

THE UNIVERSITY OF CALGARY
FACULTY OF SCIENCE
FINAL EXAMINATION
CHEMISTRY 353

April 25th, 1998

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 - 51 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**.

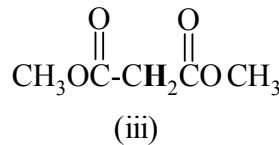
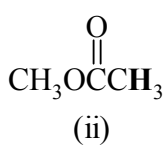
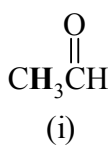
Value**PART 1: RELATIVE PROPERTIES****9% ANSWER ANY SIX (6) OF QUESTIONS 1-10.**

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

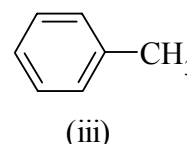
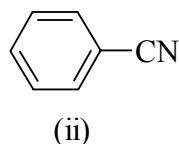
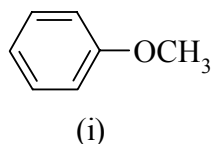
Use the following code to indicate your answers.

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

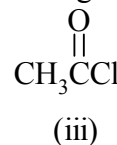
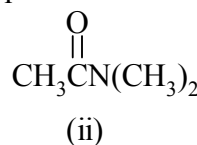
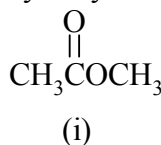
1. The acidity of the protons **H** in each of the following:



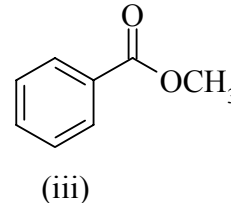
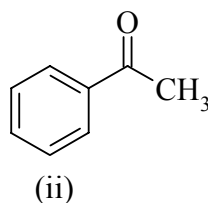
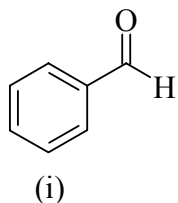
2. Rate of reaction of $\text{HNO}_3 / \text{H}_2\text{SO}_4$ with each of the following



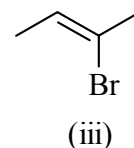
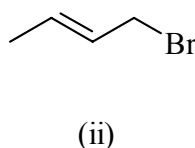
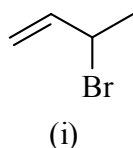
3. Reactivity towards hydrolysis using aqueous acid of the following



4. Reactivity of the following towards reaction with LiAlH_4 :



5. The relative yields of the following alkenyl bromides from the reaction of 1,3-butadiene with HBr (dark, N_2 atmosphere) at -15°C .

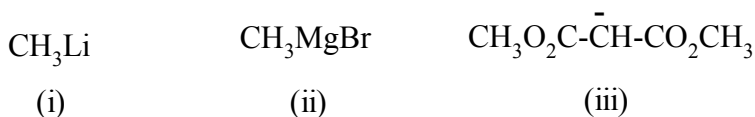


Value

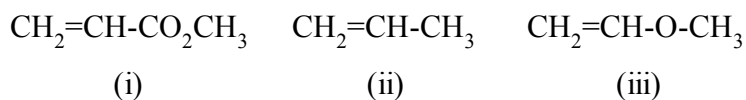
Use the following code to indicate your answers.

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

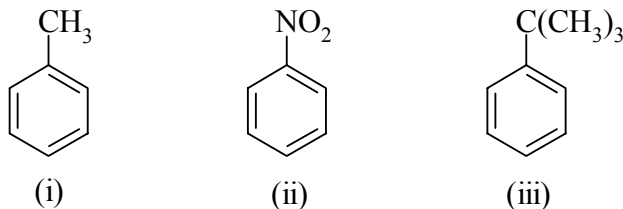
6. The amount of conjugate addition obtained in the reaction of the following with 3-butenone:



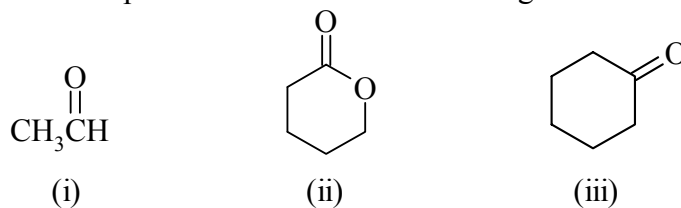
7. The relative reactivity towards Br_2 in CHCl_3 of the following::



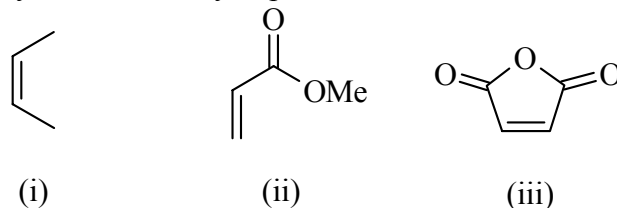
8. The % of the para product produced in the reaction of $\text{Br}_2 / \text{FeBr}_3$ with each of the following



9. The number of enolizable protons in each of the following



10. The relative reactivity towards 1,3-cyclopentadiene of each of the following.



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

The final two weeks of the CHEM 353 laboratory course were dedicated to the analysis of five common unknowns and one individual unknown. The following series of questions ALL relate to the five common unknowns A-E, actually used in the lab (here labelled *V-Z*).

<i>V</i>	<i>W</i>	<i>X</i>	<i>Y</i>	<i>Z</i>
<u>physical properties</u>				
b. 184°/760	b. 86°/760	m. 122°	b. 227°/760	m. 43°
<u>NMR data shift</u> (multiplicity; integration)				
δ 3.3 (m; 2)*	δ 2.1 (s)	δ 7.0-8.3 (m; 5)	δ 1.0 (t; 3)	δ 6.0(s; 1)*
δ 6.2-7.2 (s, 5)		12.8 (s; 1)*	δ 3.6 (s; 2)	δ 6.5-7.3 (m; 5)
			δ 3.9 (q,2)	
			δ 7.2 (s,5)	

*signal exchangeable with D₂O

IR data (major diagnostic absorptions only)

3510 cm ⁻¹	1710 cm ⁻¹	3500-2500 cm ⁻¹	1735 cm ⁻¹	3600 cm ⁻¹
3500 cm ⁻¹		1700 cm ⁻¹		

Value

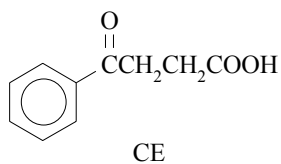
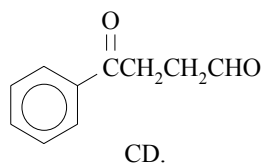
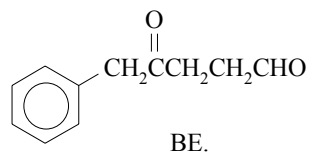
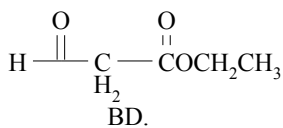
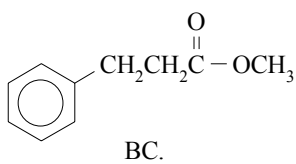
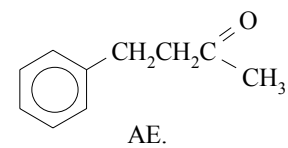
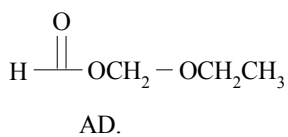
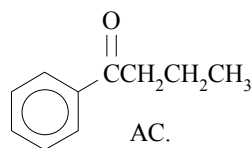
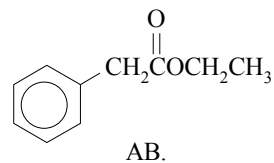
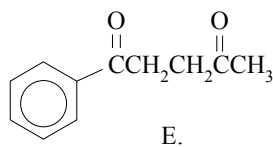
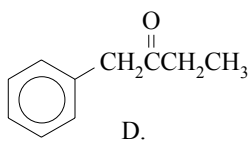
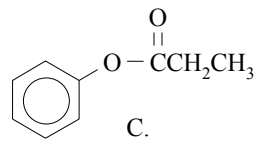
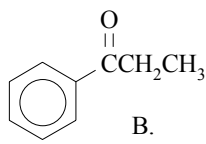
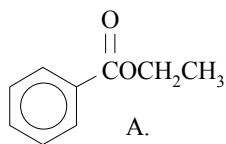
The six possible categories to which the unknowns belong are shown below. Use this key to answer Questions 11-15. No two compounds belong to the same category.

- A. aldehyde or ketone
- B. alcohol
- C. phenol
- D. carboxylic acid
- E. ester
- AB. amine

11. Compound *V* belongs to which category?
12. Compound *W* belongs to which category?
13. Compound *X* belongs to which category?
14. Compound *Y* belongs to which category?
15. Compound *Z* belongs to which category?

The remaining questions - all refer to Unknown *Y* only.

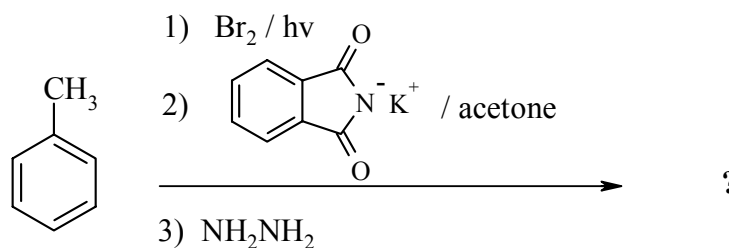
16. Compound *Y* is:-
 - A. Aromatic only
 - B. Aliphatic only
 - C. Both aromatic and aliphatic
17. Which of the following tests would be positive for unknown *Y* ? Blacken in the space if the test would be positive; leave the space blank if the test would be negative.
 - A. Soluble in water
 - B. Soluble in 5% NaOH
 - C. 2,4-Dinitrophenylhydrazine test
 - D. Ferric chloride test
 - E. Iodoform test

Value18. Which of the following compounds is *Y* ?

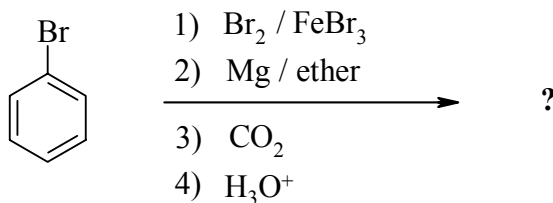
Value**PART 3: PRODUCTS OF SYNTHESIS****10% ANSWER ANY FIVE (5) OF QUESTIONS 19-25.**

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.

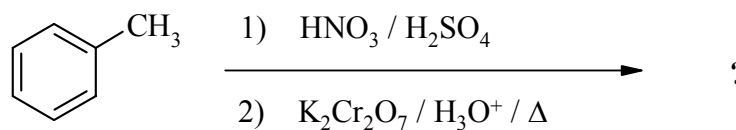
19.



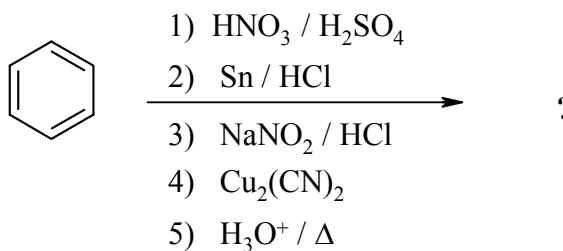
20.



21

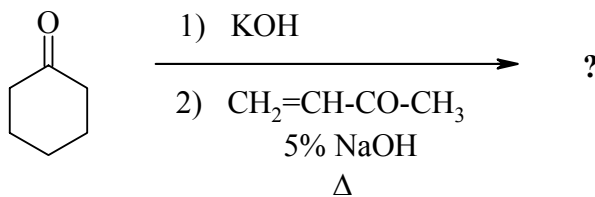


22.

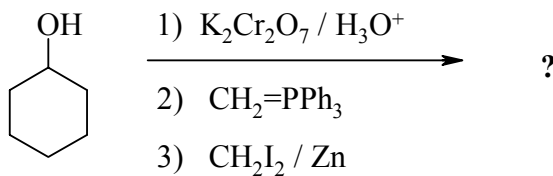


Value

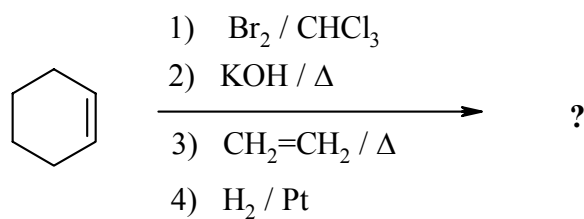
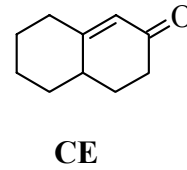
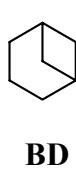
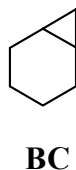
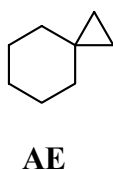
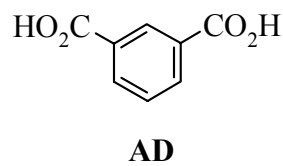
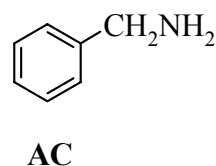
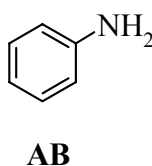
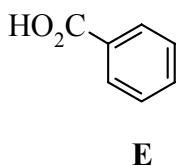
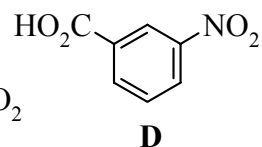
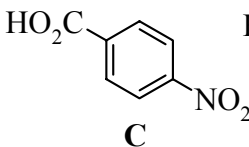
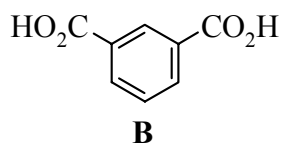
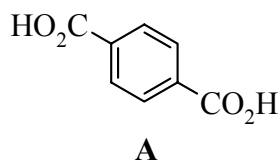
23.



24.



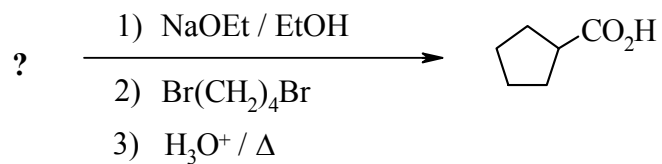
25.

List of possible answers for Questions 19 to 25

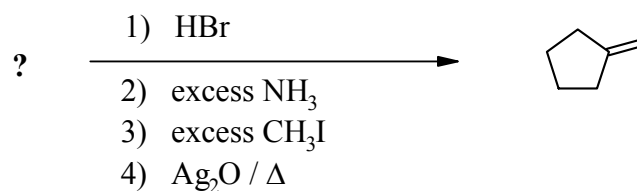
Value**PART 4: STARTING MATERIALS FOR SYNTHESIS****10% ANSWER ANY FIVE (5) OF QUESTIONS 26-32.**

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

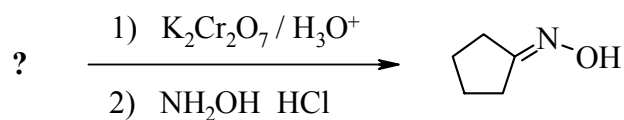
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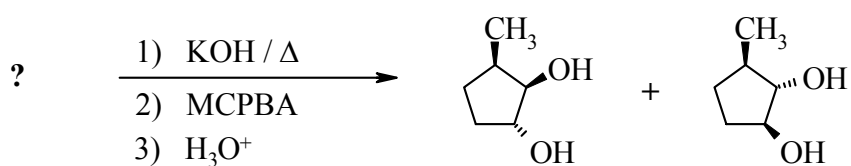
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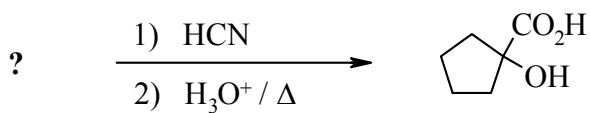
28.



29.

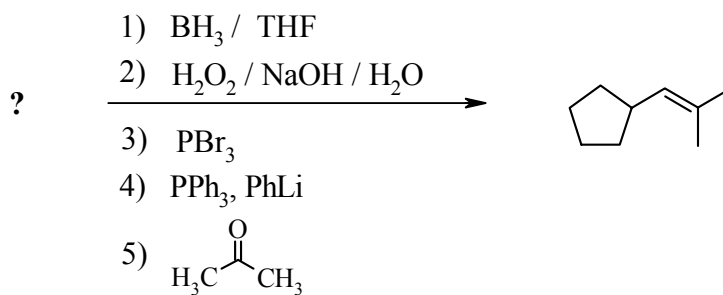


30.

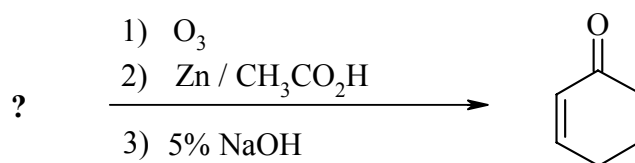
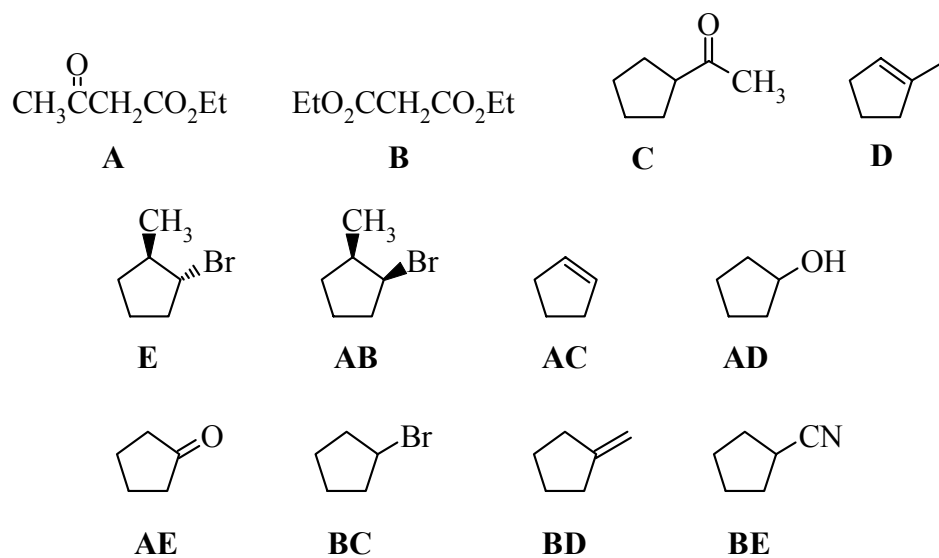


Value

31.

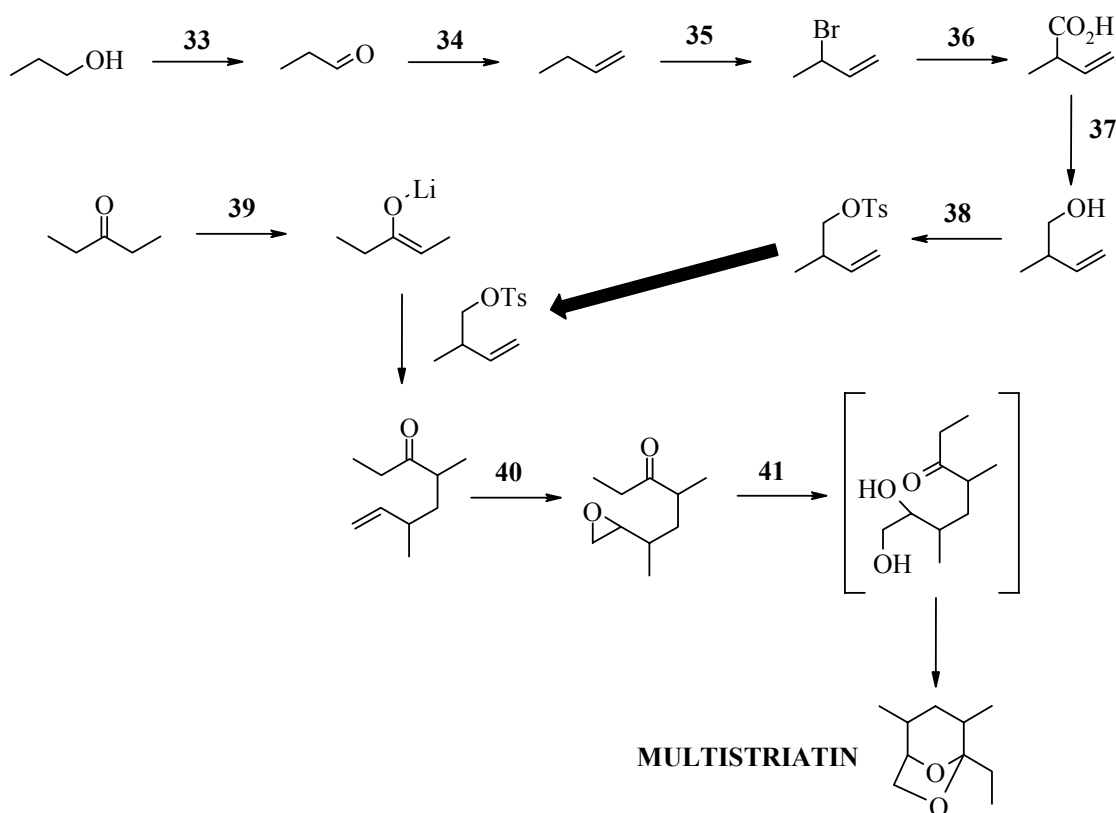


32.

List of possible answers for Questions 26 to 32

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

The following reaction scheme shows a potential synthesis of MULTISTRIATIN, an aggregation pheromone of the European Elm Beetle (*scolytus multistriatus*), the vector for Dutch Elm Disease. 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.

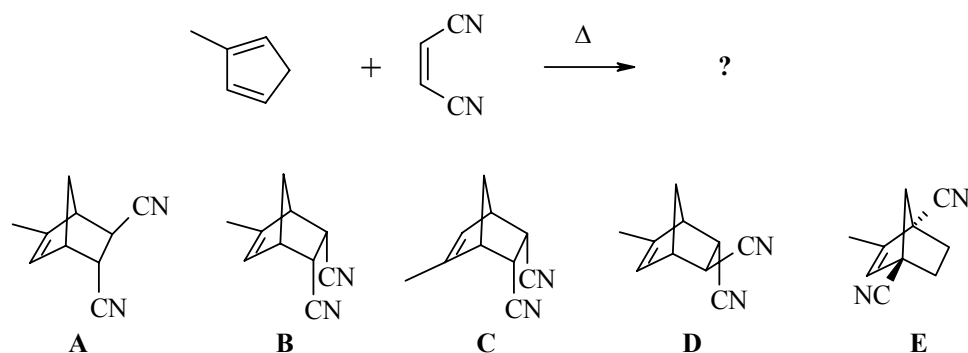


A. 1 eq NaBH_4 then H_3O^+	AE. Mg then CO_2 then H_3O^+
B. 1 eq LiAlH_4 then H_3O^+	BC. H_3O^+
C. Ph_3PCH_2	BD. Conc. $\text{H}_2\text{SO}_4 / \Delta$
D. $\text{NaTs} / \text{DMSO}$	BE. $\text{TsCl} / \text{pyridine}$
E. MCPBA	CD. $\text{NaOEt} / \text{EtOH}$
AB. $\text{Br}_2 / h\nu$	CE. $\text{Li NiPr}_2 / \text{THF}$
AC. PBr_3	DE. LiCl / DMF
AD. Pyridinium chlorochromate	ABC. NaOH then $\text{CrO}_3 / \text{pyridine}$

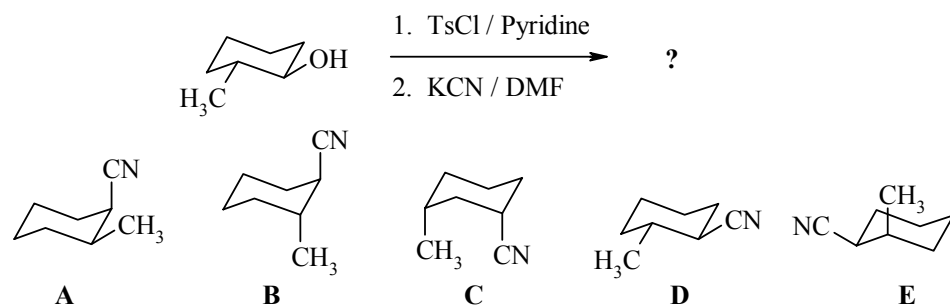
Value**PART 6: STEREOCHEMISTRY OF REACTIONS****10% ANSWER ANY FOUR (4) OF QUESTIONS 42 - 46**

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.

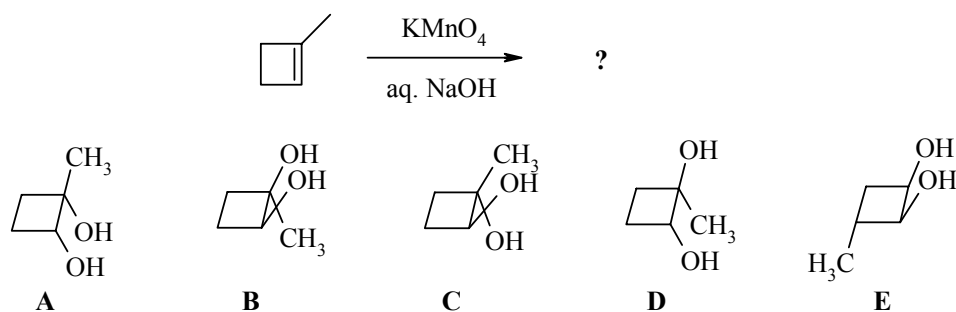
42.



43.

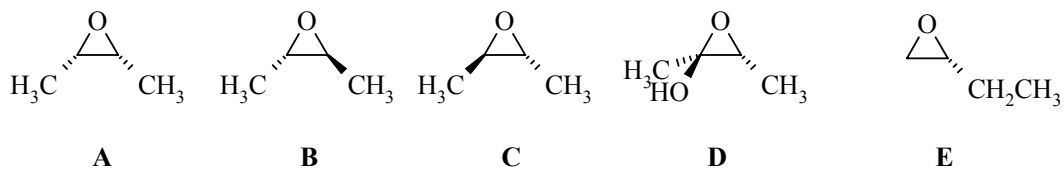
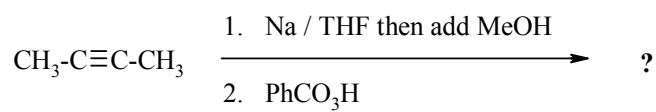


44.

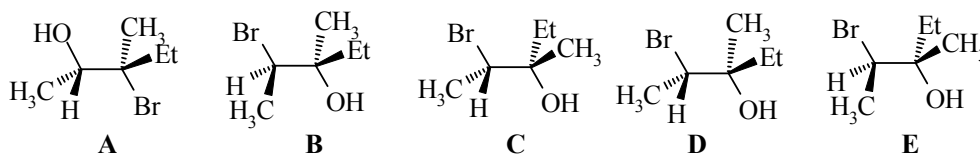
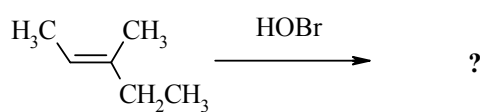


Value

45.

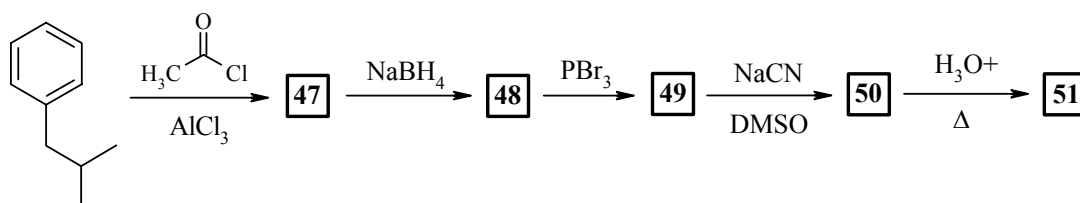


46.



Value**PART 7: APPLIED SPECTROSCOPY****10% ANSWER ALL OF THE QUESTIONS 47 - 51.**

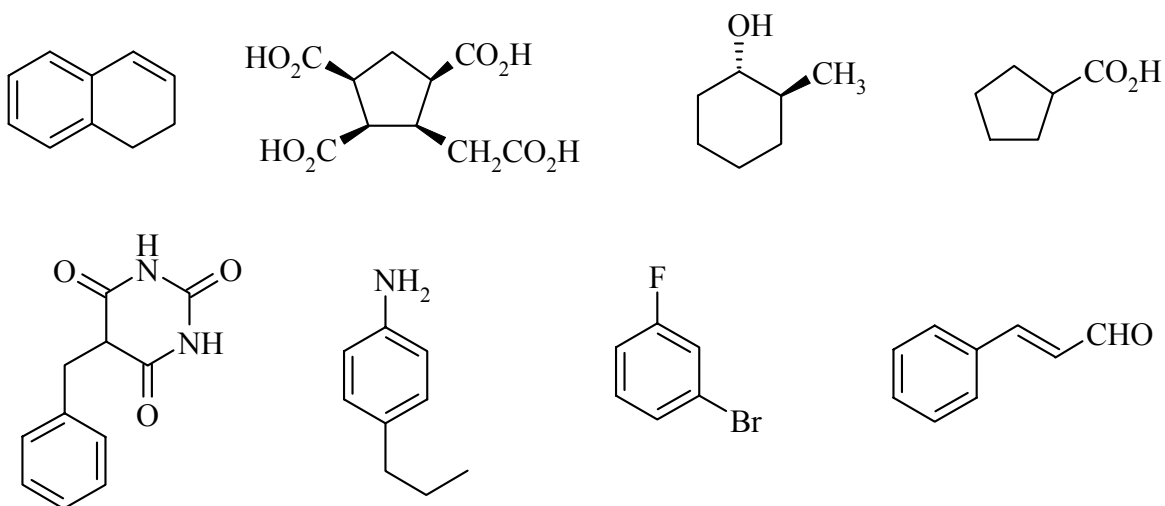
Our old friend has not learnt. The novice organic chemist was carrying out the synthesis shown below of Ibuprofen. However, once again, he managed to mix up all of his $^1\text{H-NMR}$ spectra ! For each of the **BOXED NUMBERS** in the scheme, which indicates a compound, select from the $^1\text{H-NMR}$ spectra provided the spectra that corresponds to that compound.



DIGITAL SPECTRA WILL BE ADDED AS SOON AS TIME ALLOWS

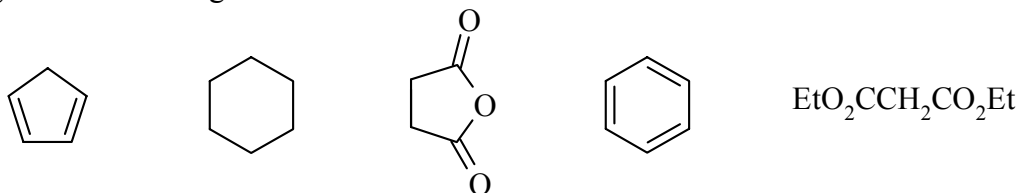
Value**PART 8: TOTAL SYNTHESIS****WRITE YOUR ANSWER ON ONE OF BLANK PAGES PROVIDED**

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 2 carbons
- Triphenyl phosphine
- MCPBA
- Any of the following:



Value**PART 9: STRUCTURE DETERMINATION****14% WRITE YOUR ANSWER ON ONE OF BLANK PAGES PROVIDED**

Compound **A**, $C_7H_{15}N$, was basic and existed as a pair of enantiomers. On treatment with excess CH_3I , **A** reacted with 2 equivalents of CH_3I ; subsequently Ag_2O was added and the mixture heated. Compound **B**, $C_9H_{19}N$, was isolated from the reaction mixture as a racemic mixture. Compound **B** was then reacted with excess CH_3I followed by heating with Ag_2O . In this reaction, 1 equivalent of CH_3I was consumed, and compound **C**, C_7H_{12} , and trimethylamine were obtained from the reaction mixture. **C** was then reacted with aqueous $Hg(OAc)_2$ ($OAc = acetate$) followed by $LiAlH_4$. This treatment produced **D**, $C_7H_{16}O_2$, an optically inactive mixture of 3 diastereomers. **D** was treated with $K_2Cr_2O_7 / H^+$ and **E** $C_7H_{12}O_2$ was isolated from the reaction mixture. **E** was also obtained in a separate reaction by treating 1,2-dimethylcyclopentene with ozone followed by work-up with zinc and acetic acid. **E** was reacted with 5% $NaOH$ solution and **F**, $C_7H_{10}O$, was obtained. On ozonolysis of **F** followed by reductive work-up with Zn / CH_3CO_2H , 2,6-dioxoheptanal (also called 2,6-diketoheptanal) was obtained.

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

A - 4, **B** - 9, **C** - 4, **D** - 4, **E** - 4, **F** - 7.

What are **A - F** ?

Show the step-by-step mechanism (use curly arrows) for the conversion of **E** to **F**.

Value

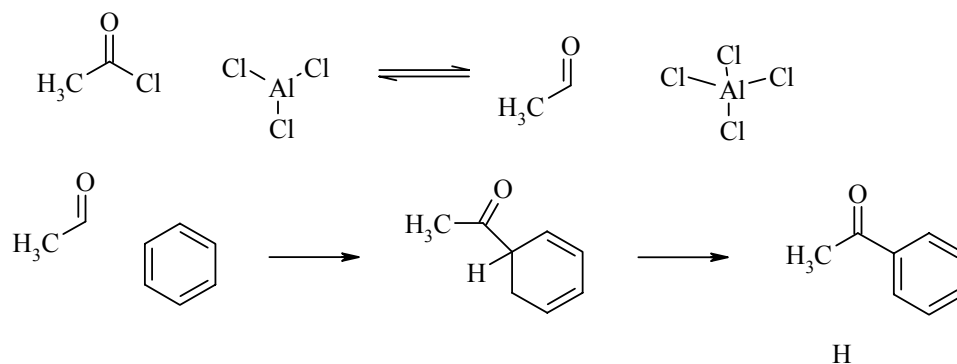
NAME _____

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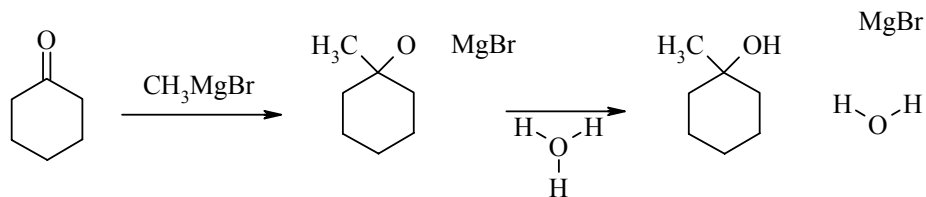
PART 10: MECHANISMS**8% ANSWER ALL OF THE QUESTIONS 52 - 55 BY DRAWING ON THIS PAGE**

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

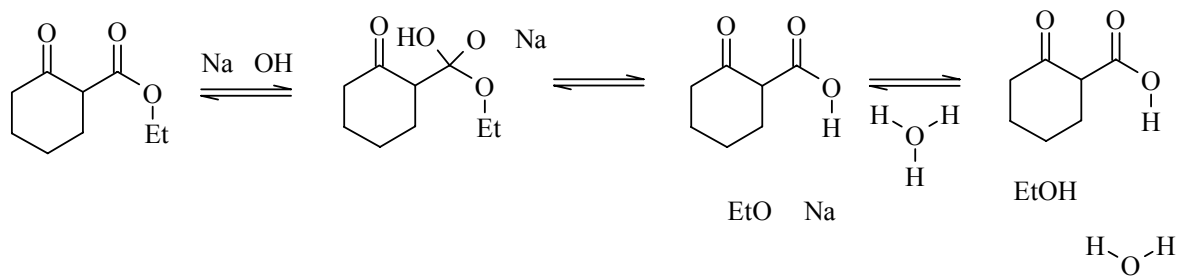
52.



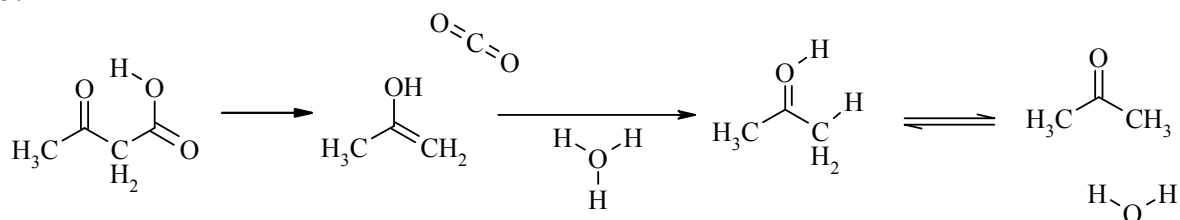
53.



54.



55.



Value

PART 8:

NAME

ID

Value

PART 9: **NAME ID** _____