

THE UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

FINAL EXAMINATION

CHEMISTRY 353

April 21st, 2001

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 - 50 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 (inside front cover) and tables of spectroscopic data (appended to the end of the exam) are provided.

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

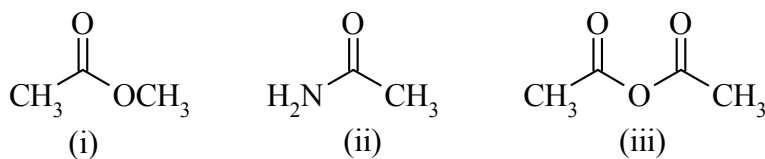
Value**PART 1: RELATIVE PROPERTIES****9% ANSWER ANY SIX (6) OF QUESTIONS 1-10.**

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

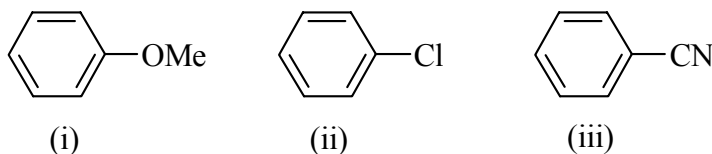
Use the following code to indicate your answers.

- | | | | |
|----|---------------------------|-----|---------------------------|
| A. | i > ii > iii | D. | ii > iii > i |
| B. | i > iii > ii | E. | iii > i > ii |
| C. | ii > i > iii | AB. | iii > ii > i |

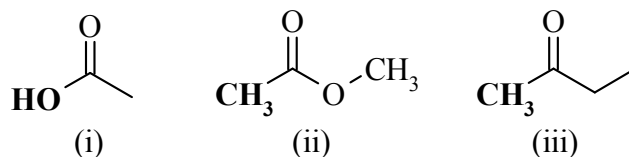
1. The relative rate of hydrolysis using dilute aq. NaOH of the following:



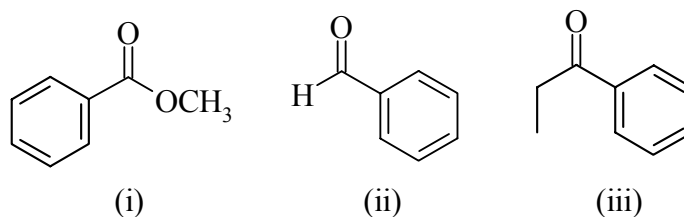
2. The relative rate of reaction of HNO₃ / H₂SO₄ with each of the following:



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



4. The relative reactivity towards LiAlH₄ / dry THF of each of the following:

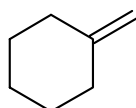


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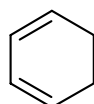
Use the following code to indicate your answers.

- | | | | |
|----|---------------------------|-----|---------------------------|
| A. | i > ii > iii | D. | ii > iii > i |
| B. | i > iii > ii | E. | iii > i > ii |
| C. | ii > i > iii | AB. | iii > ii > i |

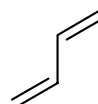
5. The relative reactivity of each of the following towards methyl propenoate:



(i)

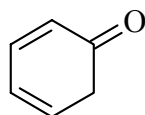


(ii)

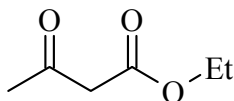


(iii)

6. The relative stability of the enols of each of the following:



(i)

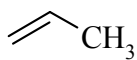


(ii)

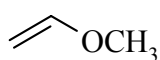


(iii)

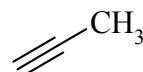
7. The relative reactivity of each of the following towards aqueous H₂SO₄:



(i)



(ii)



(iii)

8. The relative reactivity of each of the following towards 2-butene:

HI

(i)

HBr

(ii)

H₂O

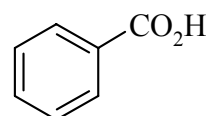
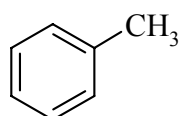
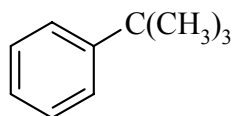
(iii)

Value

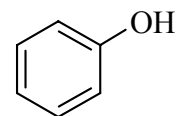
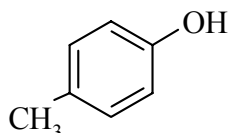
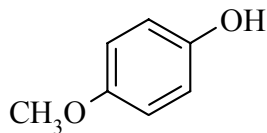
Use the following code to indicate your answers.

- | | | | |
|----|---------------------------|-----|---------------------------|
| 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 each of the following with bromine / FeBr₃:



10. The relative acidity of the following:



Value**PART 2: LABORATORY****9% ANSWER ALL NINE (9) 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.

Stu Dent had unknown **#0001**, which was a colourless liquid. He measured the boiling point to be 193°C (uncorrected). The IR and H-nmr of **#0001** are shown below. Stu carried out a series of chemical tests on **#0001** the results of which are shown in the table below. Stu also isolated a liquid product, **STU-2**, from the dichromate test on **#0001**. The results of chemical test on **STU-2** are also shown in the table below. The crystalline product, **STU-3**, from the reaction of **STU-2** with 2,4-dinitrophenylhydrazine was isolated and the melting point measured as 200°C.

DIGITAL SPECTRA WILL BE ADDED AS SOON AS TIME ALLOWS

Chemical Test	Observations for #0001	Observations for STU-2
Water solubility	Partially soluble	Insoluble
5% NaHCO ₃	Insoluble	Insoluble
5% NaOH	Insoluble	Insoluble
5% HCl	Insoluble	Insoluble
Lucas	Colourless layer formed rapidly	No noticeable change
2,4-Dinitrophenylhydrazine	No visible reaction	Red precipitate formed
Iodoform	No visible reaction	Yellow precipitate formed
Ferric Chloride	No significant colour change	No significant colour change
Dichromate	Changed from orange to green	No noticeable change

Value

Value

11. The corrected boiling point for unknown **#0001** should be approximately:
- A** 183°C **B** 188°C **C** 193°C **D** 203°C **E** 253°C
12. Based on the chemical tests *alone* on unknown **#0001** which of the following statements is / are true ?
- A.** The unknown could be a phenol
B. The unknown must be a tertiary alcohol
C. The unknown could be an aldehyde
D. The unknown could be an alcohol OR an amine
E. The unknown could be an alcohol
13. Which of the following statements about the 2,4-dinitrophenylhydrazine test on **STU-2** is / are true ?
- A.** **STU-2** contains an alcohol functional group
B. **STU-2** contains a C=O group
C. **STU-2** could be an aldehyde or a ketone
D. **STU-2** is a carboxylic acid derivative
E. **STU-2** is an aromatic compound
14. Which of the following statements about the iodoform test on **STU-2** is / are true ?
- A.** **STU-2** is an alcohol
B. The yellow precipitate is due to CHI_3
C. The yellow precipitate is due to the carboxylic acid product
D. **STU-2** is a methyl ketone
E. **STU-2** is an aromatic compound
15. Which of the following statements about the Lucas test is / are true ?
- A.** It indicates the presence of a halide in **#0001**
B. **#0001** is a primary alcohol
C. The Lucas test is an example of a substitution reaction
D. The Lucas test is an example of an addition reaction
E. The Lucas reagent is $\text{Br}_2 / \text{CHCl}_3$
16. Which of the following statements about the dichromate test is / are true ?
- A.** The initial oxidation state for Cr is VII
B. Cr^{3+} is green
C. Tertiary alcohols are oxidised to chromate esters
D. Secondary alcohols are oxidised to ketones
E. During the test, Cr is reduced.

Value

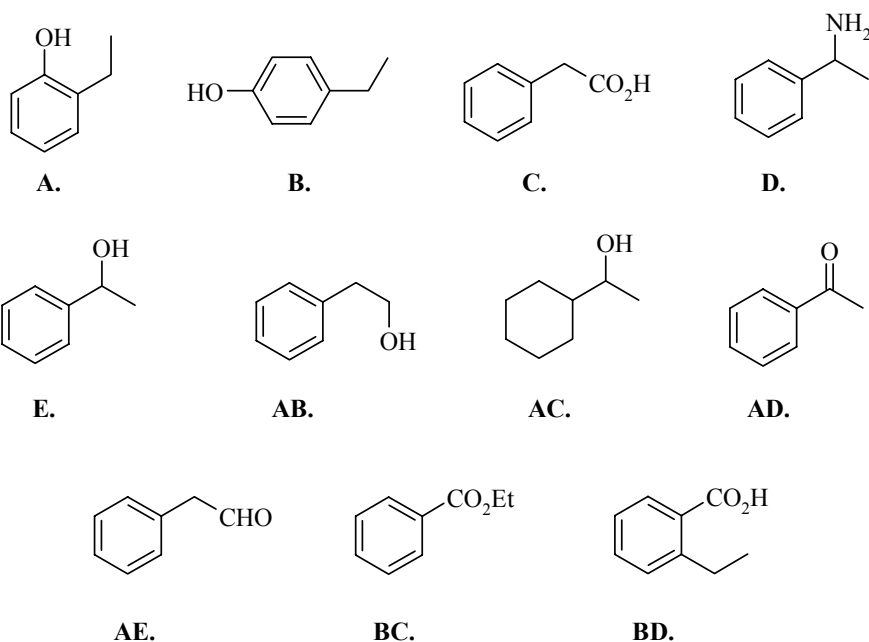
17. The correct melting point for **STU-3** should be approximately:

- A** 180°C **B** 190°C **C** 200°C **D** 210°C **E** 250°C

ANSWER QUESTIONS 18 & 19 FROM THE LIST OF COMPOUNDS GIVEN BELOW.

18. Which of the compounds shown below is unknown **#0001** ?

19. Which of the compounds shown below is **STU-2** ?

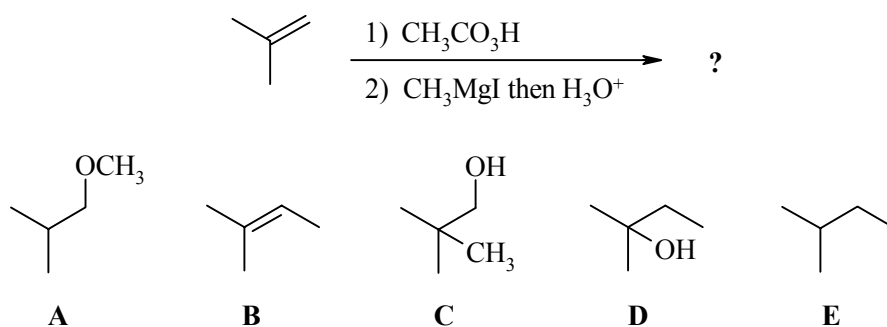


Value

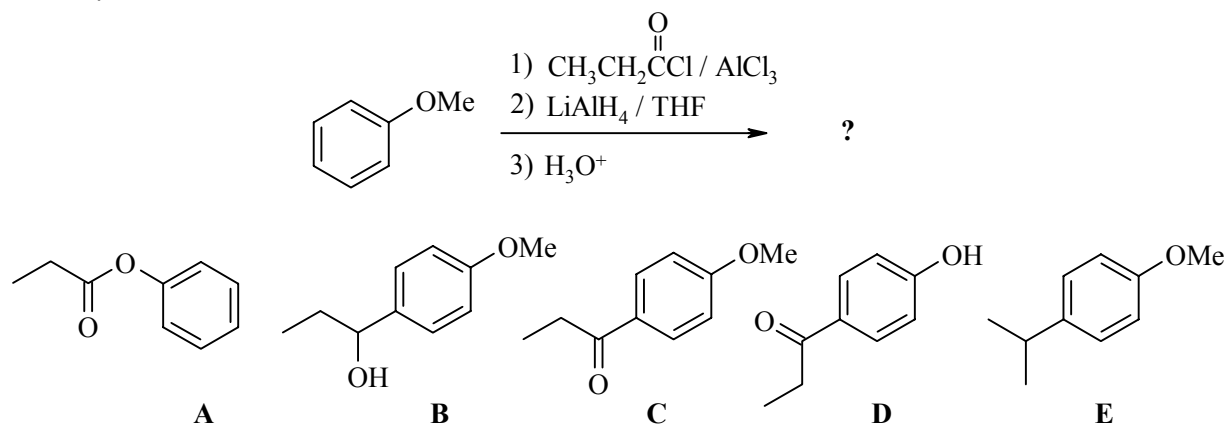
PART 3: PRODUCTS OF SYNTHESIS**10% ANSWER ANY FIVE (5) OF QUESTIONS 20-26.**

For each of the questions 20 to 26 identify the major product obtained from each of the reaction sequences shown by selecting from the list of possible products provided.

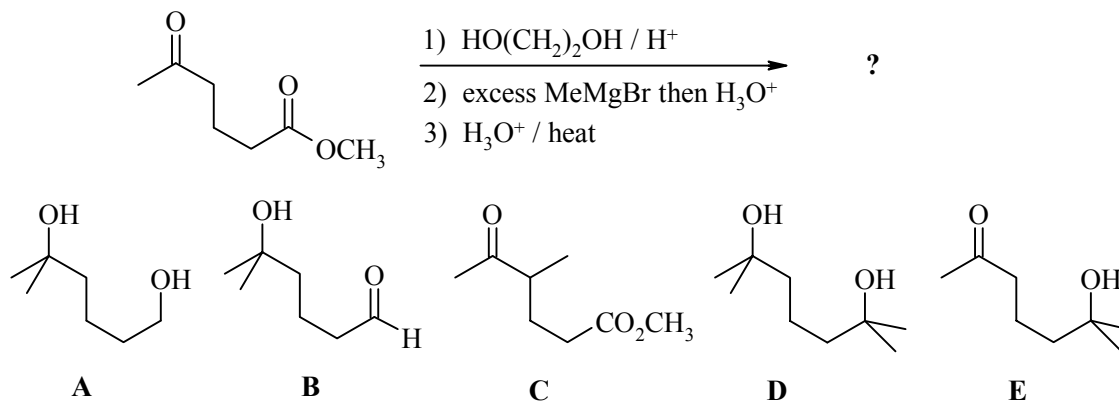
20.



21.

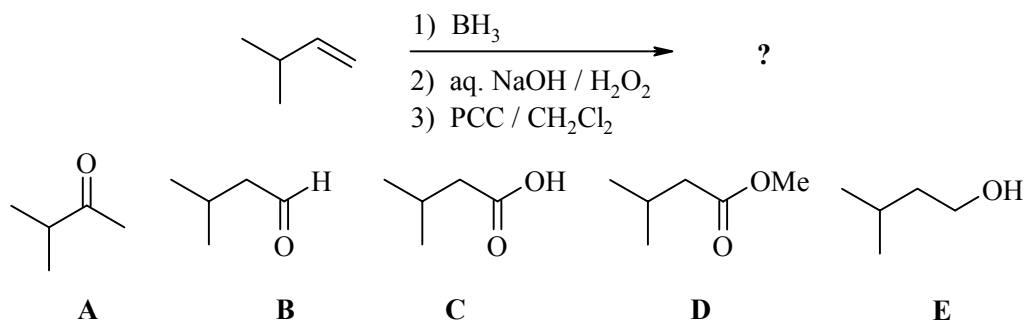


22.

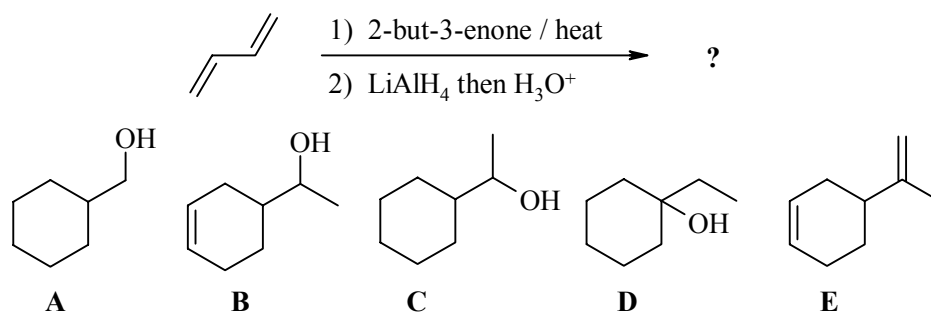


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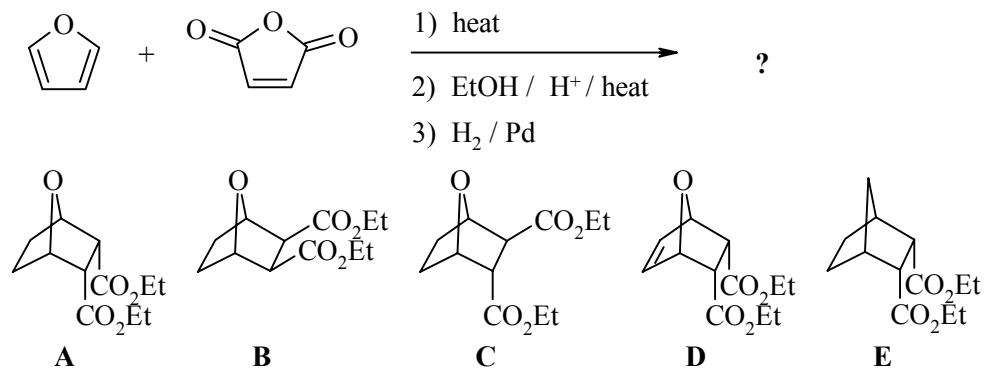
23.



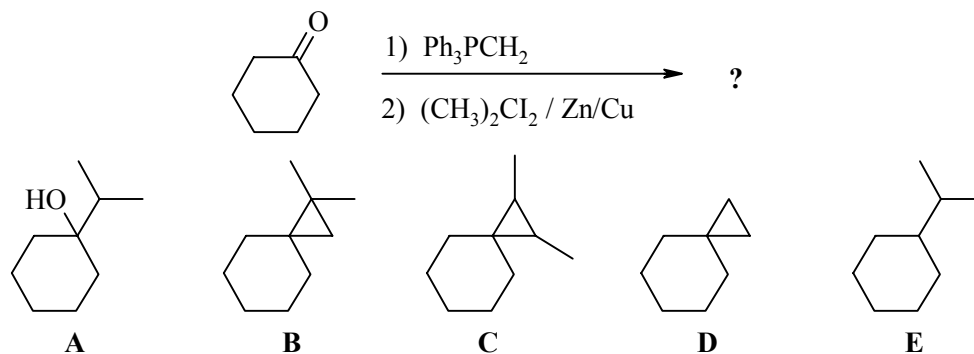
24.



25.



26.

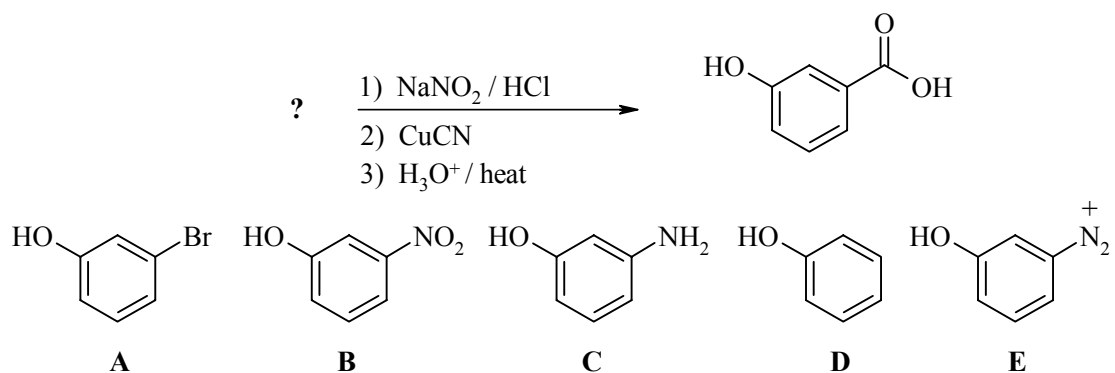


Value

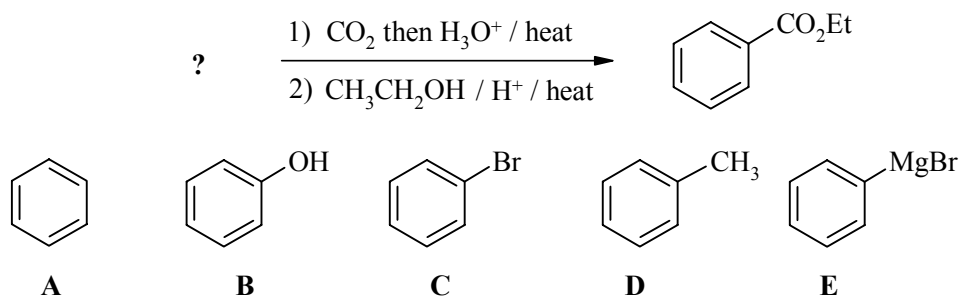
PART 4: STARTING MATERIALS FOR SYNTHESIS**10% ANSWER ANY FIVE (5) OF QUESTIONS 27-33.**

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

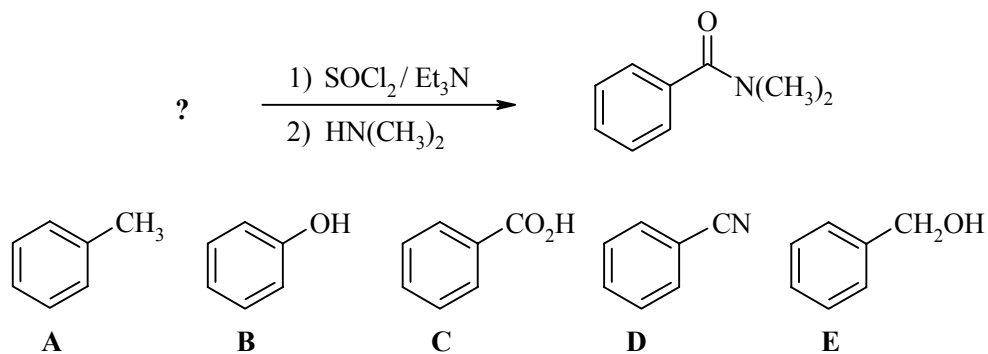
27.



28.

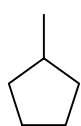
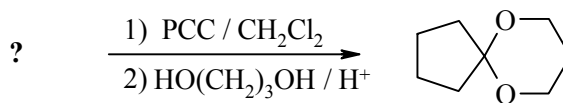
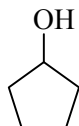
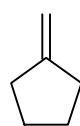
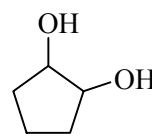


29.

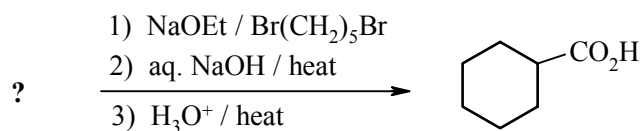
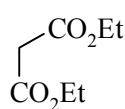
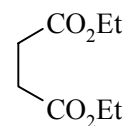
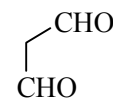


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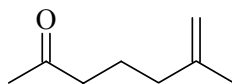
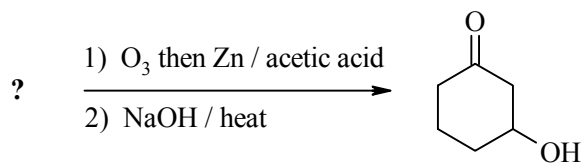
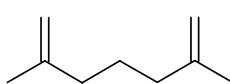
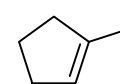
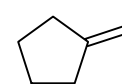
30.

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

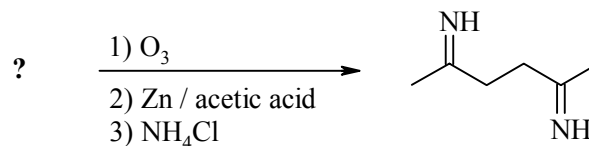
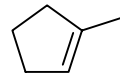
31.

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

32.

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

33.

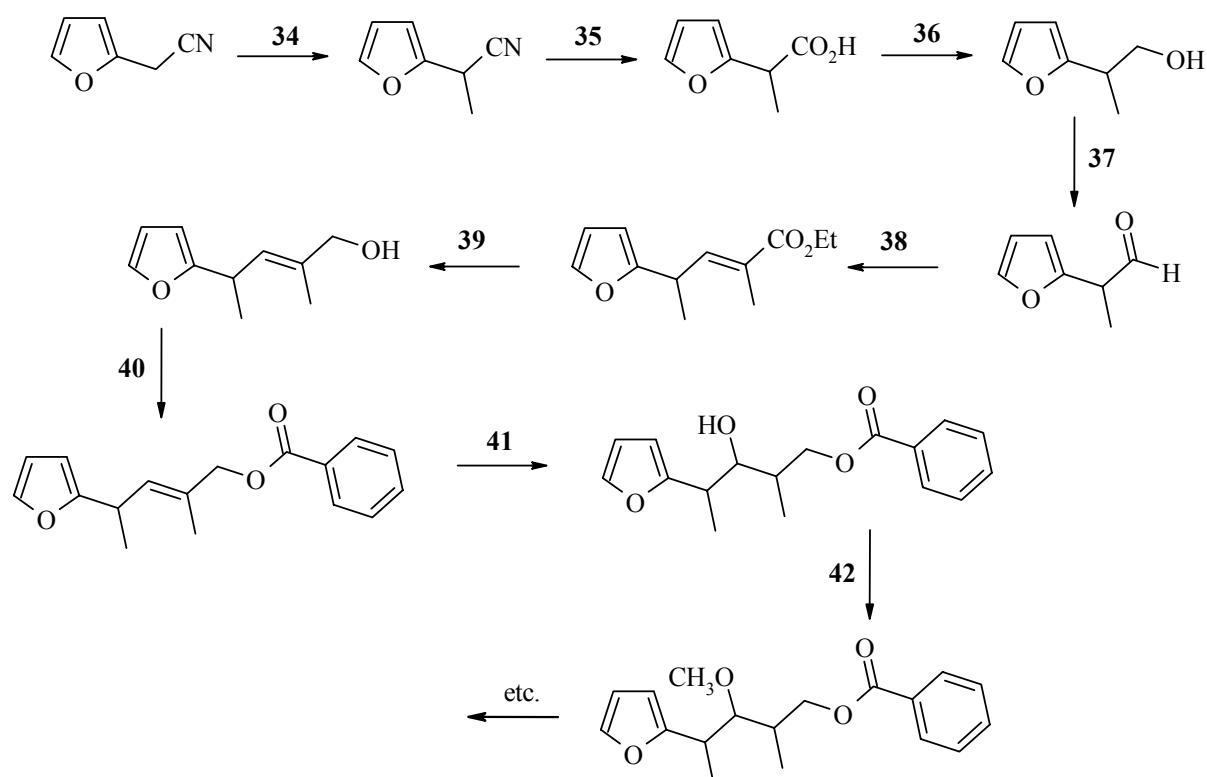
**A****B****C****D****E**

Value

PART 5: REAGENTS FOR SYNTHESIS

9% ANSWER ALL OF THE QUESTIONS 34 - 42

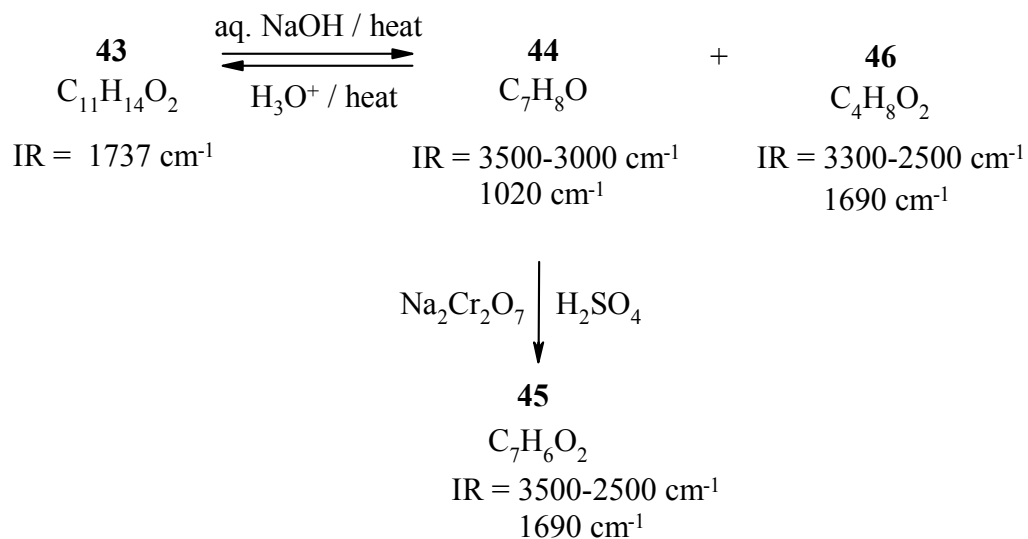
The following reaction scheme is based on *part* of the Kishi synthesis of the left segment of the antibiotic, MONENSIN. From the list of reagents provided in the table below, select the best reagent combination to carry out each of the reactions required at each numbered step.

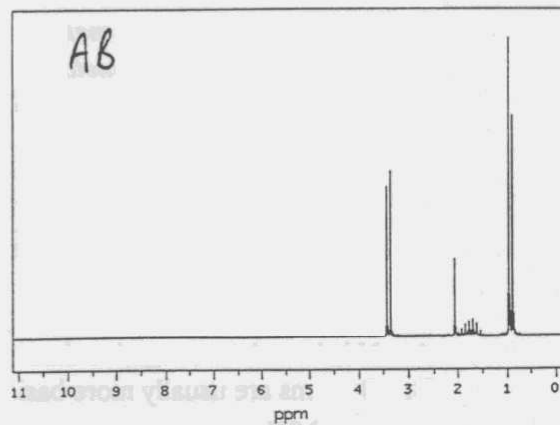
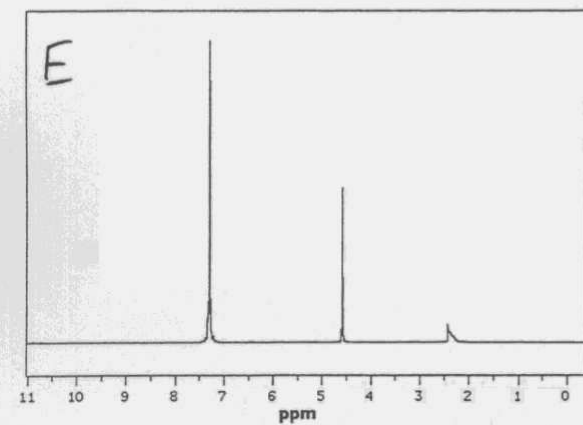
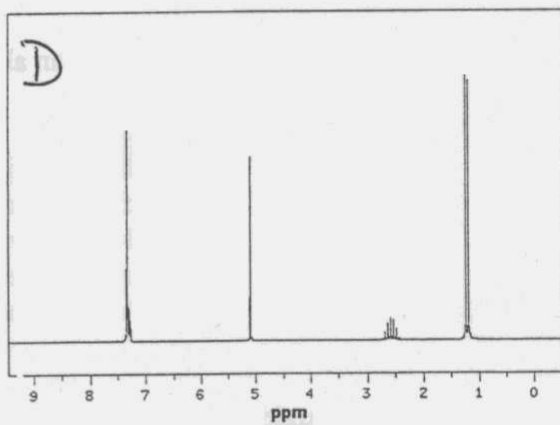
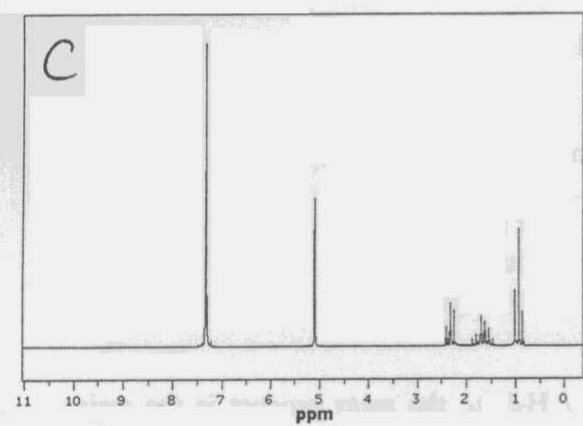
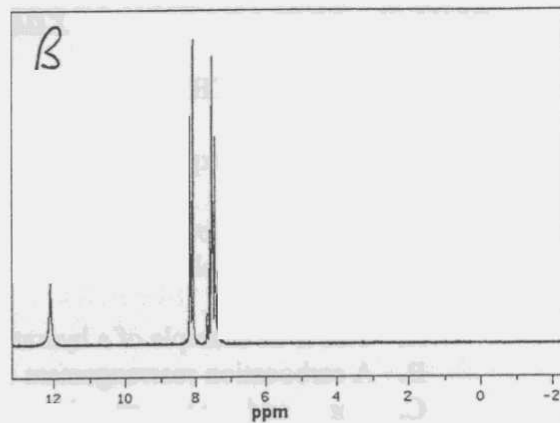
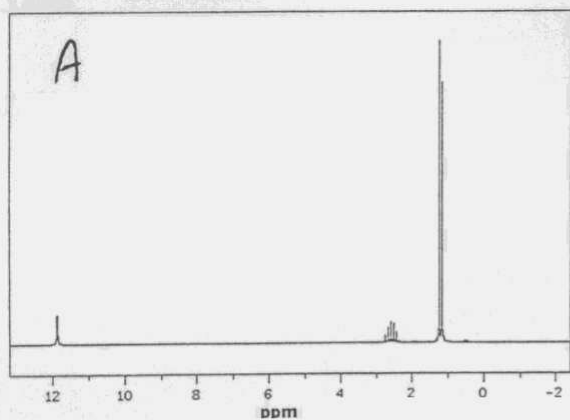


- | | |
|--|---|
| A. LiAlH_4 then H_3O^+ | AE. O_3 then Zn / AcOH |
| B. $\text{NaBH}_4 / \text{EtOH}$ | BC. H_3O^+ |
| C. $\text{KOH} / \text{aq. CH}_3\text{OH} / \text{heat}$ | BD. BH_3 then $\text{NaOH} / \text{H}_2\text{O}_2$ |
| D. $\text{C}_6\text{H}_5\text{COBr} / \text{base}$ | BE. $\text{Ph}_3\text{PC}(\text{CH}_3)\text{CO}_2\text{Et}$ |
| E. $\text{C}_6\text{H}_5\text{Br} / \text{base}$ | CD. MeMgBr then H_3O^+ |
| AB. Pyridinium chlorochromate | CE. Na then CH_3I |
| AC. MCPBA | DE. BuLi then CH_3I |
| AD. $\text{Na}_2\text{Cr}_2\text{O}_7 / \text{aq. H}_2\text{SO}_4$ | ABC. CH_3OH |

Value**PART 6: APPLIED SPECTROSCOPY****8% ANSWER ALL FOUR (4) OF QUESTIONS 43 - 46**

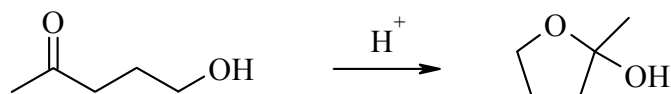
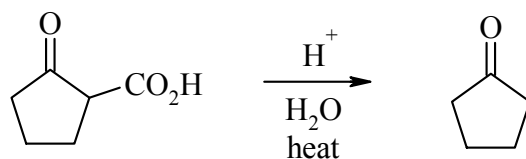
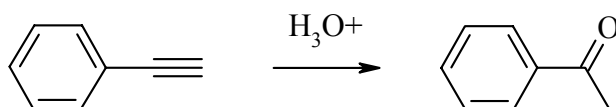
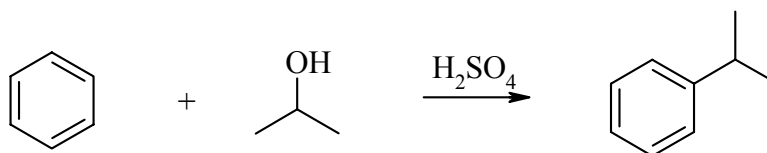
For each of the questions **43 - 46**, select the H-NMR spectra from the following page that corresponds to each of the compound numbers in the reaction scheme shown below.



Value

Value**PART 7: EXPLANATION OF PHENOMENA****8% ANSWER ALL OF THE QUESTIONS 47 - 50.**Choose the **SINGLE** explanation that **BEST** describes the phenomenon indicated.

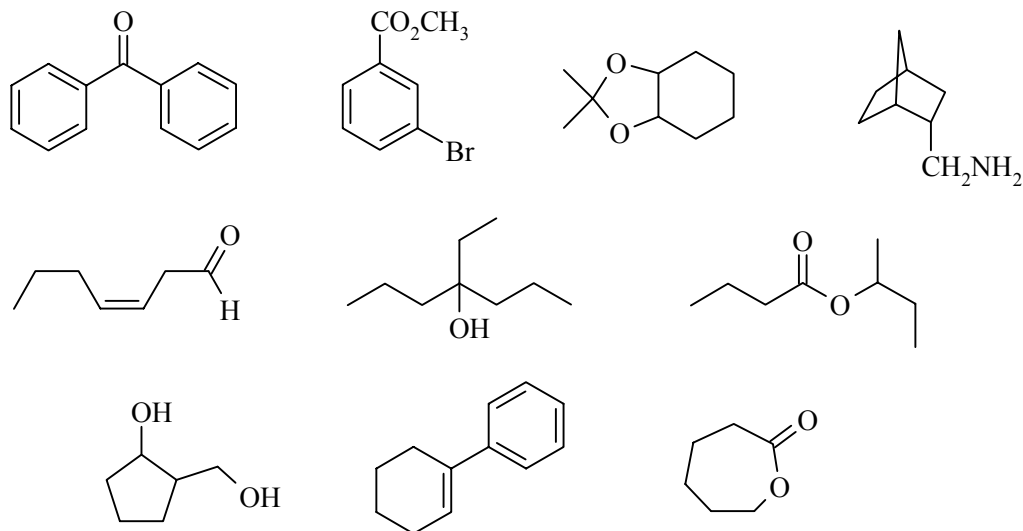
47. When 2-methyl-2-butene is reacted with BH_3 then aq. $\text{NaOH} / \text{H}_2\text{O}_2$ the major product is 3-methyl-2-butanol. This is because:
- A. This is an example of a hydration reaction.
 - B. A carbocation rearrangement occurs.
 - C. Boron adds as a nucleophile, later to be replaced by an oxygen nucleophile.
 - D. Boron adds as a electrophile, later to be replaced by an oxygen nucleophile.
 - E. This is an example of a radical addition.
48. When benzene is reacted with an alkyl chloride / AlCl_3 , polyalkylation can be a problem. 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 and activates the product to further reaction.
 - D. Alkyl groups are activating groups so the product is more reactive than benzene.
 - E. The reaction proceeds via carbocation that rearranges to a more stable carbocation.
49. When benzaldehyde is nitrated using $\text{HNO}_3 / \text{H}_2\text{SO}_4$, the *meta* product is the major product. This is because:
- A. The $-\text{C}(=\text{O})\text{CH}_3$ group is a *meta* director.
 - B. The $-\text{CHO}$ group is a *meta* director.
 - C. The $-\text{NO}_2$ group is a *meta* director.
 - D. Nitration usually occurs at the *meta* position.
 - E. Statistically, the *meta* position is preferred over the *para* position.
50. When amides react with acid, they protonate on the oxygen rather than the nitrogen. This is because:
- A. N is less electronegative than O.
 - B. O atoms are usually more basic than N atoms in similar environments.
 - C. There are more lone pairs on the O atom.
 - D. There is more resonance stabilisation when O is protonated compared to N.
 - E. There is more resonance stabilisation when N is protonated compared to O.

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

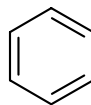
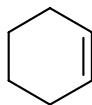
PART 9: TOTAL SYNTHESIS**WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED**

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
- MCPBA
- Any of the following:



Value**PART 10: STRUCTURE DETERMINATION****13% WRITE YOUR ANSWERS IN THE BOOKLET PROVIDED**

Compound **A** C_7H_{12} was treated with ozone followed by a work-up using H_2O_2 giving **B** $C_7H_{12}O_4$. This compound was then heated with ethanol and a few drops of conc. H_2SO_4 to give **C** $C_{11}H_{20}O_4$. **C** was heated with sodium ethoxide to give **D** $C_9H_{14}O_3$. On further heating with aqueous acid, **D** gave **E** $C_6H_{10}O$ and a gas was evolved. When **D** was reacted with an excess of methyl magnesium iodide, 1,2-dimethyl-5-(1-hydroxy-1-methylethyl)-cyclopentanol was produced.

When **E** was reacted with lithium aluminium hydride in dry ether, followed by an aqueous acidic work-up, **F**, $C_6H_{12}O$ was isolated which could be readily dehydrated to give **G**, an achiral compound, C_6H_{10} .

When **E** was treated with a peracid, **H**, $C_6H_{10}O_2$ was isolated. **H** was prepared in a separate synthesis by heating 5-hydroxyhexanoic acid with an acid catalyst.

A - F and **H** were all chiral.

What are **A - H** ?

What are the names of the reactions that convert **C** to **D** and **E** to **H** ?

THE END