THE UNIVERSITY OF CALGARY

FACULTY OF CONTINUING EDUCATION

FINAL EXAMINATION

CHEMISTRY 353

August 17th, 1998 Time: 3 Hours

READ THE ALL INSTRUCTIONS CAREFULLY

PLEASE WRITE YOUR **NAME, STUDENT I.D. NUMBER** ON THE **COMPUTER ANSWER SHEET** AND THE **3 PAGES** FOR THE WRITTEN ANSWER QUESTIONS.

The examination consists of Parts 1 - 10, each of which should be attempted. Note that some Parts provide you with a choice of questions, if you answer more than the required number of questions, they will be marked in numerical order until the required number have been graded. 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

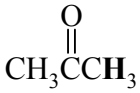
12% **ANSWER ANY SIX (6) OF QUESTIONS 1-10.**

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

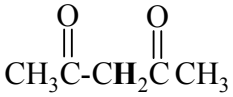
Use the following code to indicate your answers.

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:



(i)



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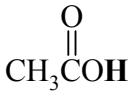
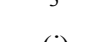
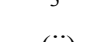


(iii)

2. The relative nucleophilicity in polar protic solvents of each of the following:



(i)



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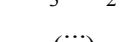
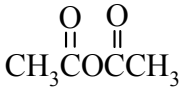
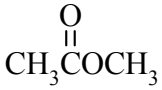


(iii)

3. Reactivity towards NH_3 of each of the following



(i)



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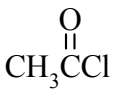
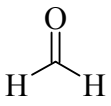
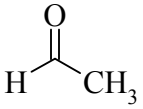


(iii)

4. Reactivity of the following towards reaction with $NaBH_4$:



(i)



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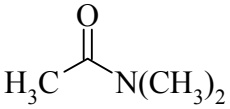
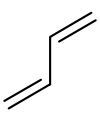


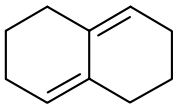
(iii)

5. The relative reactivity towards 1-buten-3-one of each of the following.



(i)

(ii)



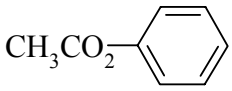
(iii)

Value

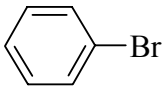
Use the following code to indicate your answers.

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

6. Rate of reaction of CH_3COCl / $AlCl_3$ with each of the following



(i)



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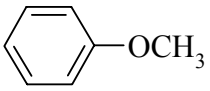
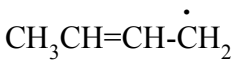
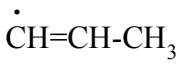


(iii)

7. The relative stability of the following radicals:



(i)



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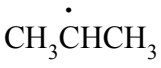
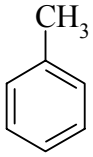
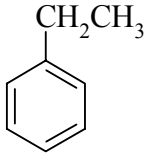


(iii)

8. The *ortho* / *para* product ratio produced in the reaction of Br_2 / $FeBr_3$ with each of the following



(i)



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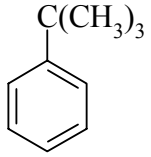
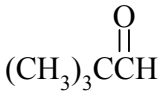
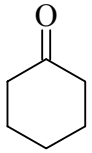


(iii)

9. The amount of the enol form present at equilibrium for each of the following:



(i)



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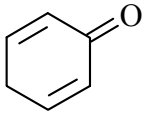


(iii)

10. The relative yields of the following alkenes produced by the reaction of *trans*-1-chloro-2-methylcyclohexane with KOH / heat:

(i) 1-methylcyclohexene

(ii) methylenecyclohexane

(iii) 3-methylcyclohexene

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.

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** and isolated the liquid product, **STU-2**, from the dichromate test on **#0001** for further tests. The results of all the tests are shown in the table below. The crystalline product, **STU-3**, from the 2,4-dinitrophenylhydrazine procedure 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		Red precipitate formed
Iodoform		Yellow precipitate formed
Ferric Chloride	No significant colour change	
Dichromate	Colour changed from orange to green	No noticeable change

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 Br_2 / $CHCl_3$

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

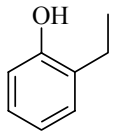
A 180°C **B** 190°C **C** 200°C **D** 210°C **E** 250°C

Value

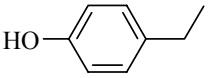
ANSWER QUESTIONS 17 & 18 FROM THE LIST OF COMPOUNDS GIVEN BELOW.

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

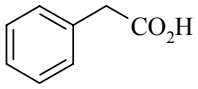
18. Which of the following compounds shown below is **STU-2** ?



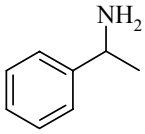
A.



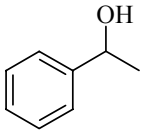
B.



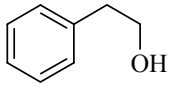
C.



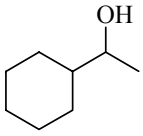
D.



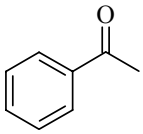
E.



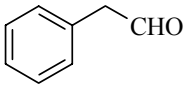
AB.



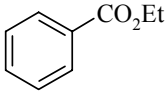
AC.



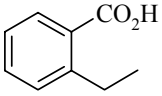
AD.



AE.



BC.



BD.

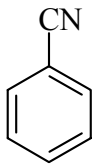
Value

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.

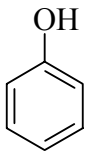
19.



1) Br_2 , $FeBr_3$
2) H_3O^+, heat
3) $SOCl_2$
4) CH_3OH

→ **?**

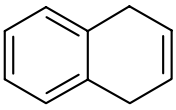
20.



1)  , Et_3N
2) HNO_3, H_2SO_4
3) Zn / HCl
4) $NaNO_2$, H_2SO_4
5) CuBr

→ **?**

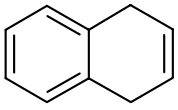
21



1) BH_3, H_2O_2
2) $Na_2Cr_2O_7$
3) LDA, THF, -78°C
4) CH_3Br

→ **?**

22.

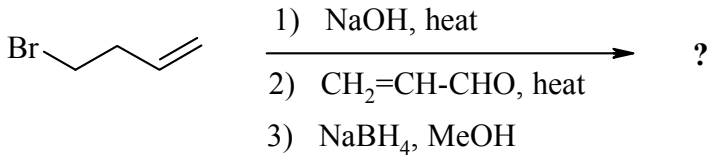


1) hot $KMnO_4$
2) P_2O_5
3) Br_2, $FeBr_3$

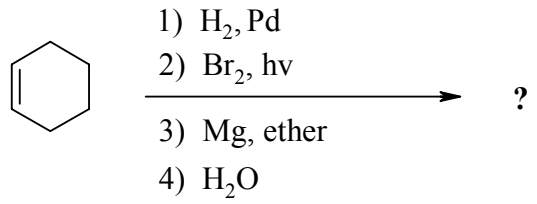
→ **?**

Value

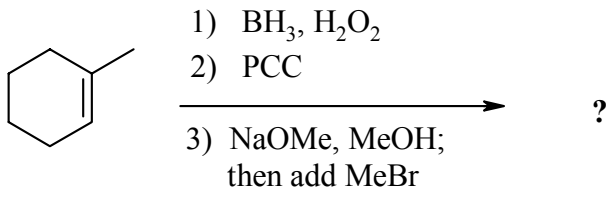
23.



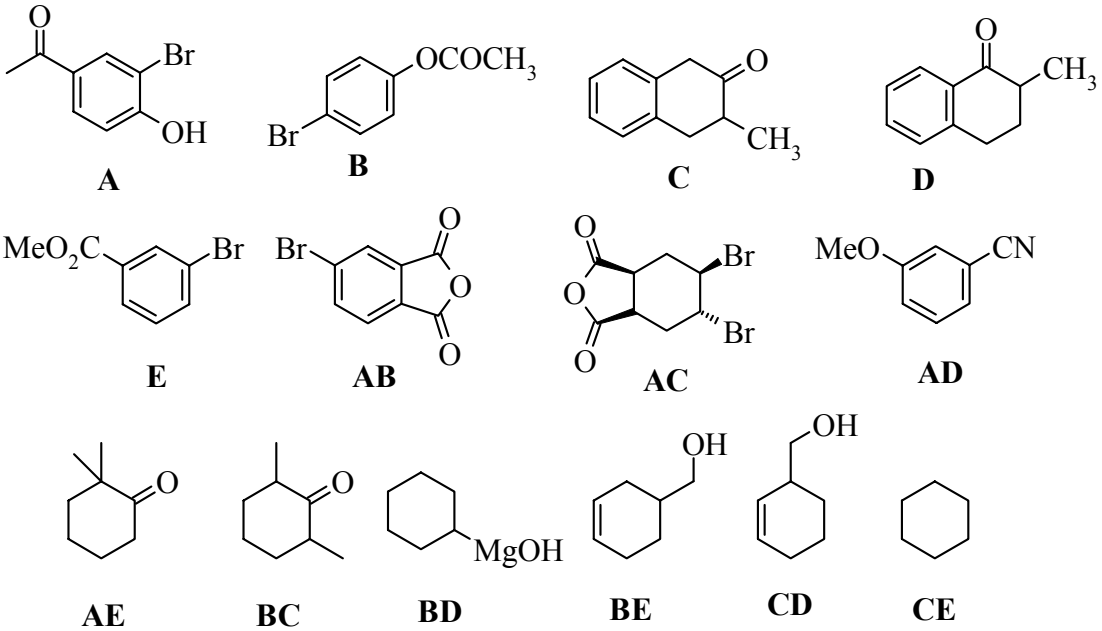
24.



25.



List of possible answers for Questions 19 to 25



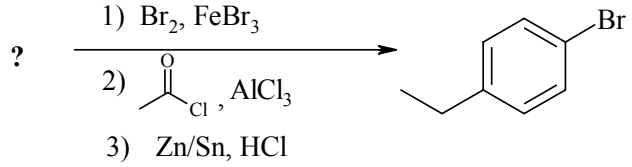
Value

PART 4: STARTING MATERIALS FOR SYNTHESIS

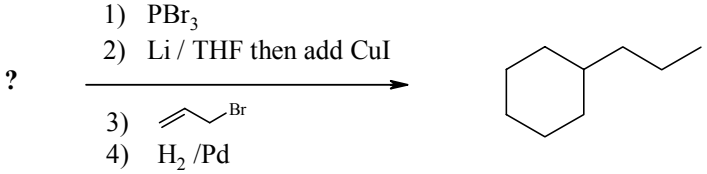
10% **ANSWER ANY FIVE (5) OF QUESTIONS 26-32**.

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

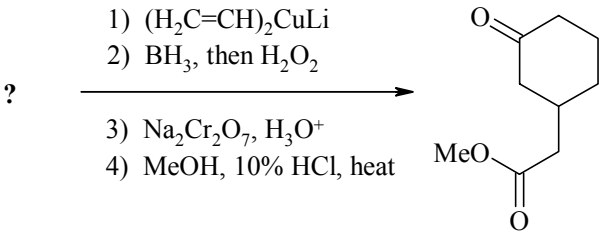
26.



27.



28.



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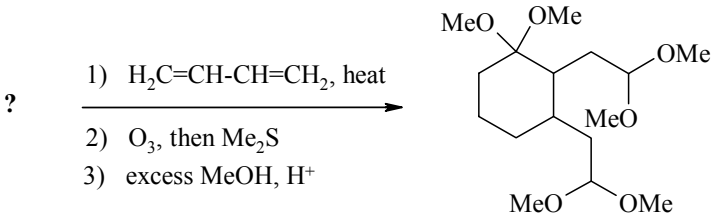

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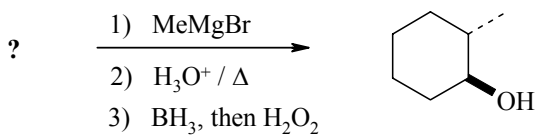
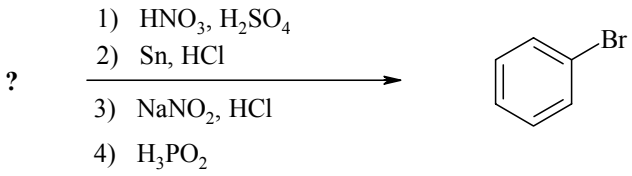
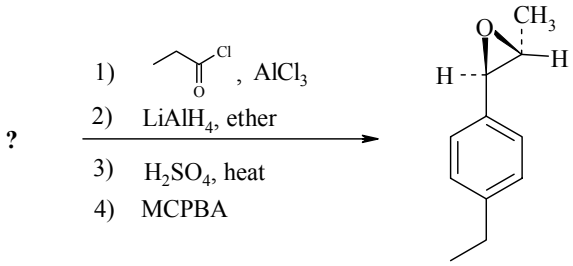


Value

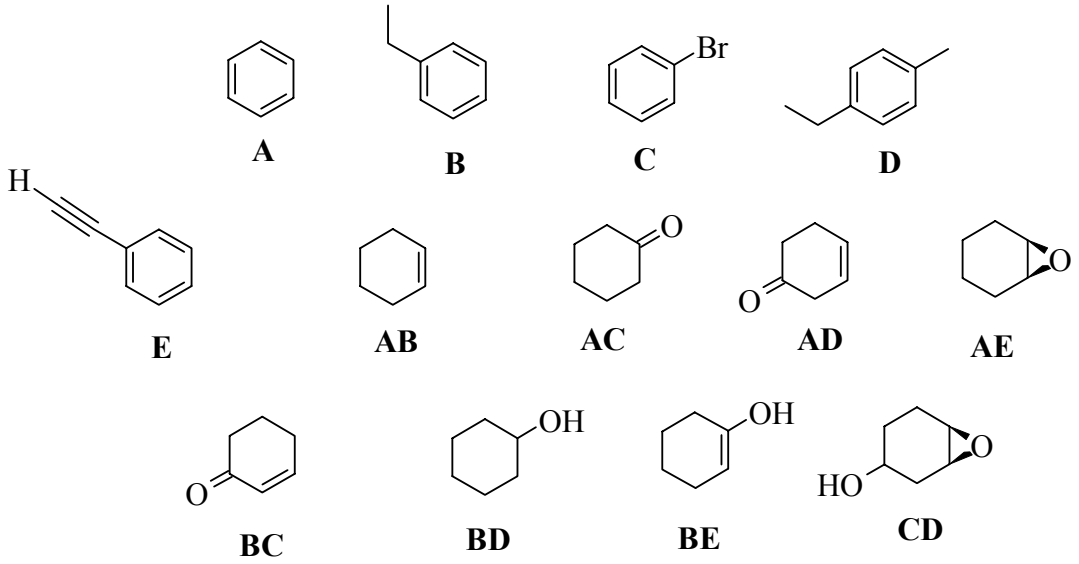
31.



32.



List of possible answers for Questions 26 to 32

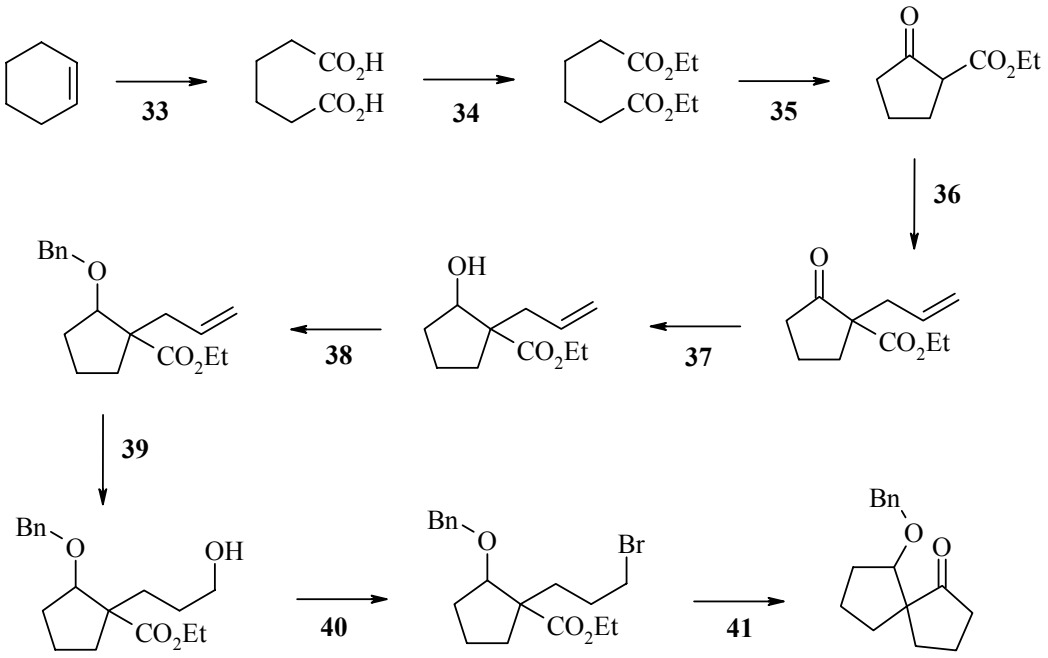


Value

PART 5: REAGENTS FOR SYNTHESIS

9% **ANSWER ALL OF THE QUESTIONS 33 - 41**

The following reaction scheme shows a new synthesis of a chiral ligand being carried out by a summer student in Dr. Keay's research laboratory. 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.



NOTE: Bn = Benzyl group, $PhCH_2$-

A. $NaBH_4$ then H_3O^+	**BD.** Pyridinium chlorochromate
B. $LiAlH_4$ then H_3O^+	**BE**. $Na_2Cr_2O_7$ / H_3O^+
C. O_3 then Zn / CH_3CO_2H	**CD**. NaBr / acetone
D. O_3 then H_2O_2	**CE**. PBr_3
E. NaOH	**DE**. Br_2 / hv
AB. Na dissolved in EtOH	**ABC**. LDA / THF / -78°C
AC. H_3O^+	**ABD**. Mg / Et_2O
AD. BH_3 then NaOH / H_2O_2	**ABE**. EtOH / H^+ / heat
AE. Na then add PhBr	**ACD**. CH_2=CH-CH_2MgBr
BC. Na then add $PhCH_2Br$	**ACE**. NaOEt then CH_2=CH-CH_2Br

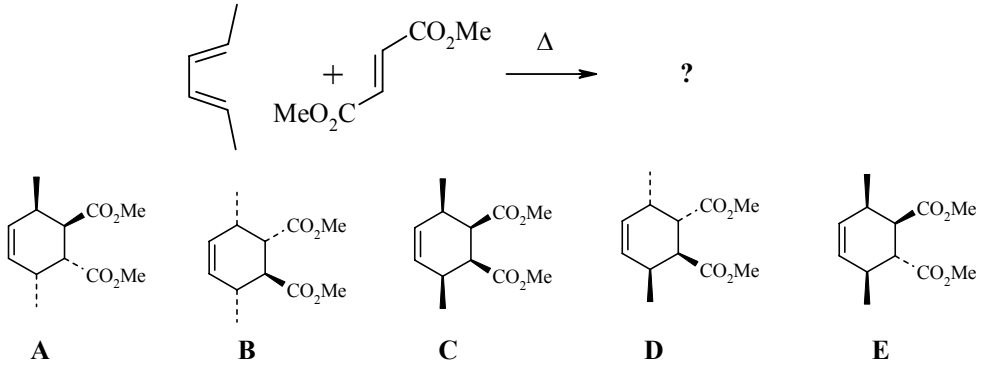
Value

PART 6: STEREOCHEMISTRY OF REACTIONS

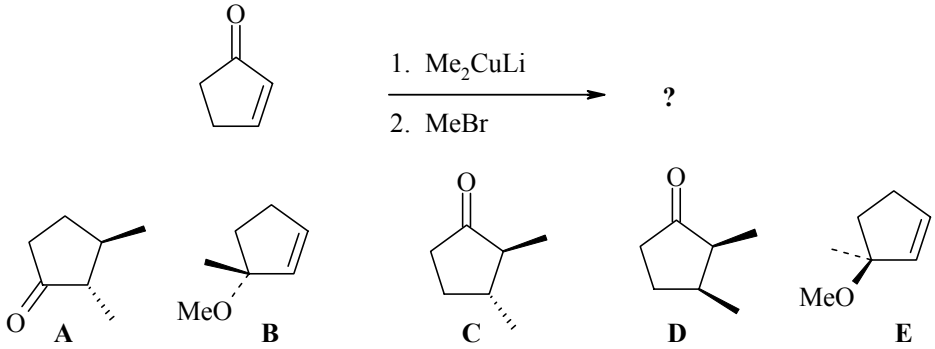
10% **ANSWER ANY FOUR (4) OF QUESTIONS 42 - 46**

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.

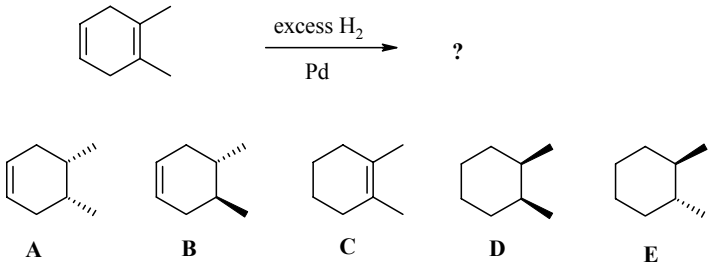
42.



43.

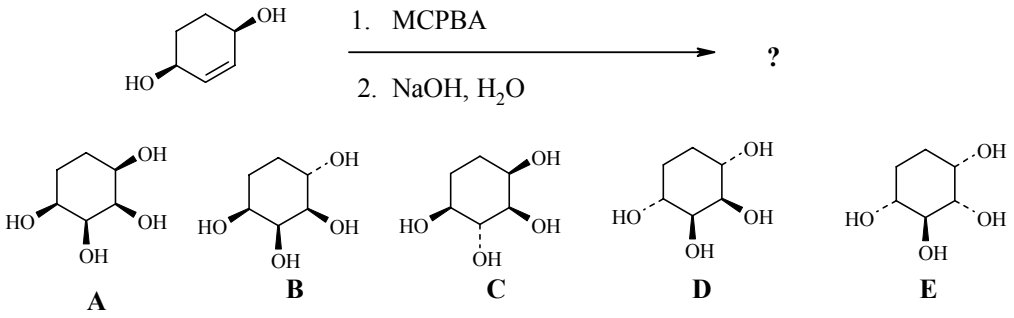


44.

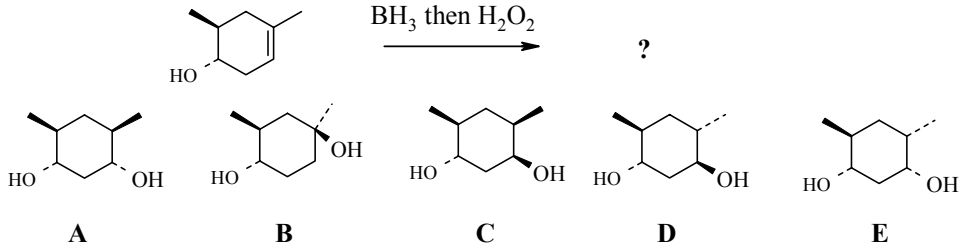


Value

45.



46.



Value

PART 7: EXPLANATION OF PHENOMENA

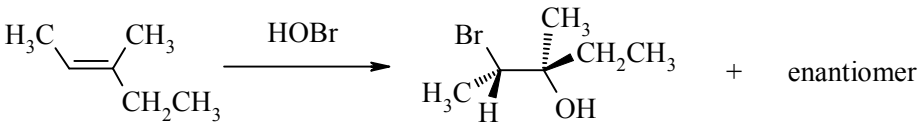
8% **ANSWER ALL OF THE QUESTIONS 47 - 50.**

Choose the SINGLE explanation that BEST describes the phenomenon.

47. The α-hydrogens of ketones typically have a pKa = 20, whereas for esters pKa =25. This is because:

A. The resonance stabilisation in ester enolates is better than that in ketones
B. The resonance stabilisation in ketone enolates is better than that in esters
C. There is no resonance stabilisation of the enolates of esters
D. The α-hydrogens in ketones are more accessible
E. The inductive effect of the extra oxygen in the ester destabilises the ester enolate

48. In the addition of HOBr (hypobromous acid) to alkenes the selectivity shown below is observed. This is because:



A. Since the halogen is more electronegative, the O is electrophilic and adds to the alkene first.
B. This is a concerted syn-addition like hydroboration
C. The reaction is radical in character and proceeds with anti-Markovnikov selectivity
D. Oxygen is more electronegative, so Br^+ is the electrophile that adds to give a bromonium ion that is opened in an anti fashion when HO^- attacks.
E. An epoxide forms which is then attack in an SN1 like fashion by bromide

49. 4-Nitrophenol is more acidic than 3-nitrophenol. This is because:

A. The *ortho*-nitro group destabilises the phenolate due to a steric effect
B. The lone pair on the nitrogen stablises the phenolate when it is in the *para* position
C. Inductive stabilisation of the phenolate is better in the *meta* position.
D. There are more stabilising resonance structures when the nitro group is para to the phenol group
E. There are more electronegative atoms in 4-nitrophenol

50. When HBr is added to 1,3-butadiene at room temperature, 1-bromo-2-butene is formed. This is because:

A. The reaction is under kinetic control and is irreversible
B. The reaction is under kinetic control and is reversible
C. The reaction is under thermodynamic control and is irreversible
D. The reaction is under thermodynamic control and is reversible
E. The reaction is a radical process

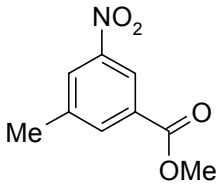
Value

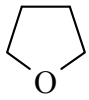
PART 8: TOTAL SYNTHESIS

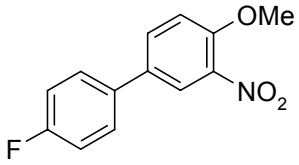
WRITE YOUR ANSWER ON ONE OF BLANK PAGES PROVIDED

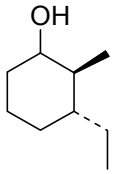
12% Design an efficient synthesis for any **THREE (3)** of the following six target molecules using any of the starting materials and reagents given in the accompanying list. Show the product of each step and clearly identify the reagents.

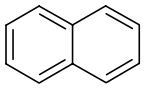
DO NOT SHOW MECHANISMS.

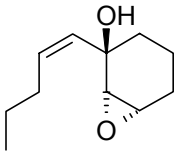
1. 

2. 

3. 

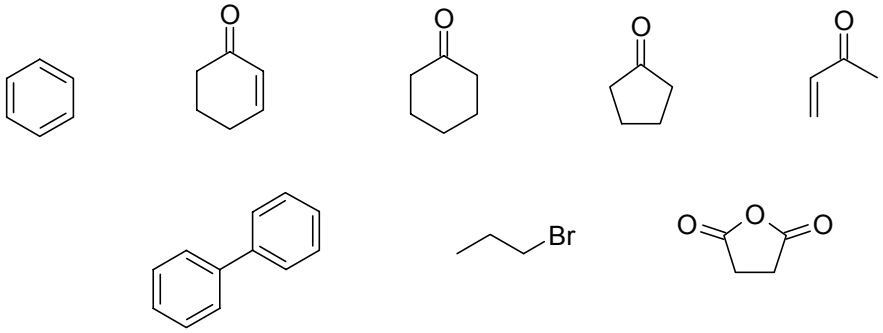
4. 

5. 

6. 

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

Value

PART 9: STRUCTURE DETERMINATION

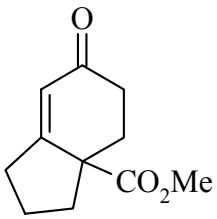
13% **WRITE YOUR ANSWER ON ONE OF BLANK PAGES PROVIDED**

Compound **A** ($C_8H_{14}O_4$; IR 1725 cm^{-1}; NMR δ 3.78 (s, 3H), 2.10 (t, 2H), 1.52 (t, 2H)) did not decolourize Br_2 nor did it react with ozone.

When **A** was treated with excess $LiAlH_4$ with work-up, product **B** (IR 3340 very broad) was obtained. When **B** was treated with excess PCl_3, a dichloride **C** was formed that when treated with hot KOH (excess) provided compound **D**. When compound **D** was reacted with excess ozone followed by a reductive workup (with $(H_3C)_2S$), 2 moles of formaldehyde and butandial were obtained. Compound **D** did **not** react with 1-buten-3-one when heated.

When compound **A** was placed in a flask containing NaOMe/MeOH an exothermic reaction took place to form **E** (IR 1725, 1715 cm^{-1}; NMR 3.8 (s, 3H), 3.7 (t, 1H), 2.2 (t, 2H), 1.7 (pentet, 2H), 1.5 (q, 2H).

Unlike compound **D**, compound **E** was found to react with 1-buten-3-one when the two were mixed in a solution of NaOMe/MeOH and gave compound **F** as a solid.



F

Answer the following questions.

Determine the structures of compounds **A-E**

Why does compound **D** not react with 1-buten-3-one ?

What is the name of the reaction for **A**→**E**?

What is the name of the reaction for **E**→**F**?

Value

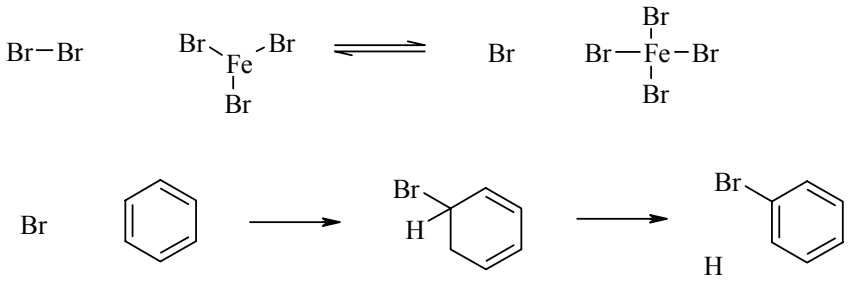
NAME **ID**

PART 10: MECHANISMS

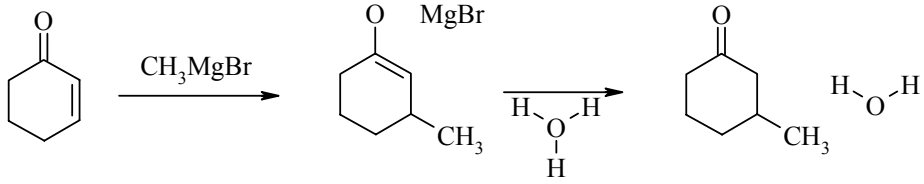
8% **ANSWER ALL OF THE QUESTIONS 51 - 54 BY DRAWING ON THIS PAGE**

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.

51.



52.



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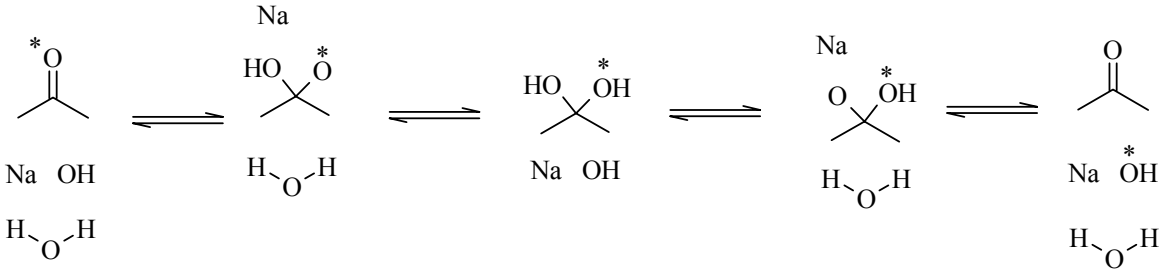
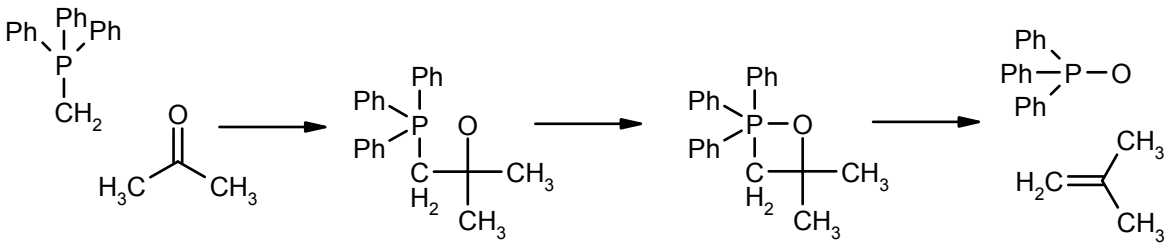


* denotes O^{18}

54.



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PART 8: **NAME** **ID**

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PART 9: NAME ID