THE UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

FINAL EXAMINATION

CHEMISTRY 353

April 29th, 2002 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, *e.g.* answer 5 out of 6. These will be graded in numerical order 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 - 52 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***.

Value

PART 1: RELATIVE PROPERTIES

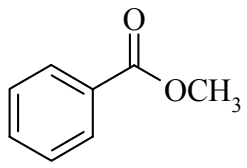
9% **ANSWER ANY SIX (6) OF QUESTIONS 1-10.**

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

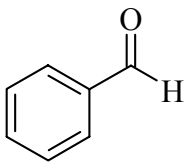
Use the following code to indicate your answers.

A	**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 rate of reaction of $NaBH_4$ with each of the following:



i



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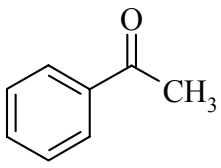
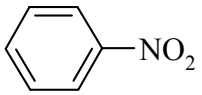
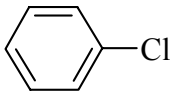


iii

2. The relative rate of reaction of fuming H_2SO_4 with each of the following:



i



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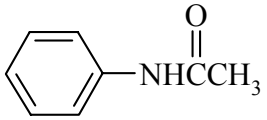
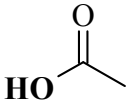
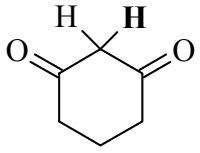


iii

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



i



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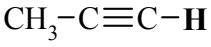


iii

Value

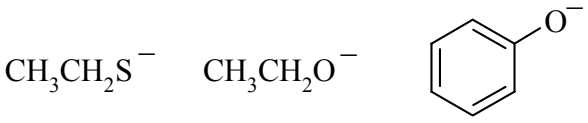
Use the following code to indicate your answers.

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

4. The relative reactivity of the following towards benzaldehyde in dry THF of each of the following:

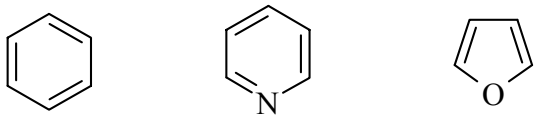
i **ii** **iii**

5. The relative nucleophilicities in aqueous solution of each of the following:



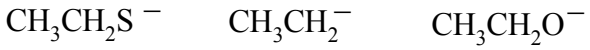
i **ii** **iii**

6. The resonance energies of each of the following:



i **ii** **iii**

7. The relative basicity of each of the following:



i **ii** **iii**

8. The relative reactivity with aqueous H_2SO_4 of each of the following:

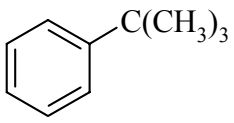
i **ii** **iii**

Value

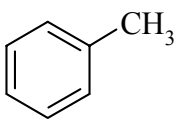
Use the following code to indicate your answers.

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

9. The yield of the *para* product from the reaction of $(CH_3)_3CCl$ / $AlCl_3$ with each of the following :



i



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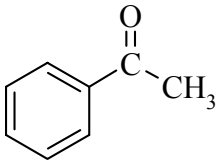
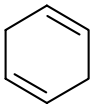
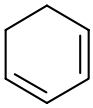


iii

10. The relative stability of the following isomers:



i



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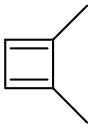


iii

Value

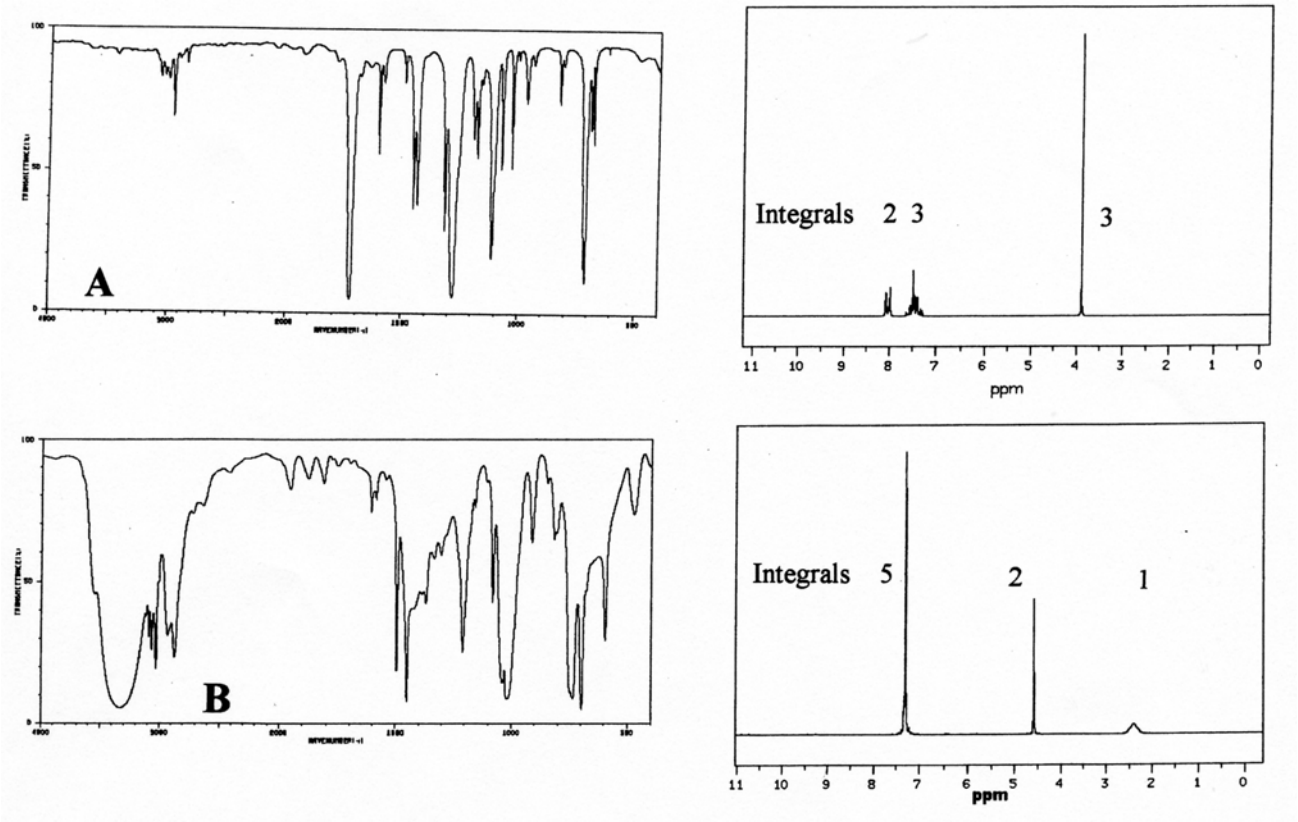
PART 2: LABORATORY

9% **ANSWER ANY SIX (6) OF THE QUESTIONS 11-18.**

The following questions are based on the experiments you have done this semester.

The IR and H-nmr of 6 compounds **A - AB** are provided. For each of the questions **11-18**, select one of the 6 compounds A - AB that matches the functional group test results given in each question.

NOTE :
The numbers on the scales under all of the IR spectra from left to right read 4000, 3000, 2000, 1500, 1000 and 500 cm^{-1} respectively.



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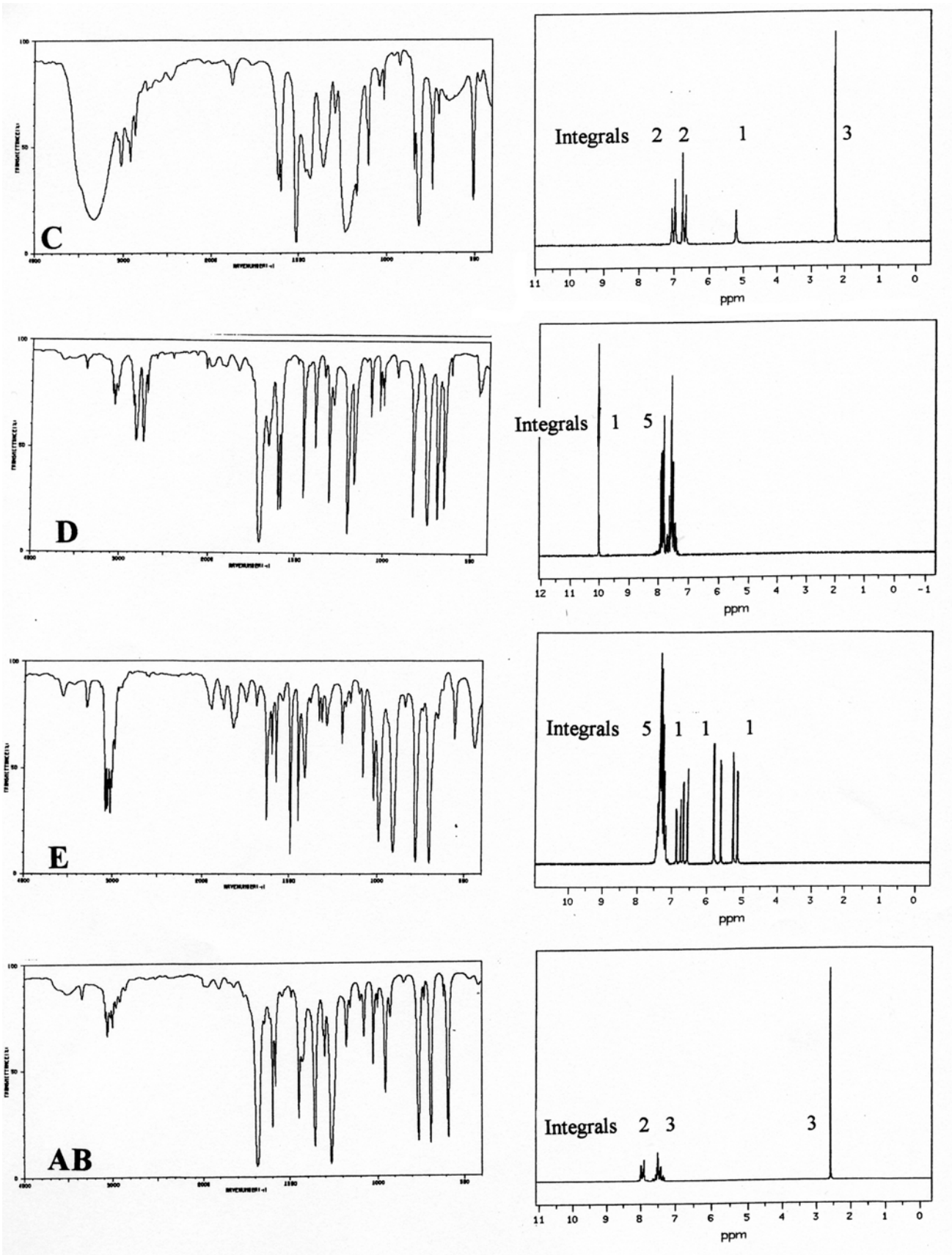

C
Integrals 2 2 1 3
ppm
D
Integrals 1 5
ppm
E
Integrals 5 1 1 1
ppm
AB
Integrals 2 3 3
ppm

Value

11. A compound that will react 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 will cause a dichromate solution to change from orange to green *and* a red solution with 2,4-dinitrophenylhydrazine

15. A compound that will give a yellow precipitate when treated with a basic solution containing iodine.

16. A compound that will react with bromine in chloroform to give a colourless solution.

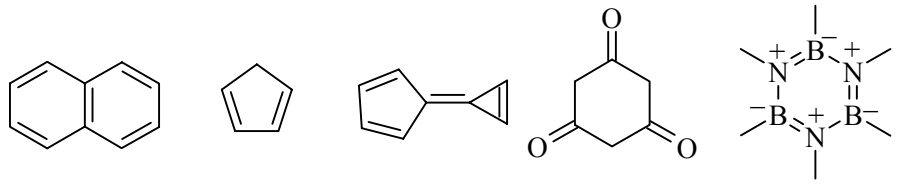
17. A compound that will give an orange precipitate with 2,4-dinitrophenylhydrazine *and* a clear solution when treated with a basic solution containing iodine.

18. A compound that contains a carbonyl group, but gives no precipitate when reacted with 2,4-dinitrophenylhydrazine.

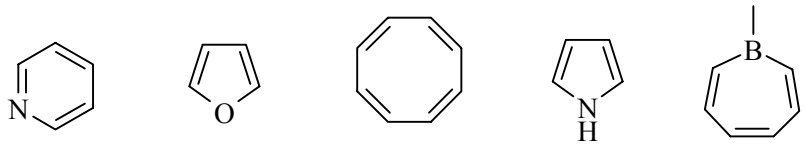
Value

PART 3: AROMATICITY AND RESONANCE

9% **ANSWER ANY SIX (6) of the questions 19-25.**



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



AB **AC** **AD** **AE** **BC**

For each of the questions **19-25** select **a single compound** from the list above that is **best** described as:

19. A heterocyclic aromatic compound with a moderately basic N atom.

20. A 4n + 2 π-electron aromatic system where n = 2 in the Huckel rule.

21. A 4n π-electron system that is non-aromatic because it is non-planar.

22. Aromatic as drawn that also has an aromatic conjugate acid

23. Non-aromatic as drawn but has an aromatic conjugate base.

24. Non-aromatic as drawn but has an aromatic tautomer.

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

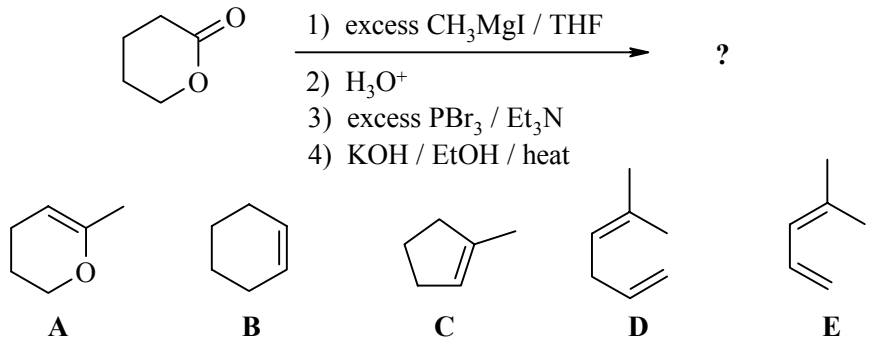
Value

PART 4: PRODUCTS OF SYNTHESIS

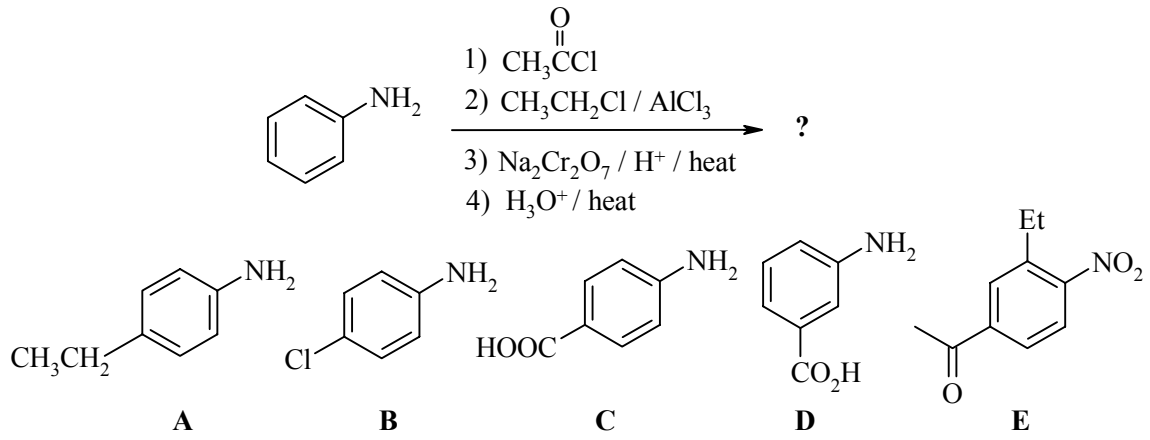
10% **ANSWER ANY FIVE (5) OF QUESTIONS 26-32**.

For each of the questions **26-32** identify the major product obtained from each of the reaction sequences shown by selecting from the list of possible products provided.

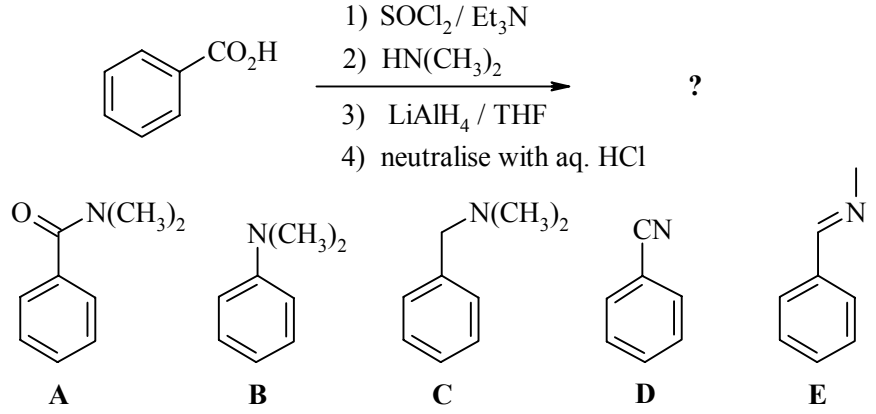
26.



27.

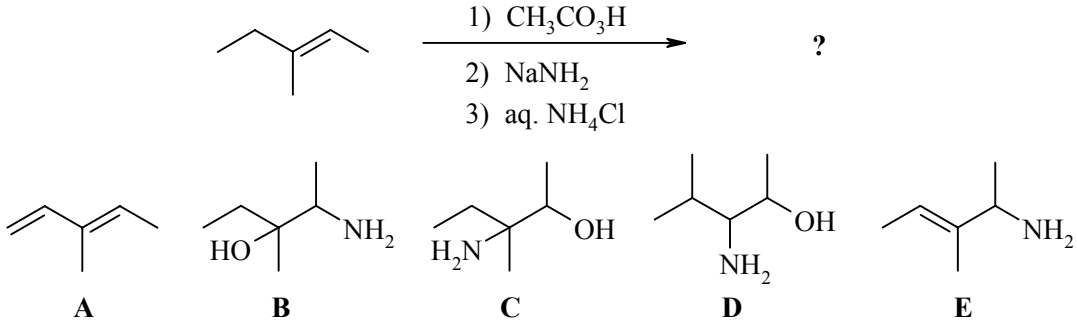


28.

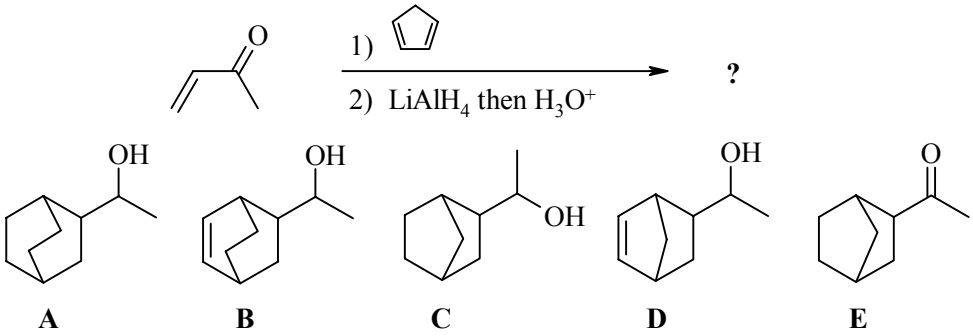


Value

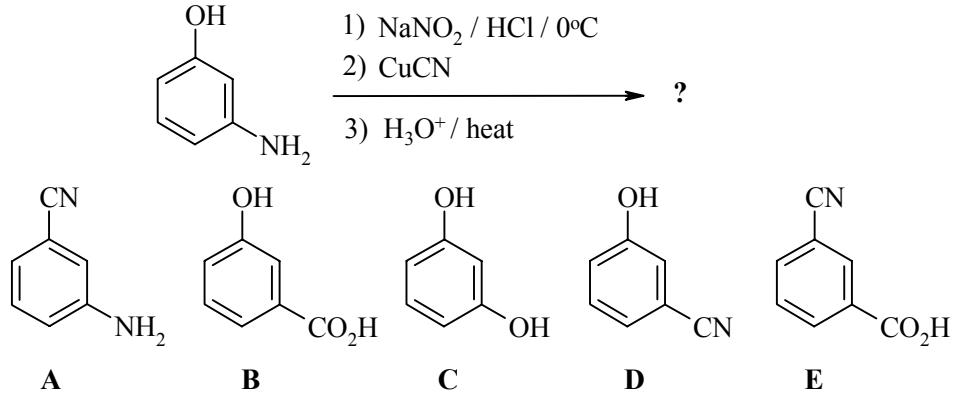
29.



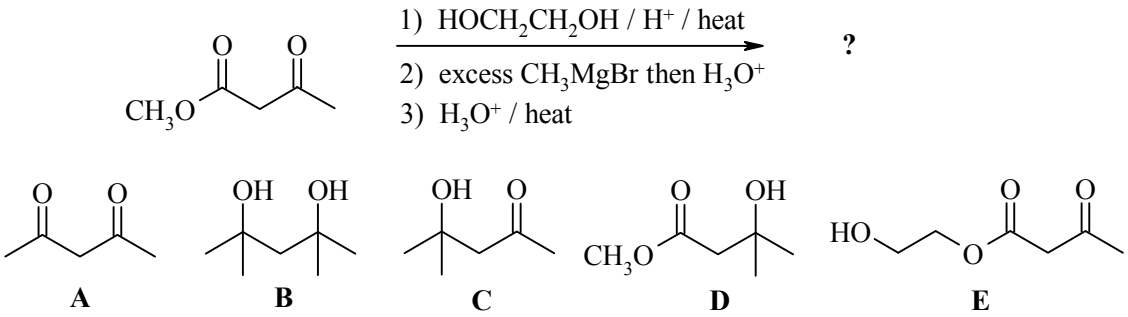
30.



31.



32.



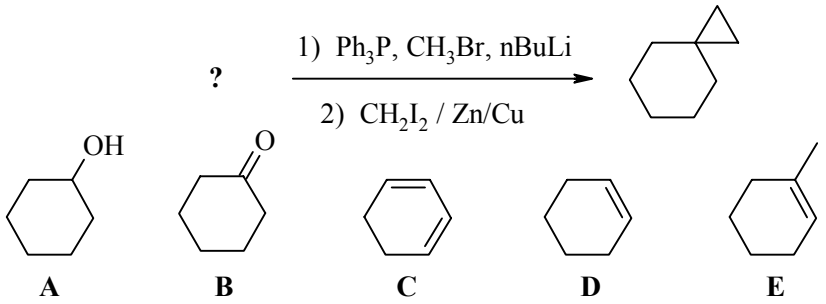
Value

PART 5: STARTING MATERIALS FOR SYNTHESIS

10% **ANSWER ANY FIVE (5) OF QUESTIONS 33-39**.

For each of the questions **33-39**, choose the starting material from the selection provided that gives the product indicated via the transformations shown.

33.



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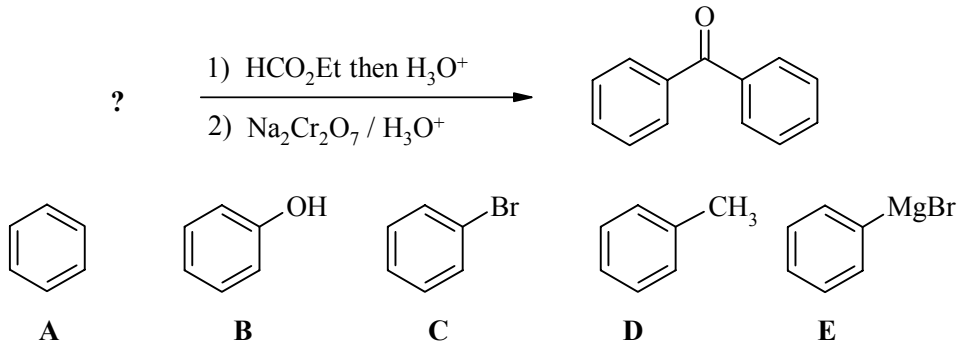

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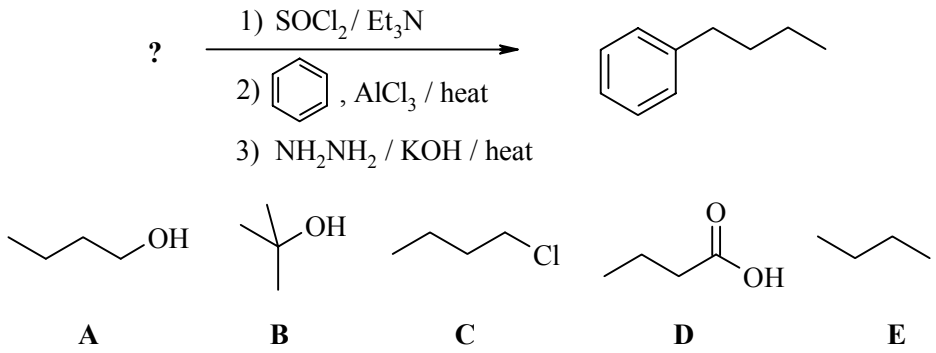

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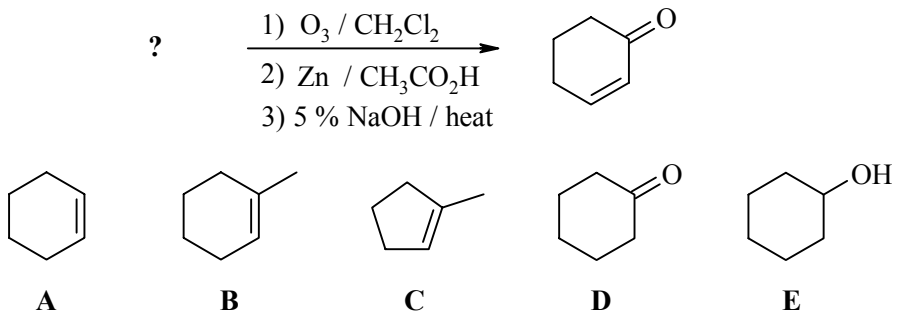

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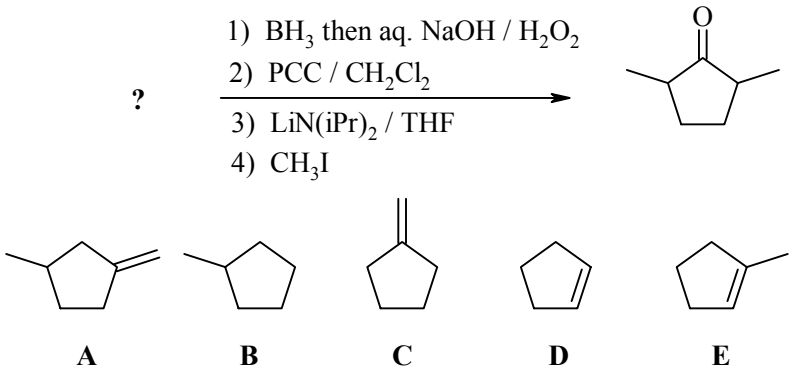

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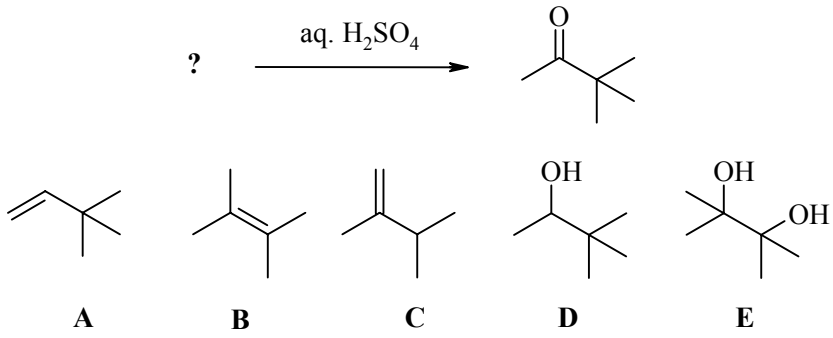

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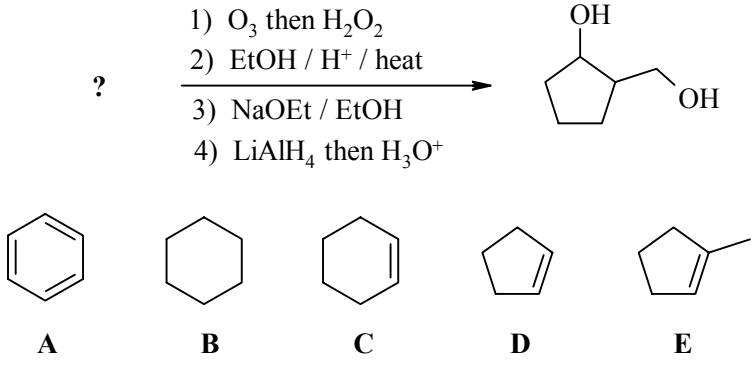
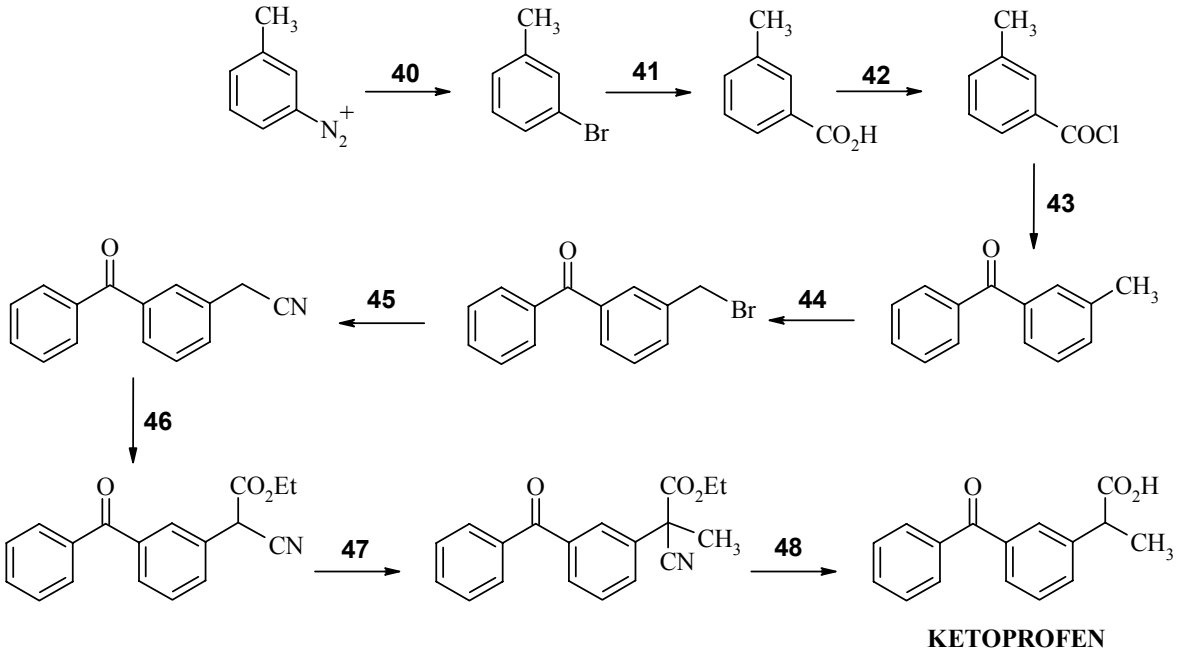


Value

PART 6: REAGENTS FOR SYNTHESIS

9% **ANSWER ALL OF THE QUESTIONS 40 - 48**

The following reaction scheme shows a synthesis of KETOPROFEN, an analgesic similar to Ibruprofen. 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.



KETOPROFEN

A. HBr	AE. MeMgBr / THF
B. Br_2 / hv	BC. Mg then CO_2 then H^+
C. CuBr	BD. Conc. H_2SO_4 / Δ
D. $SOCl_2$ / Et_3N	BE. H_3O^+ / Δ
E. NaCl / DMF	CD. NaOEt then $ClCO_2Et$
AB. $AlCl_3$ / benzene	CE. $LiAlH_4$ then H_3O^+
AC. HCN	DE. Aq. NaOH
AD. NaCN / DMSO	ABC. NaOEt then MeI

Value

PART 7: EXPLANATION OF PHENOMENA

8% **ANSWER ALL OF THE QUESTIONS 49 - 52.**

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

49. When 2-methyl-2-butene is reacted with Cl_2 in H_2O the major product is 3-chloro-2-methyl-2-butanol. This is because:

A. This is an example of a hydration reaction.
B. A carbocation rearrangement occurs.
C. Water adds giving a carbocation intermediate that then reacts with a chloride ion.
D. Chlorine adds forming a cyclic halonium ion that is opened when water acts as a Nu
E. This is an example of a radical addition.

50. 1,3-cyclopentadiene has a pKa = 15 whereas simple cycloalkanes have pKa > 50 with respect to their conjugate bases. This is because:

A. 1,3-cyclopentadiene is aromatic.
B. 1,3-cyclopentadiene is anti-aromatic.
C. 1,3-cyclopentadiene is non-aromatic.
D. 1,3-cyclopentadiene is non-aromatic with an aromatic conjugate base.
E. 1,3-cyclopentadiene is a conjugated diene.

51. When HCl is added to 1,3-butadiene at elevated temperature, 1-chloro-2-butene is formed. This is because:

A. The reaction is under thermodynamic control and is irreversible.
B. The reaction is under thermodynamic control and is reversible.
C. The reaction is under kinetic control and is irreversible.
D. The reaction is under kinetic control and is reversible
E. The reaction is controlled by steric effects

52. Tertiary alcohols cannot easily be oxidised by aqueous dichromate but secondary alcohols can. This is because:

A. Ketones are less electrophilic than aldehydes
B. The oxidation occurs via a 1,2-elimination of a chromate ester and a tertiary alcohol lacks the appropriate H atom for this.
C. The tertiary alcohol is too hindered to react.
D. The secondary carbocation is less stable and therefore more reactive.
E. Tertiary alcohols are insoluble in the reaction medium.

Value

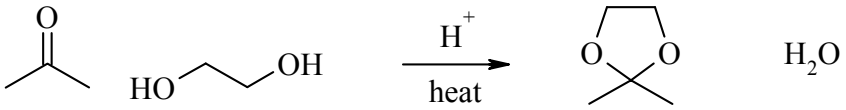
PART 8: MECHANISM

12% **ANSWER ANY THREE (3) OF QUESTIONS A - D**

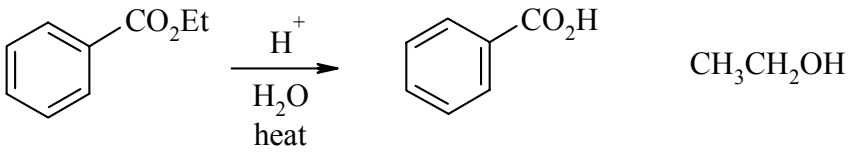
WRITE YOUR ANSWER IN THE BOOKLET PROVIDED

Use curly arrow mechanisms to show the mechanisms for ANY THREE (3) of the following transformations

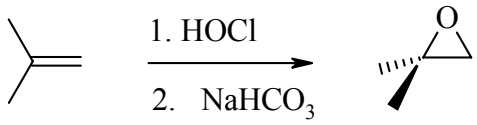
A.



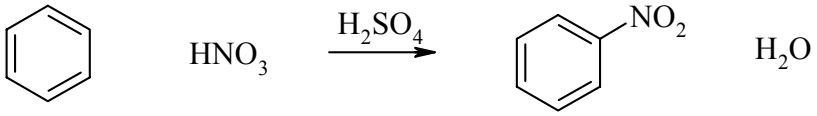
B.



C.



D.



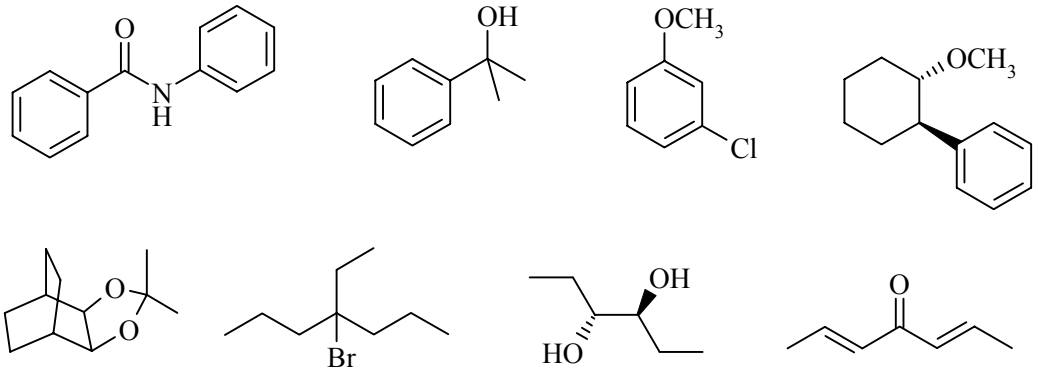
Value

PART 9: TOTAL SYNTHESIS

WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED

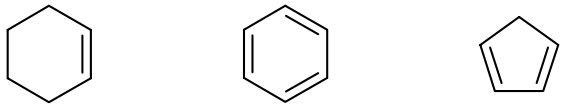
12% Design an efficient synthesis for any **THREE (3)** of the following target molecules using any of the starting materials and reagents given in the accompanying list. Show the product of each step and clearly identify the reagents.

DO NOT SHOW MECHANISMS.



Permitted Starting Materials and Reagents

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



Value

PART 10: STRUCTURE DETERMINATION

12% **WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED**

Compound **A** contains 91.25% C and 8.75% H by weight. When **A** was heated with succinic anhydride (also known as butandioic anydride) and $AlCl_3$, followed by an aqueous acid work-up, the major product was **B**, $C_{11}H_{12}O_3$. **B** was then treated with Zn / Hg in conc. HCl to give **C** $C_{11}H_{14}O_2$. **C** was then reacted with thionyl chloride / Et_3N then heated with $AlCl_3$ to give **D** $C_{11}H_{12}O$ as the major product. When **D** was reacted with methyl magnesium iodide in dry THF, followed by an acidic work-up, **E**, $C_{12}H_{14}$ was obtained. **E** was then thermally dehydrogenated over a platinum catalyst to provide **F**, $C_{12}H_{12}$. When **F** was heated with acidic potassium permanganate, the product was 1,7-naphthalenedicarboxylic acid.
None of the compounds **A-F** are chiral.

What are **A - F** ?

Draw the mechanism for the conversion of **D** to **E**.

ANSWER ONE OF THE FOLLOWING:

EITHER

Suggest a reason why the formation of **E** is favoured.

OR

Suggest a reason why **E** hydrogen is lost so readily to give **F**.

THE END