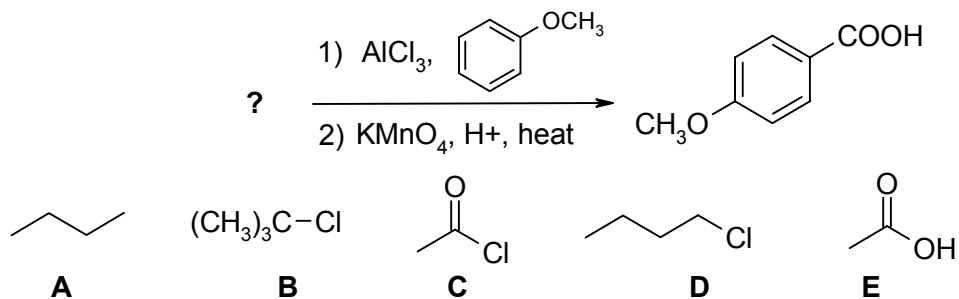
41.



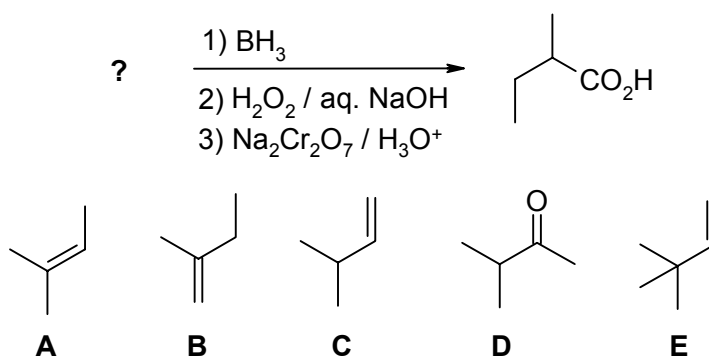
42.



43.

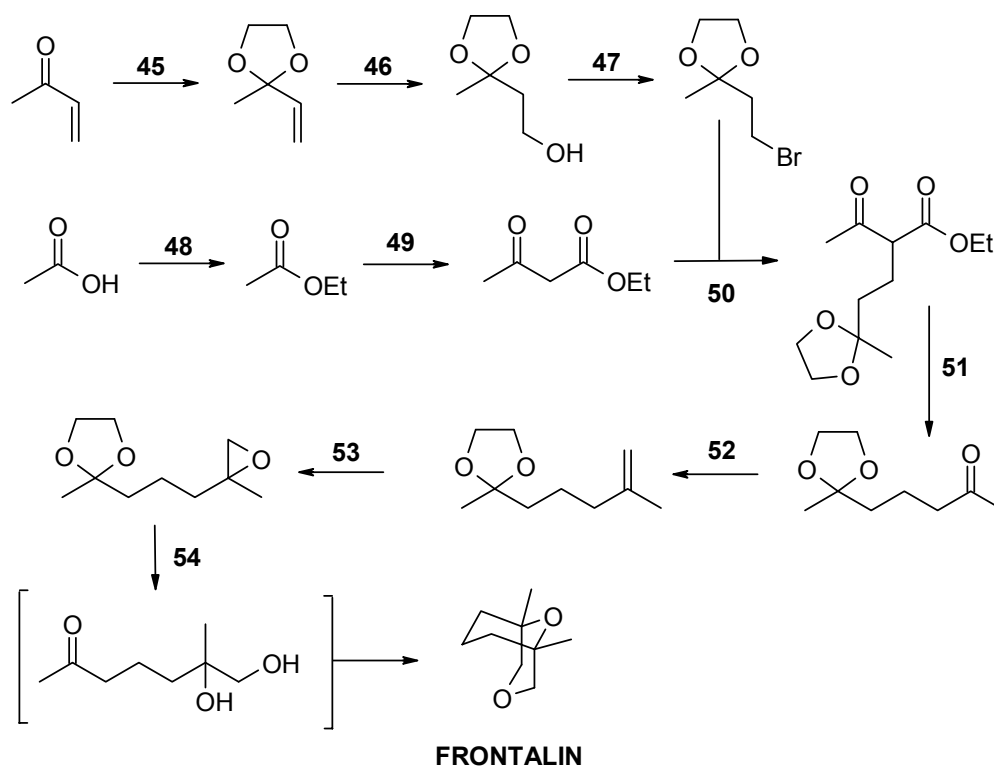


44.



**PART 6: REAGENTS FOR SYNTHESIS****10% ANSWER ALL OF THE QUESTIONS 45 - 54**

The following reaction scheme shows a possible synthesis of **FRONTALIN**, a pheromone of the Southern Pine Beetle. 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. $(\text{CH}_3)_2\text{C}=\text{O} / \text{H}^+$	AE. $\text{CH}_3\text{MgBr} / \text{THF}$ then $\text{H}_3\text{O}^+$
B. $\text{CH}_3\text{CO}_2\text{H}$	BC. $\text{BH}_3$ then aq. $\text{NaOH} / \text{H}_2\text{O}_2$
C. $\text{CH}_3\text{CO}_3\text{H}$	BD. Conc. $\text{H}_2\text{SO}_4 / \text{heat}$
D. $\text{HOCH}_2\text{CH}_2\text{OH} / \text{H}^+$	BE. $\text{H}_3\text{O}^+ / \text{heat}$
E. $\text{NaBr} / \text{DMSO}$	CD. $\text{NaOH} / \text{H}_2\text{O} / \text{heat}$
AB. $\text{PBr}_3 / \text{Et}_3\text{N}$	CE. $\text{LiAlH}_4$ then $\text{H}_3\text{O}^+$
AC. $\text{Ph}_3\text{P}=\text{CH}_2$	DE. $\text{NaOEt} / \text{EtOH}$
AD. $\text{PPh}_3$ then $\text{BuLi}$	ABC. $\text{EtOH} / \text{H}^+ / \text{heat}$

**PART 7: EXPLANATION OF PHENOMENA**

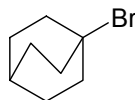
**8% ANSWER ALL OF THE QUESTIONS 55 - 58.**

Choose the **SINGLE** explanation that **BEST** describes the phenomenon indicated.

55. When acetone is reacted with 1,2-ethanediol in the presence of acid, the yield of the product increases if water is removed during the reaction. THIS IS BECAUSE:

- A. The product is unstable in the presence of water.
- B. The product is formed under equilibrium conditions.
- C. The reaction is under kinetic control.
- D. The starting materials are oxidised in the presence of water.
- E. Rearrangements occur in the presence of water.

56. The tertiary alkyl bromide shown below undergoes solvolysis very, very slowly. THIS IS BECAUSE:



- A. The alkyl groups stabilize the bromide.
- B. The alkyl groups make the bromide too sterically hindered.
- C. The cyclic structure prevents the formation of a planar carbocation.
- D. Tertiary alkyl bromides prefer to react under SN2 conditions.
- E. Water is too weak a nucleophile.

57. The pKa of 1,3-cyclopentadiene is 15, whereas that for cyclopentane is > 50. THIS IS BECAUSE

- A. Cyclopentadiene is aromatic.
- B. Cyclopentane is non-aromatic.
- C. Cyclopentadiene is a 4  $\pi$  anti-aromatic system.
- D. The conjugate base of cyclopentane is a 2  $\pi$  aromatic system.
- E. The conjugate base of cyclopentadiene is a 6  $\pi$  aromatic system.

58. Primary alcohols are easily oxidized to carboxylic acids with  $\text{Na}_2\text{Cr}_2\text{O}_7$ ,  $\text{H}_2\text{SO}_4$ ,  $\text{H}_2\text{O}$ . On the other hand, oxidation of primary alcohols with PCC,  $\text{CH}_2\text{Cl}_2$  stops at the aldehyde stage. THIS IS BECAUSE:

- A. PCC,  $\text{CH}_2\text{Cl}_2$  is a milder and less reactive oxidising reagent.
- B. Water is required for the oxidation to proceed to the carboxylic acid.
- C. PCC is not a chromate reagent and therefore cannot do the second oxidation step.
- D. Aldehydes are insoluble in  $\text{CH}_2\text{Cl}_2$ .
- E. The oxidation step is an example of an E2 elimination.

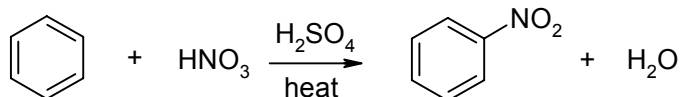
**PART 8: MECHANISM**

**10% ANSWER TWO(2) QUESTIONS IN THIS SECTION, ONE FROM A AND ONE FROM B**

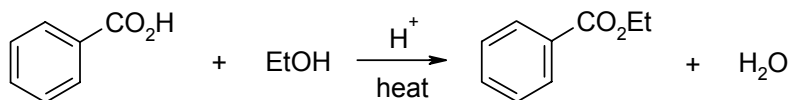
**WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED  
NO other reagents are required for any of these questions.**

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

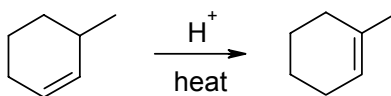
i.



ii.

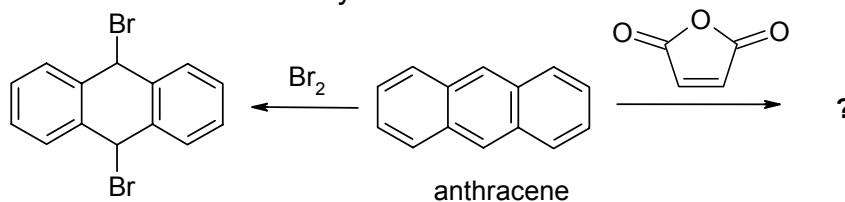


iii.

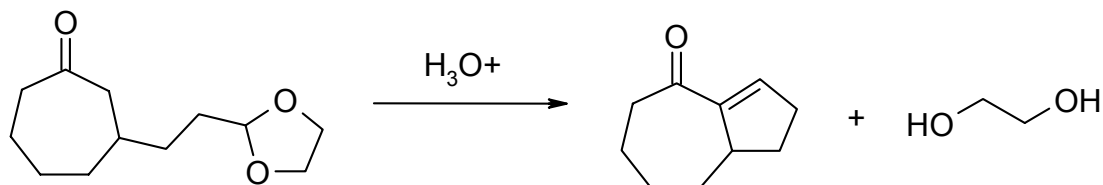


**(6) B : Use curly arrow mechanisms and a *short* paragraph (max. 25 words) to answer ONE of the following :**

i. Account for the reaction of anthracene with bromine shown below, and hence predict the outcome of the reaction with maleic anhydride :



ii. Provide a detailed mechanism showing all the steps for the following multi-step transformation:

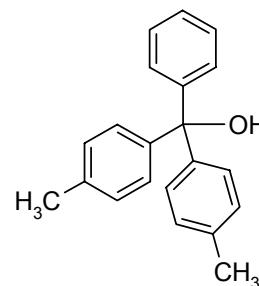
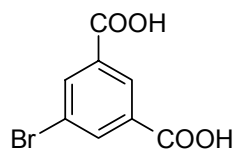
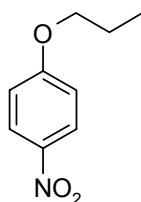
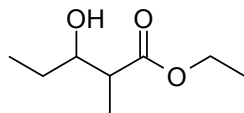
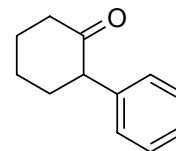
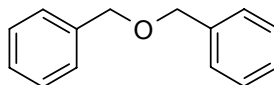
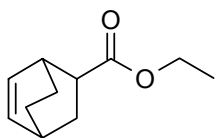
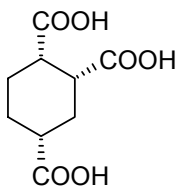


## PART 9: TOTAL SYNTHESIS

**WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED**

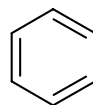
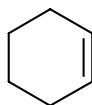
**12%** Design an efficient synthesis for any **THREE (3)** of the following target molecules using any of the starting materials and reagents given in the accompanying list. Show the product of each step and clearly identify the required reagents.

**DO NOT SHOW MECHANISMS**



### Permitted Starting Materials and Reagents\*

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



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

**PART 10: STRUCTURE DETERMINATION**

**11% WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED**

Compound, **A** is achiral, has elemental analysis 71.95% C and 12.08% H, IR absorption at  $3400\text{ cm}^{-1}$  (strong broad) and has 4 peaks in the  $^{13}\text{C}$  nmr spectra (70, 36, 26 and 24 ppm).

When **A** was heated with concentrated sulphuric acid, hydrocarbon **B** was obtained. **B** was found to have IR absorption at  $1604\text{ cm}^{-1}$  and has 3 peaks in the  $^{13}\text{C}$  nmr spectra (127, 25 and 23 ppm). **B** was then reacted with  $\text{O}_3$  followed with Zn / acid work-up to give **C**. **C** was found to have IR absorptions at  $1730\text{ cm}^{-1}$  (strong) and **C** reacted with 2,4-DNP to give a yellow precipitate.

When **C** was dissolved in ethanol and refluxed for 24hrs with sodium ethoxide, **D** was obtained as the major product. **D** was found to have IR absorptions  $1710\text{ cm}^{-1}$  (strong),  $1620\text{ cm}^{-1}$  and has 6 peaks in the  $^{13}\text{C}$  nmr spectra (195, 150, 141, 39, 33, and 25 ppm). **D** also reacted with 2,4-DNP, giving a precipitate that was orange.

Reaction of **D** with the ylid formed by the reaction of triphenyl phosphine, iodoethane and n-butyl lithium gave hydrocarbon **E**. Catalytic hydrogenation of **E** using excess  $\text{H}_2/\text{Pt}$  gave (1-propyl)cyclopentane. When **E** was heated with *cis*-dimethyl butendioate (otherwise known as dimethyl maleate), the major product was a bicyclic compound **F**. When **F** was reacted with lithium aluminium hydride in THF, followed by a dilute acid work-up, 4,5-di(1-hydroxymethyl)-3-methylbicyclo[4.3.0]non-1-ene was obtained.

- (9) Identify the compounds **A**, **B**, **C**, **D**, **E** and **F** (structures are sufficient)
- (1) What is the structure of the ylid formed by the reaction of of triphenyl phosphine, iodoethane and n-butyl lithium in the reaction of **D** to **E**?
- (1) What is the name of the reaction that leads to the bicyclic structure **F** ?

**THE END**