

THE UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

FINAL EXAMINATION

CHEMISTRY 353

April 20th, 1999

Time: 3 Hours

PLEASE WRITE YOUR **NAME, STUDENT I.D. NUMBER** AND SECTION NUMBER (01 for MWF lectures and 02 for TR lectures) ON **COMPUTER ANSWER SHEET** AND THE **3 PAGES** FOR THE WRITTEN ANSWER QUESTIONS.

READ THE INSTRUCTIONS CAREFULLY

The examination consists of Parts 1 - 10, each of which should be attempted. Note that some Parts provide you with a choice of questions. Parts 1 - 7 will be computer graded, and only Parts 8, 9 and 10 are to be answered on the pages indicated. A periodic table with atomic numbers and atomic weights, and tables of spectroscopic data are appended to the end of the exam.

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

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

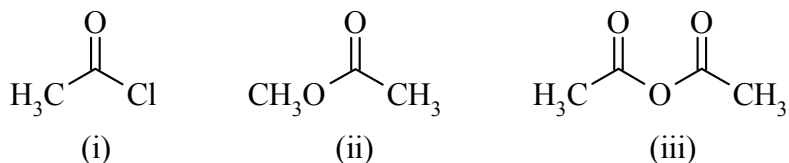
Value**PART 1: RELATIVE PROPERTIES****9% ANSWER ANY SIX (6) OF QUESTIONS 1-10.**

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

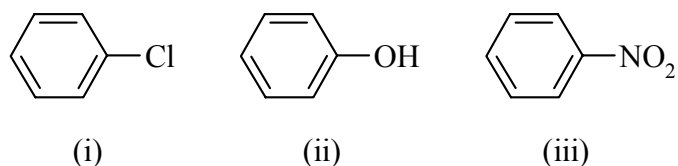
Use the following code to indicate your answers.

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

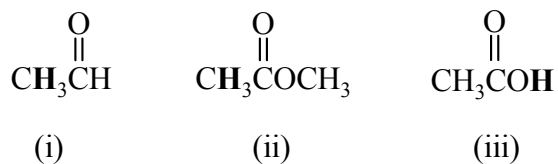
1. The relative rate of hydrolysis using dilute aq. NaOH of the following:



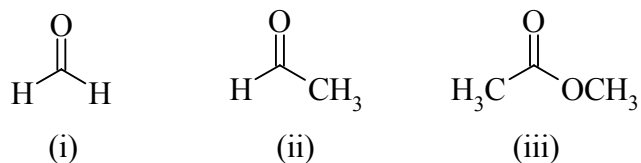
2. The relative rate of reaction of isopropyl chloride / AlCl₃ with each of the following



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



4. The relative reactivity towards reaction with MeMgBr of the following:



Value

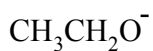
Use the following code to indicate your answers.

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

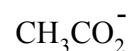
5. The relative nucleophilicity in polar, protic solvents of the following:



(i)

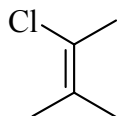


(ii)

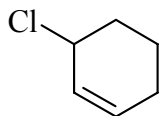


(iii)

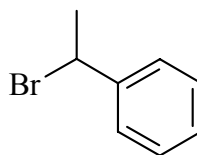
6. The relative rate of reaction with aq. EtOH / AgNO₃ of the following:



(i)

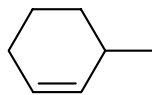


(ii)

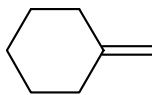


(iii)

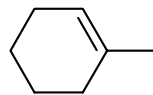
7. The relative yields of the following products produced by the reaction of conc. H₂SO₄ with 1-methylcyclohexanol:



(i)

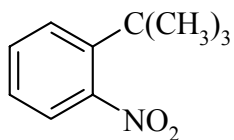


(ii)

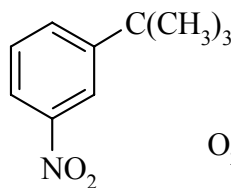


(iii)

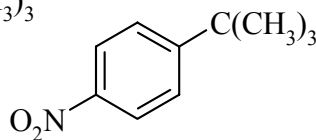
8. The relative yields of the following products produced in the nitration reaction of t-butylbenzene:



(i)



(ii)



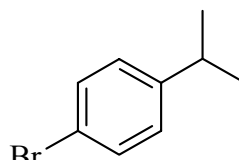
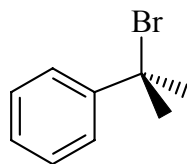
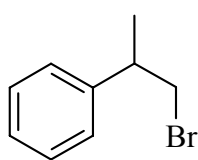
(iii)

Value

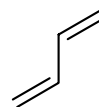
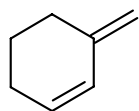
Use the following code to indicate your answers.

- | | | | |
|----|--------------|-----|--------------|
| 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 relative yields of the following products produced by the reaction of isopropyl benzene with Br₂ / uv light:



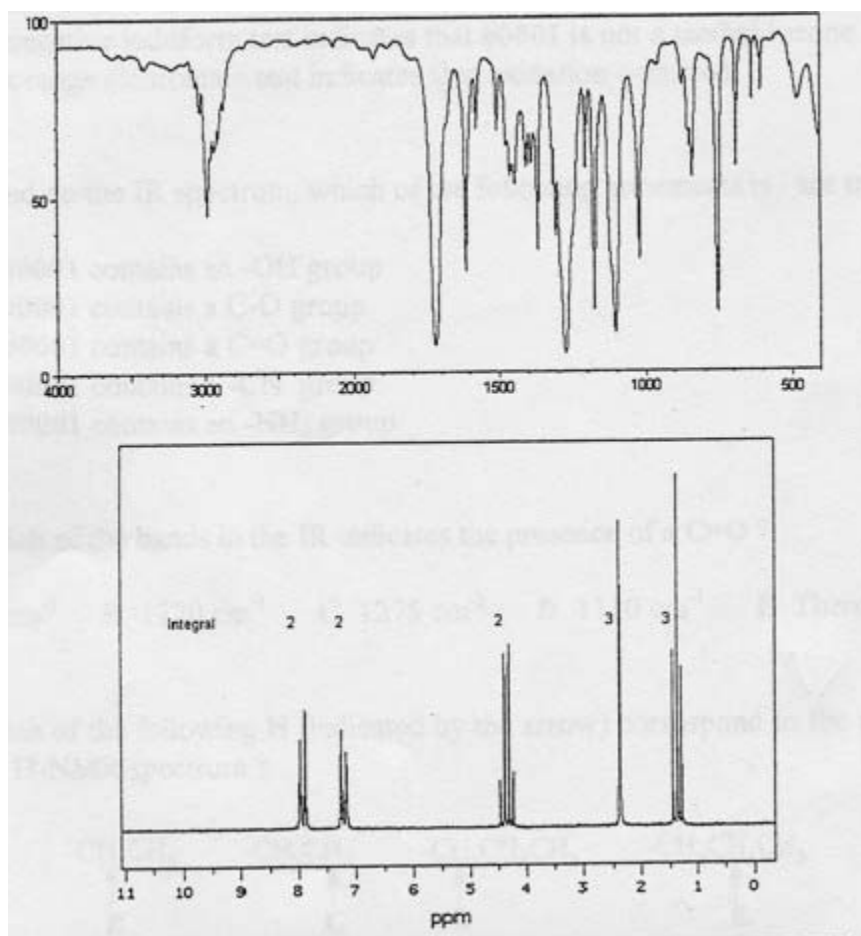
10. The relative reactivity towards dimethyl *cis*-butendioate (also called dimethyl maleate) of the following.



Value**PART 2: LABORATORY****8% ANSWER ALL OF THE QUESTIONS 11-18.**

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

Sue Dent had unknown **#0001**, which was a colourless, sweet smelling liquid. She measured the boiling point to be 223 °C (uncorrected). IR and H-NMR spectra of **#0001** are shown below. Sue also carried out a series of chemical tests on **#0001**. The results of these tests are also shown below.



Value

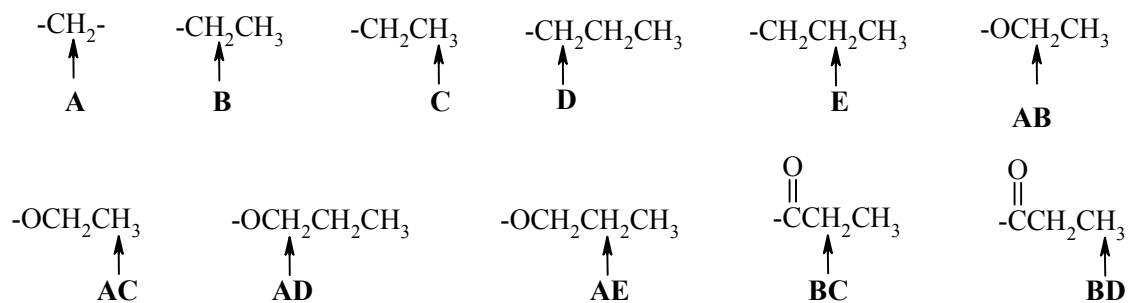
Chemical Test	Observations for #0001
Water solubility	Insoluble
5% NaHCO ₃	Insoluble
5% NaOH	Insoluble
5% HCl	Insoluble
Lucas	Clear solution obtained
2,4-Dinitrophenylhydrazine	Clear red solution obtained
Iodoform	Yellow solution obtained
Ferric Chloride	No significant colour change
Dichromate	Orange solution obtained
Bromine / chloroform	Brown solution obtained

11. The corrected boiling point for the unknown #0001 should be approximately :
- A 210 °C B 223 °C C 230 °C D 235 °C E 240 °C
12. Based on the chemical tests, which of the following statements is / are true ?
- A. The Lucas and ferric chloride test results indicate that #0001 is not an alcohol or phenol
 B. The 2,4-DNP test result indicates that #0001 contains a carbonyl group.
 C. The 2,4-DNP test result indicates that #0001 is an aldehyde or ketone.
 D. The negative iodoform test indicates that #0001 is not a methyl ketone.
 E. The orange dichromate test indicates that oxidation occurred.
13. Based on the IR spectrum, which of the following statements is / are true ?
- A. #0001 contains an -OH group
 B. #0001 contains a C-O group
 C. #0001 contains a C=O group
 D. #0001 contains a -CN group
 E. #0001 contains an -NH₂ group
14. Which of the bands in the IR indicates the presence of a C=O ?

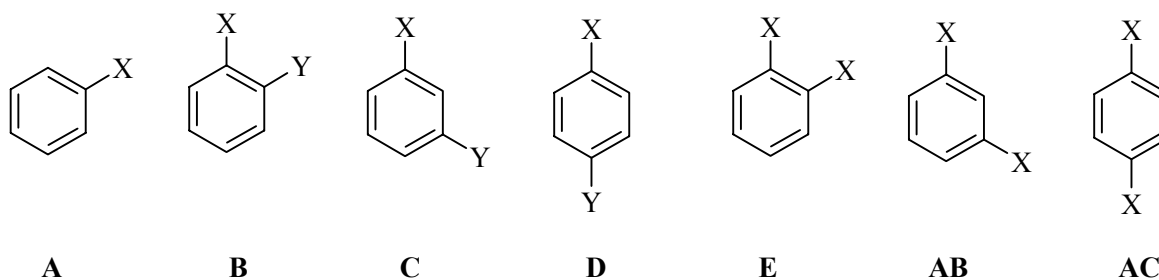
Value

A 2975 cm^{-1} B 1720 cm^{-1} C 1275 cm^{-1} D 1110 cm^{-1} E There is no C=O !

15. Which of the following H (indicated by the arrow) correspond to the peaks at 4.3ppm in the H-NMR spectrum ?



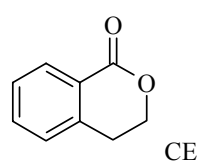
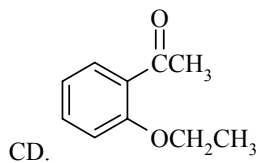
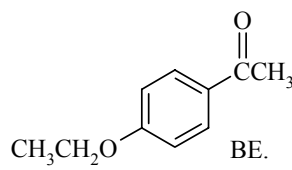
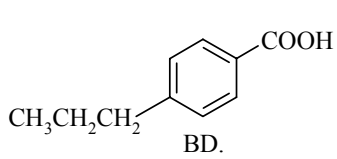
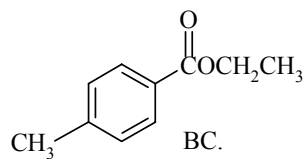
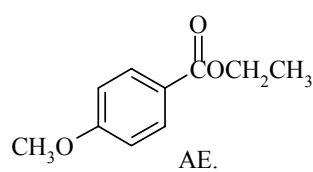
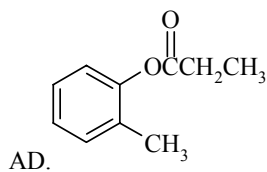
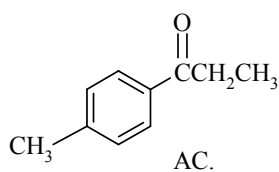
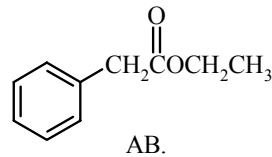
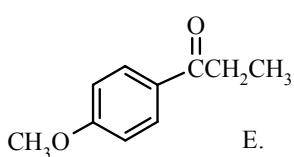
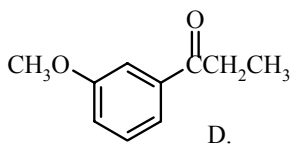
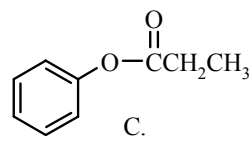
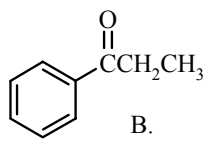
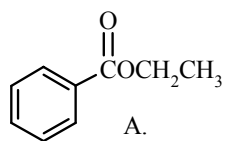
16. Which of the following partial structures best rationalise the peaks at 7 to 8ppm in the H-NMR spectrum ?



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

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

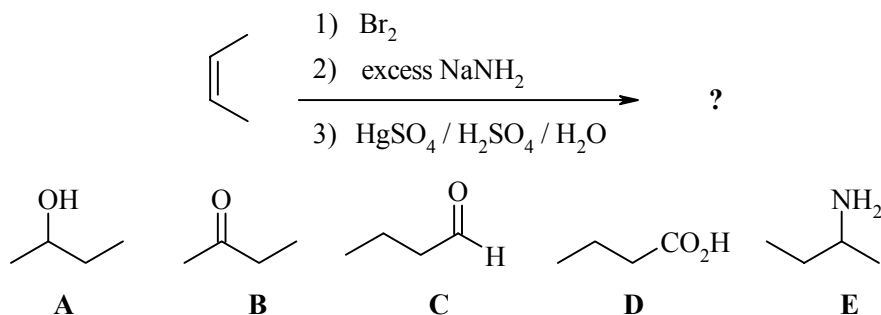
18. Which of the following compounds is #0001 ?

Value

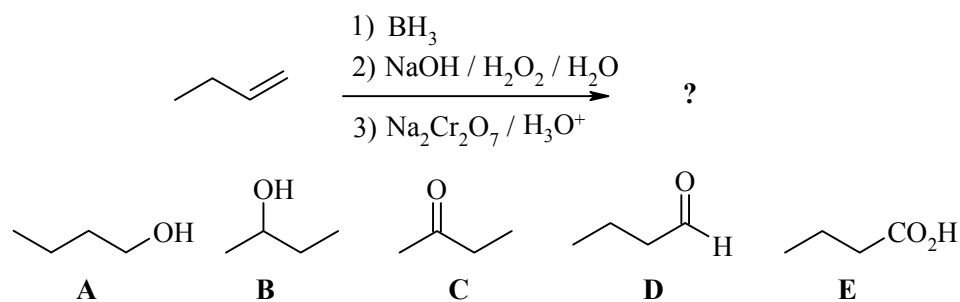
Value**PART 3: PRODUCTS OF SYNTHESIS****10% ANSWER ANY FIVE (5) OF QUESTIONS 19-25.**

For each of the questions 19 to 25 identify the major product obtained from each of the reaction sequences shown by selecting from the list of possible products provided.

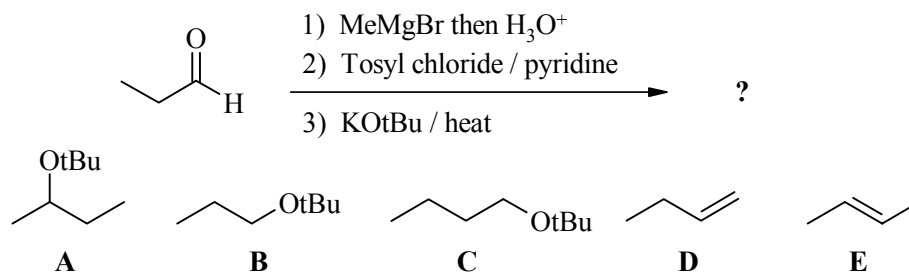
19.



20.

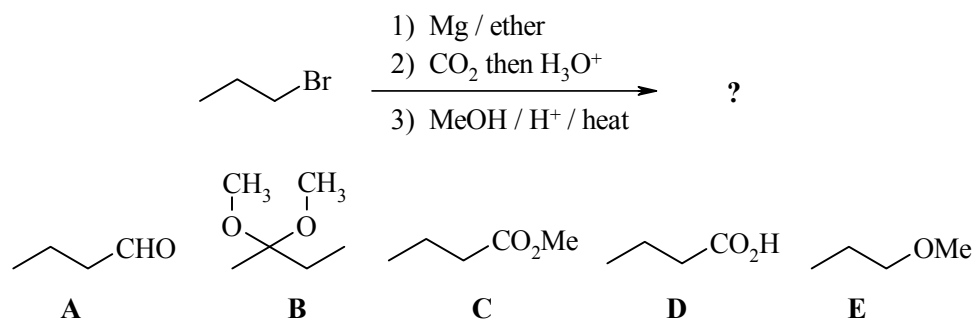


21.

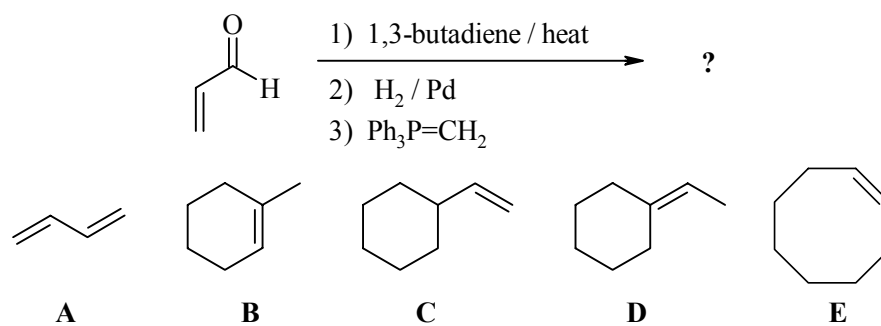


Value

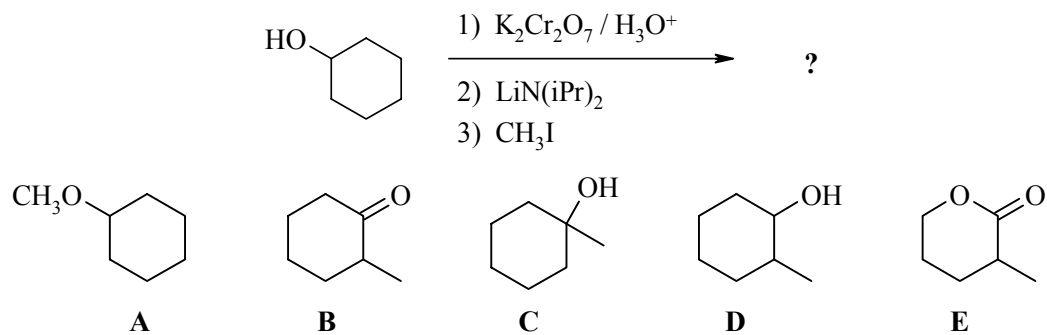
22.



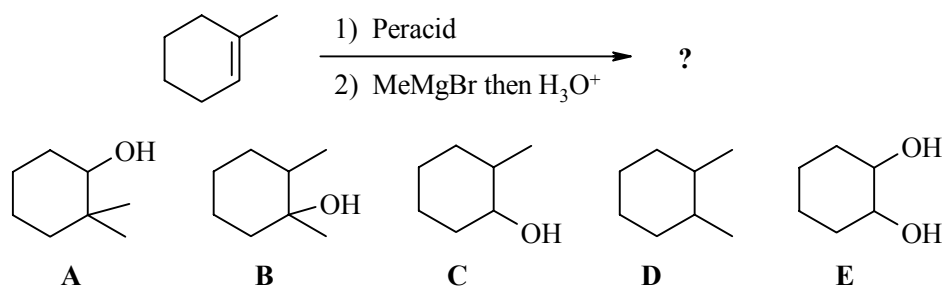
23.



24.



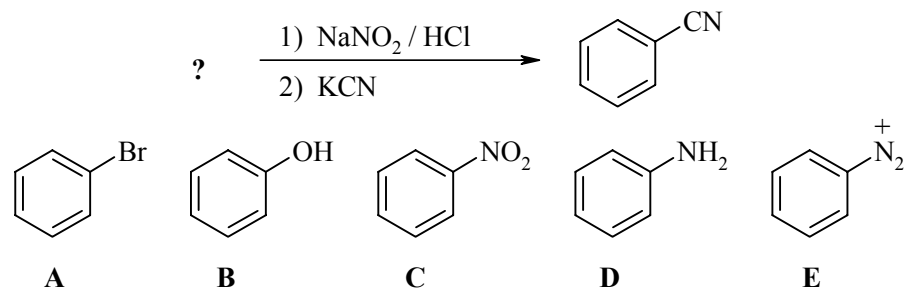
25.



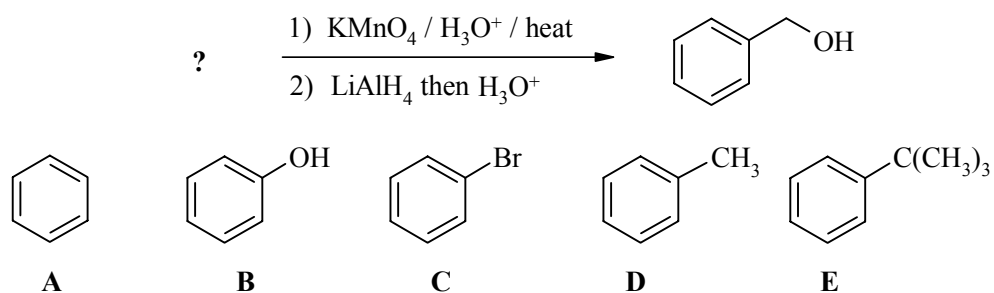
Value**PART 4: STARTING MATERIALS FOR SYNTHESIS****10% ANSWER ANY FIVE (5) OF QUESTIONS 26-32.**

For each of the questions 26-32, choose the starting material from the selection provided that gives the product indicated via the transformations shown.

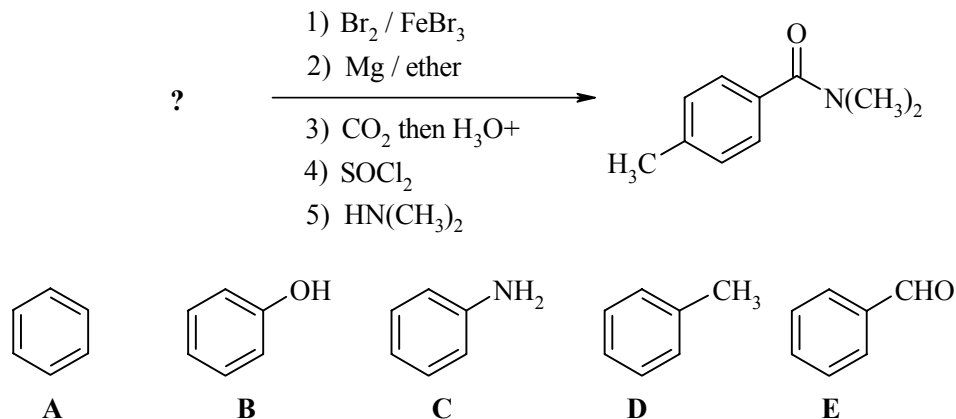
26.



27.

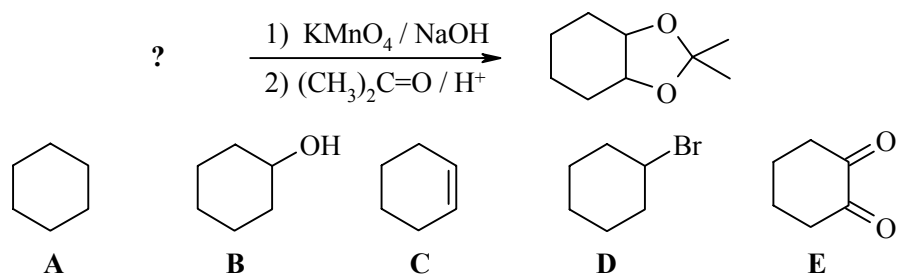


28.

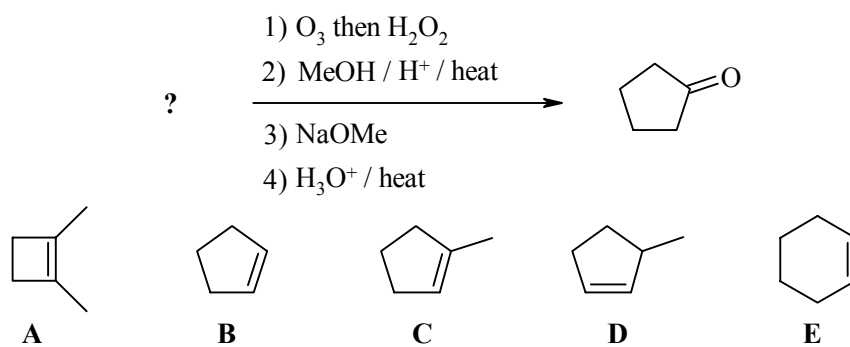


Value

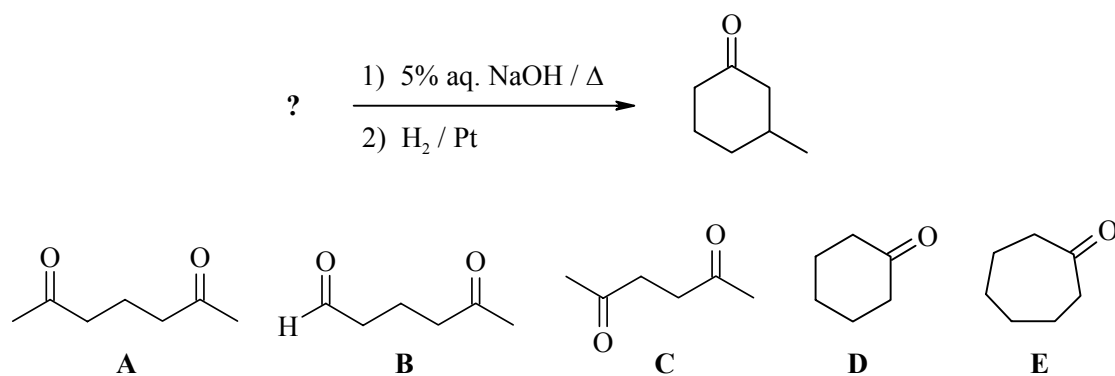
29.



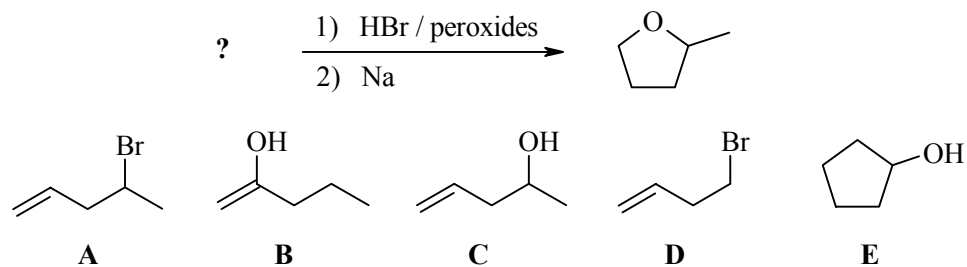
30.



31.

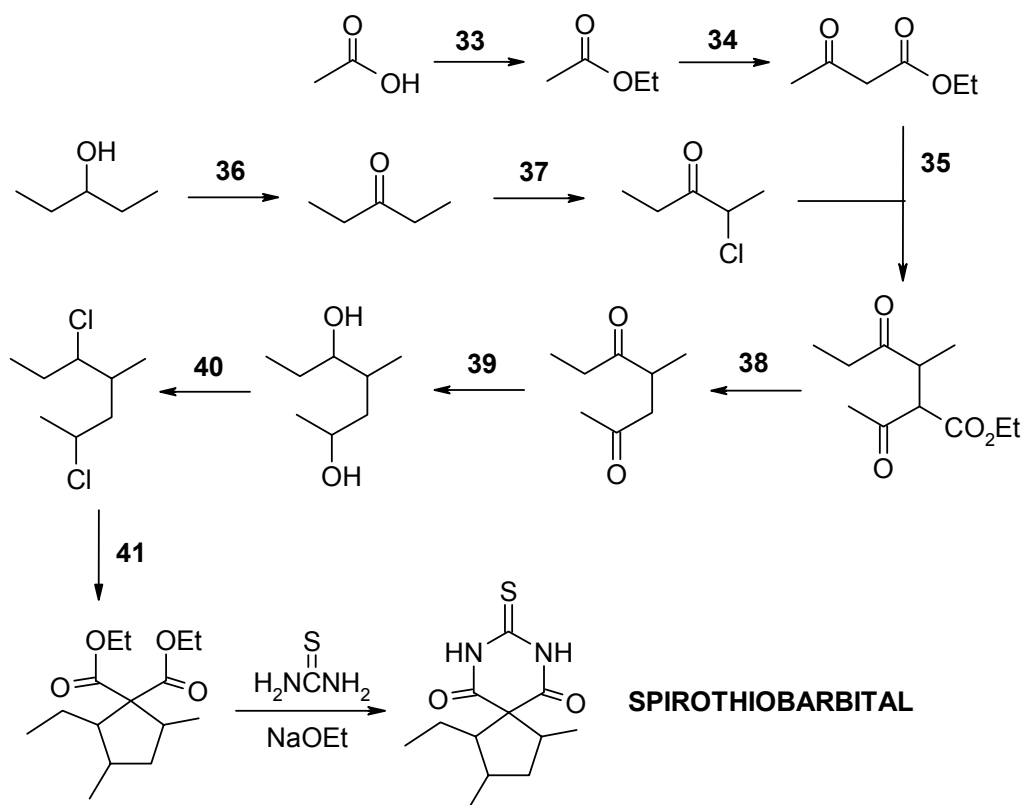


32.



Value**PART 5: REAGENTS FOR SYNTHESIS****9% ANSWER ALL OF THE QUESTIONS 33 - 41**

The following reaction scheme shows a synthesis of SPIROTHIOBARBITAL, an example of a sulfur (*thio*) barbiturate. 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.

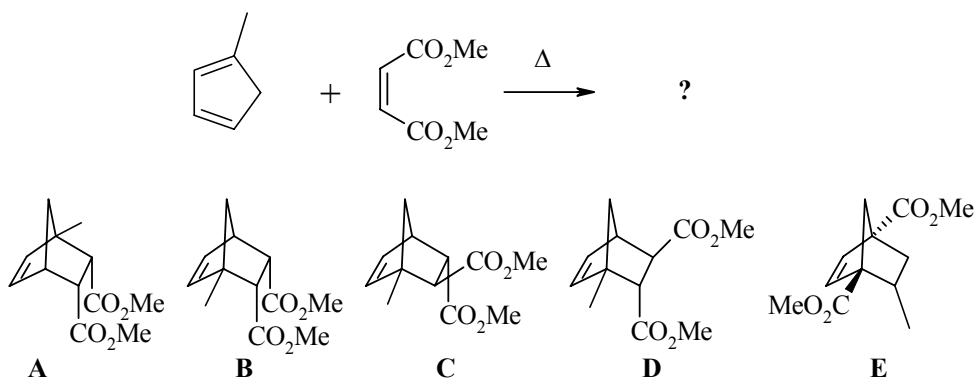


- | | |
|---|---|
| A. NaH | AE. H_2O_2 |
| B. Na / THF then MeOH | BC. $\text{H}_3\text{O}^+ / \Delta$ |
| C. H_2 / Pd | BD. $\text{Conc. H}_2\text{SO}_4 / \Delta$ |
| D. $\text{NaOH} / \text{Cl}_2$ | BE. $\text{EtOH} / \text{H}^+ / \Delta$ |
| E. HCl / Cl_2 | CD. $\text{NaOEt} / \text{EtOH}$ |
| AB. PCl_3 | CE. $\text{Li NiPr}_2 / \text{THF}$ |
| AC. 1 mol. eq. LiAlH_4 then H_3O^+ | DE. $\text{Aq. NaOH} / \Delta$ |
| AD. Pyridinium chlorochromate | ABC. $\text{NaOEt} / \text{EtOH} / \text{CH}_2(\text{CO}_2\text{Et})_2$ |

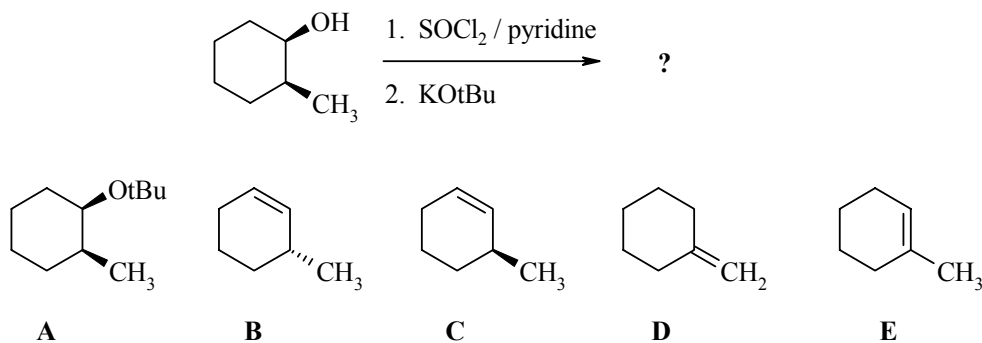
Value**PART 6: STEREOCHEMISTRY OF REACTIONS****10% ANSWER ANY FOUR (4) OF QUESTIONS 42 - 46**

For each of the questions 42 - 46, select the most abundant product. If two products are equally abundant, then indicate both. In order to indicate more than one product, blacken the spaces corresponding to each one.

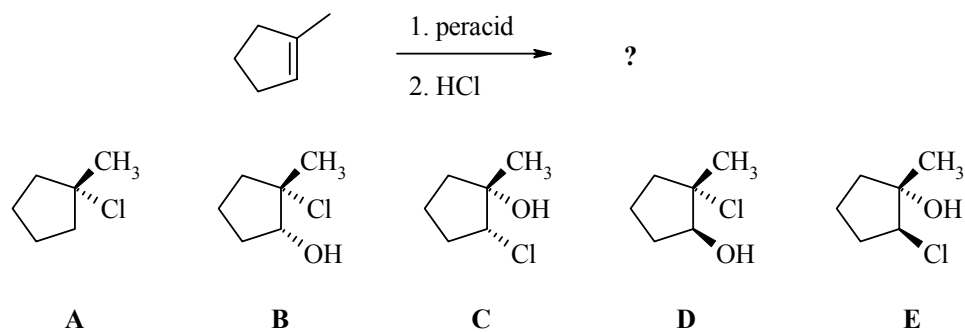
42.



43.



44.



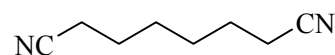
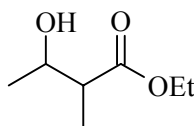
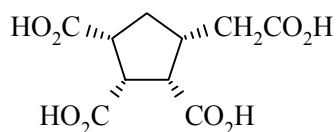
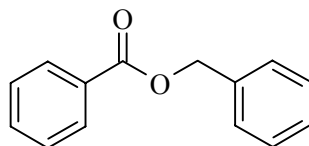
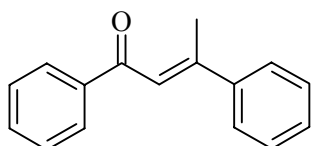
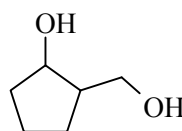
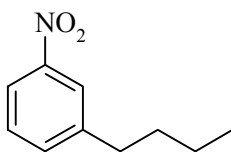
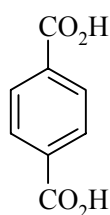
Value**PART 7: EXPLANATION OF PHENOMENA****8% ANSWER ALL OF THE QUESTIONS 47 - 50.**

Choose the SINGLE explanation that BEST describes the phenomenon indicated.

47. The α -hydrogens of esters typically have a $pK_a = 25$, whereas for amides $pK_a = 30$. This is because:
- A. The N atom in amides is less electronegative and does not stabilise the anion
 - B. The inductive effect of the nitrogen in the amide destabilises the amide enolate
 - C. There is no resonance stabilisation of the enolates of amides
 - D. The resonance stabilisation of the enolate is better in esters than in amides
 - E. The resonance stabilisation of the enolate is better in amides than in esters
48. When 3,3-dimethyl-1-butene is treated with aqueous H_2SO_4 , the major product is 2,3-dimethylbutan-2-ol. This is because:
- A. The reaction is an example of an anti-Markovnikov process
 - B. The reaction is an example of a Hofmann addition
 - C. Steric effects direct the attack of the nucleophile, H_2O
 - D. A 2° carbocation forms and rearranges to a 3° carbocation
 - E. Resonance control the attack of the nucleophile, H_2O
49. When nitrobenzene is sulphonated using sulphuric acid, the *meta* product is the major product. This is because:
- A. The SO_3H group is a *meta* director
 - B. The nitro group is a *meta* director
 - C. Statistically, the *meta* position is preferred
 - D. Sulphonation usually occurs at the *meta* position
 - E. The *ortho* positions are sterically hindered
50. The reaction of a Grignard reagent with the carbonyl group of a carboxylic acid does not give an alcohol. This is because:
- A. The carboxylic acid does not react with the Grignard reagent
 - B. The product of the reaction is a diol that is in equilibrium with a ketone
 - C. The Grignard reagent is a base, so proton abstraction generates an alkane
 - D. The carboxylic acid is too sterically hindered to react
 - E. Grignard reagents only react with aldehydes and ketones

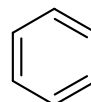
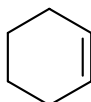
Value**PART 8: TOTAL SYNTHESIS****WRITE YOUR ANSWER ON THE BLANK PAGE PROVIDED**

12% Design an efficient synthesis for any **THREE (3)** of the following eight 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 4 carbons
- Triphenyl phosphine
- MCPBA
- Any of the following:



Value**PART 9: STRUCTURE DETERMINATION****14% WRITE YOUR ANSWER ON THE BLANK PAGE PROVIDED**

Compound **A**, C_6H_{10} , was treated with dilute H_2SO_4 to form **B**, $C_6H_{12}O$. Reaction of **B** with $K_2Cr_2O_7 / H_3O^+$ gave compound **C**, $C_6H_{10}O$. **C** was also formed in a separate reaction sequence starting from diethyl heptanedioate. This diester was treated with $NaOEt / EtOH$ to give compound **D**, $C_9H_{14}O_3$ on work-up. When **D** was heated with aqueous acid, bubbles of gas were produced and **C** was isolated from the reaction mixture.

When **C** was reacted with hydroxylamine, NH_2OH , in an acidic buffer solution, compound **E**, $C_6H_{11}NO$, was obtained. Reaction of **E** with conc. H_2SO_4 gave a rearrangement product, **F**, that was found to be an isomer of **E**. **F** was also prepared independently by heating 6-aminohexanoyl chloride. Compound **F** was then reacted with $LiAlH_4$ in anhydrous ether followed by a dilute acid work-up, to yield **G**, $C_6H_{13}N$. When **G** was reacted with excess methyl iodide followed by heating with Ag_2O , 1,5-hexadiene was obtained.

D was the only chiral molecule and existed as a pair of enantiomers that were difficult to resolve.

Compounds **A - G** showed the following numbers of signals in the ^{13}C nmr:

A = 3, **B** = 4, **C** = 4, **D** = 9, **E** = 4, **F** = 6, **G** = 3

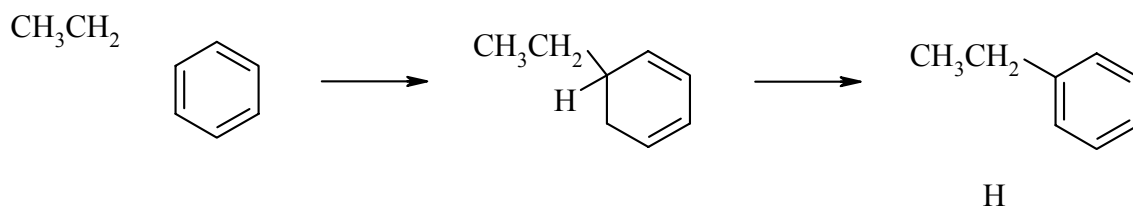
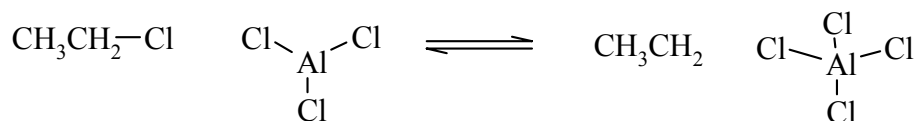
What are **A - G** ?

Postulate a step-by-step mechanism (using curly arrows) for the conversion of **E** to **F**.

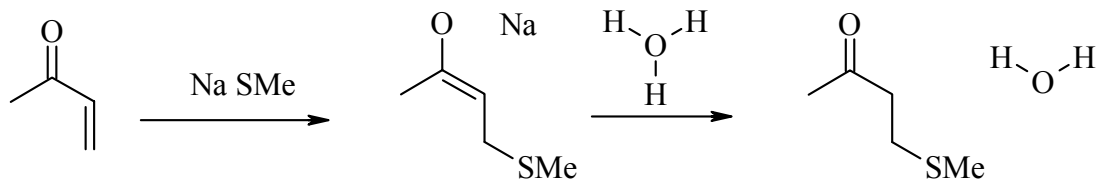
ValueNAMEID**PART 10: MECHANISMS****10% ANSWER ALL OF THE QUESTIONS 51 - 53 BY DRAWING ON THESE PAGES**

For Questions 51 and 52, DRAW in ALL of the curly arrows and any required charges to complete the step-by-step mechanisms for the following reaction schemes. All the required bonds have been shown.

51.



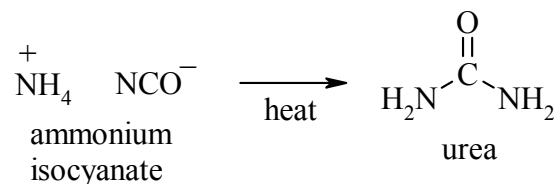
52.

**QUESTION 53 IS ON THE FOLLOWING PAGE**

Value

For Question 53 you are required to **draw a curly arrow mechanism** to complete the step-by-step mechanism for the reaction indicated. You will need to draw structures for any intermediates required.

53. In 1828, Wohler carried out the first "organic" synthesis by producing urea from ammonium isocyanate, see below. Based on the chemistry of carbonyl compounds and / or nitriles, postulate a reasonable mechanism to account for this reaction. (Hint: draw a Lewis structure of the isocyanate ion to start from)



Value

PART 8:

NAME

ID

Value

PART 9: **NAME ID** _____