THE UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

MIDTERM EXAMINATION

CHEMISTRY 353

February 19, 1998 Time: 2 Hours

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

Read the instructions carefully. The exam consists of Parts 1 - 8, each of which should be attempted. Note that some Parts provide you with a choice of questions. Parts 1 - 5 will be computer graded, and Parts 6, 7 and 8 are to be answered **ON THE PAGES PROVIDED** in this examination booklet. A periodic table with atomic numbers and atomic weights and spectroscopic data tables are appended to the exam.

Parts 1 - 5 consist of a series of multiple choice questions numbered 1 - 31 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***.

PART 1: RELATIVE PROPERTIES

15% **ANSWER ANY FIVE (5) OF QUESTIONS 1-8**.

Arrange the items in the questions in this section in **DECREASING ORDER** (greatest first) with respect to the indicated property.

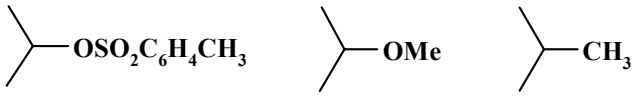
Use the following code to indicate your answers.

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 nucleophilicity of the following in polar, protic solvents:

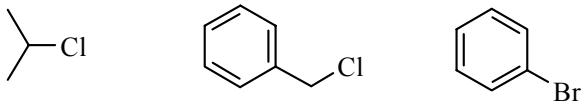
(i) (ii) (iii)

2. The leaving group ability for the indicated group (**LG**):



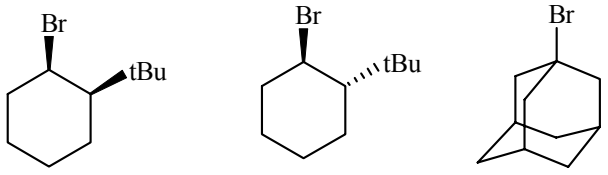
(i) (ii) (iii)

3. The rate of reaction with $AgNO_3$/EtOH (aq) of:



(i) (ii) (iii)

4. The rate of elimination (using EtONa / Δ) of:

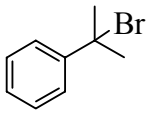


(i) (ii) (iii)

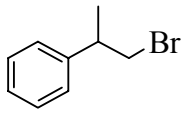
Use the following code to indicate your answers.

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

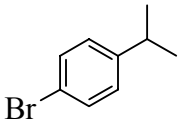
5. The % of the mono-bromination products produced by the reaction of isopropylbenzene with Br_2 in the presence of uv light:



(i)



(ii)

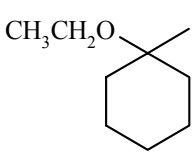


(iii)

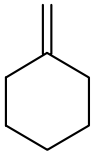
6. The relative reactivity of the following on reaction with NaF in DMSO:

$CH_3CH_2CH_2Br$ (i) CH_3Br (ii) $(CH_3)_3CBr$ (iii)

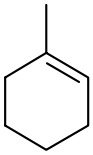
7. The yield of the products shown from reaction of 1-bromo-1-methylcyclohexane with sodium ethoxide:



(i)



(ii)



(iii)

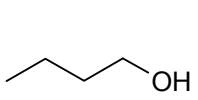
8. The relative basicity of the following species:

CH_3O^- (i) $CH_3C{\equiv}C^-$ (ii) $^-NH_2$ (iii)

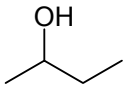
PART 2 LABORATORY

15% **ANSWER ANY FIVE (5) OF THE QUESTIONS 9-14.**

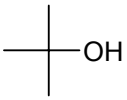
For each of the questions 9-14 below, use the following list of compounds to deduce the required structure:



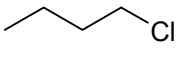
A



B



C



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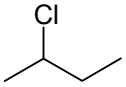
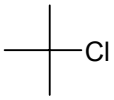
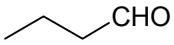


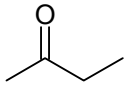
E



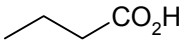
AB



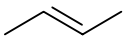
AC



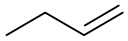
AD



AE



BC



BD

BE

9. Compound **9** was obtained when **A** was heated with aqueous chromic acid solution. Compound **9** gave a clear red solution when tested with 2,4-DNP.

10. Compound **10** reacts rapidly with $AgNO_3$ / ethanol / water but very slowly with NaI / acetone. Compound **10** was produced when **C** was treated with the Lucas reagent.

11. Compound **11** gave a colourless solution when tested with Br_2 in chloroform. Compound **11** was obtained from an alcohol by dehydration. That same alcohol when oxidised gave **AD**.

12. Compound **12** gave a colourless solution with bromine in chloroform and was obtained by dehydrating an alcohol. The alcohol used for dehydration reacted very rapidly with the Lucas reagent.

13. Compound **13** gave a precipitate when tested with 2,4-DNP. Compound **13** was produced by reacting aqueous chromic acid with an alcohol (this alcohol only reacted at a moderate rate with the Lucas reagent).

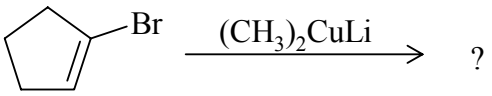
14. Compound **14** was found to react very slowly with $AgNO_3$ / ethanol / water but rapidly with NaI / acetone.

PART 3 PRODUCTS OF SYNTHESIS

12% **ANSWER ANY FOUR (4) OF QUESTIONS 15-20.**

For each of questions 15- 20 choose the most abundant product(s) from the accompanying list, that would be formed under the conditions indicated.

15.



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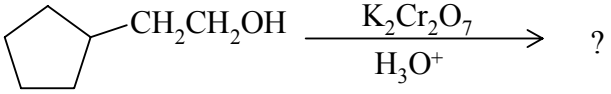

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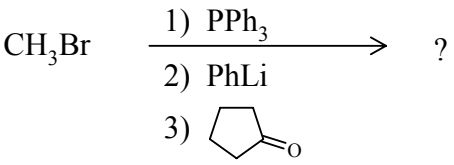

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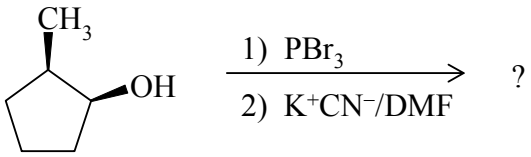

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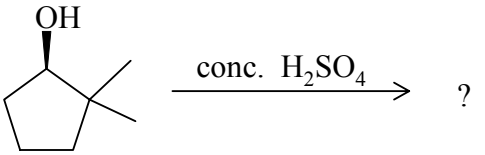
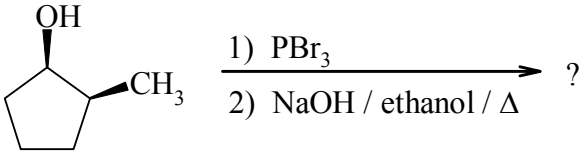
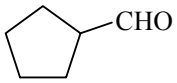


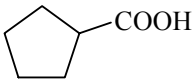
20.



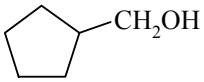
Possible products for Questions 15 - 20



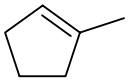
A.



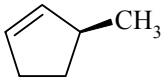
B.



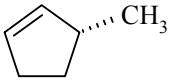
C.



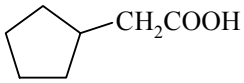
D.



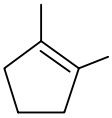
E.



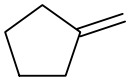
AB.



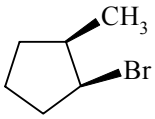
AC.



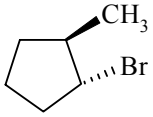
AD.



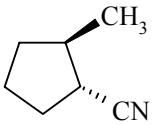
AE.



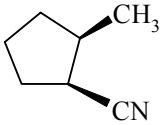
BC.



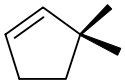
BD.



BE.



CD.



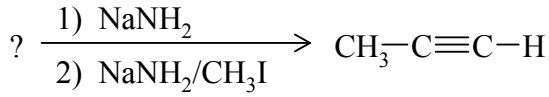
CE.

PART 4 STARTING MATERIALS

12% **ANSWER ANY FOUR (4) OF QUESTIONS 21-26**.

For each of questions 21-26 choose material from the accompanying list the appropriate starting material that would give the product(s) shown under the reaction conditions indicated:

21.



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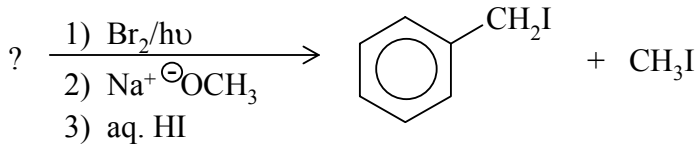

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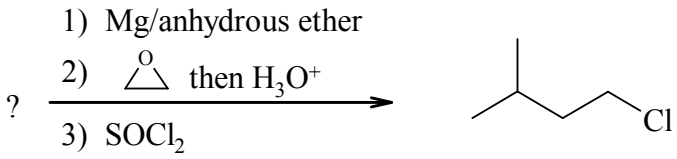

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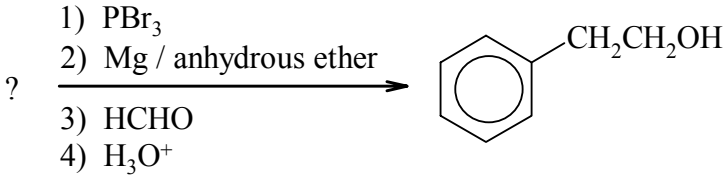

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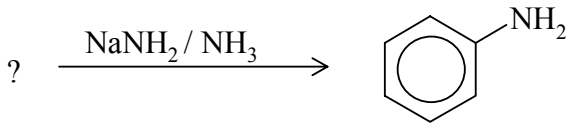
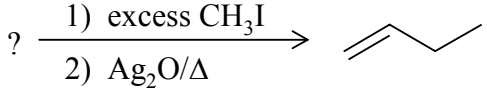
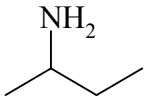


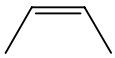
26.



Possible Starting Materials for Questions 21-26



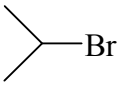
A.



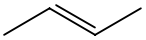
B.

CH_2BrCH_2Br

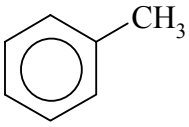
C.



D.



E.



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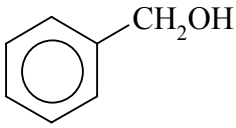

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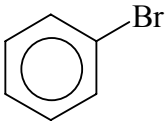

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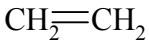
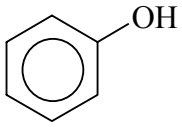
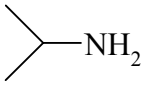


AE.



BC.



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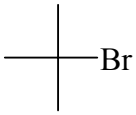
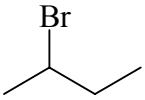


BE.

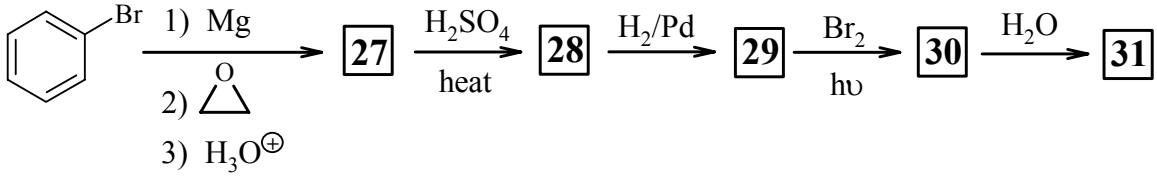


CD.

10% PART 5 APPLIED SPECTROSCOPY

ANSWER ALL OF THE QUESTIONS.27 - 31.

A novice organic chemist was carrying out the synthesis shown below. However, he managed to mix up all of his ^{1}H-NMR spectra ! For each of the **BOXED NUMBERS** in the scheme, which indicates a compound, select from the ^{1}H-NMR spectra provided the spectra that corresponds to that compound.



UNFORTUNATLEY THE SPECTRA IMAGES ARE PROVING DIFFICULT TO INCORPORATE INTO .PDF AT THIS TIME.

HOPE TO FIX AS TIME ALLOWS.

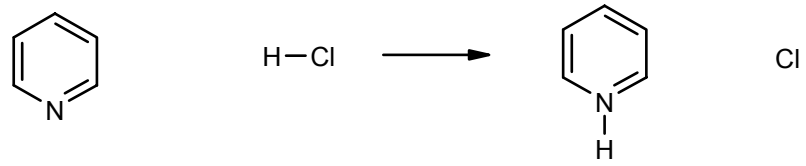
NAME _____ **ID**

PART 6: MECHANISMS

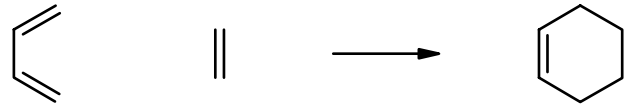
10% **ANSWER ALL OF THE QUESTIONS 32 - 35. BY DRAWING ON THIS PAGE**

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

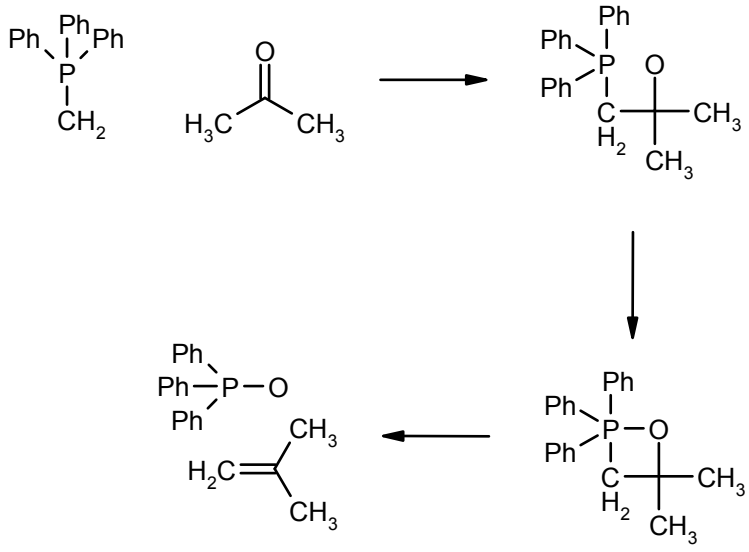
32.



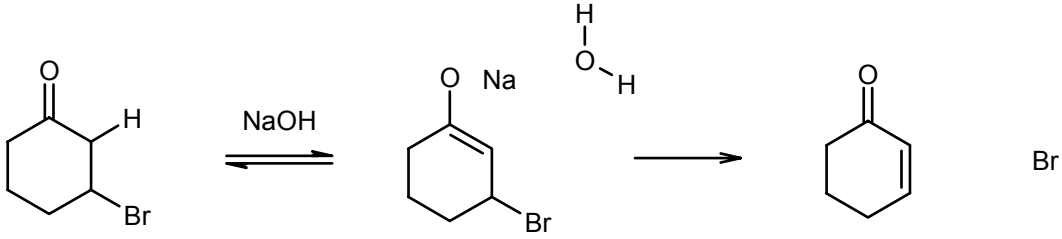
33.



34.



35.

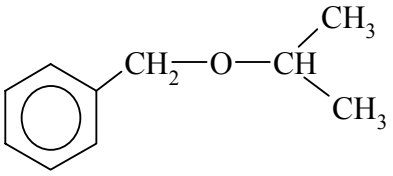


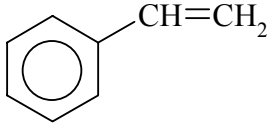
PART 7 SYNTHESIS

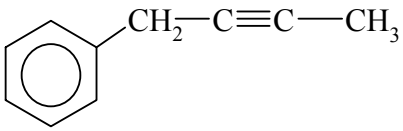
12% Using any of the starting materials shown, design efficient syntheses of any **THREE (3)** of the following molecules.

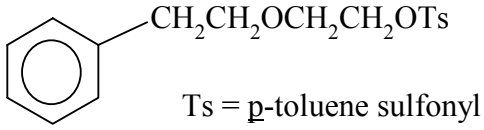
WRITE YOUR ANSWERS ON THE FOLLOWING PAGE.

DO NOT SHOW MECHANISMS.

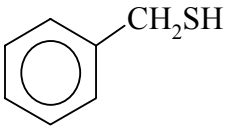


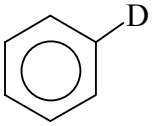




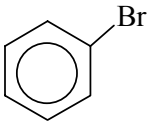


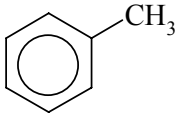
Ts = p-toluene sulfonyl





Allowed Starting Materials:





propanol
propanone
propyne
p-toluenesulfonyl chloride
Any C_1 compounds.

solvents
inorganic reagents
PPh_3

PART 8 STRUCTURE DETERMINATION

14% **WRITE YOUR ANSWER ON THE FOLLOWING PAGE**

Compound **A**, $C_6H_{14}O$, was a chiral molecule that reacted moderately quickly with Lucas Reagent ($HCl/ZnCl_2$). When **A** was treated with 10 M H_2SO_4 two isomeric compounds **B** and **C** (C_6H_{12}) were formed with **C** as the predominant isomer. Compound **C** was reacted with Br_2/CCl_4 to give a colourless compound **D** $C_6H_{12}Br_2$. **D** was hydrolysed to **E** in water. Compound **E**, $C_6H_{14}O_2$, could also be formed directly from **C**, using aqueous $KMnO_4$. During this reaction the solution turned from purple to light brown. Compound **E** was heated in conc. H_2SO_4 to give a compound **F** $C_6H_{12}O$ that gave a positive 2,4-DNP test. Compound **F** could also be formed directly from **A** by heating **A** with acidic $K_2Cr_2O_7$.

Of compounds **A** to **E** only **A** was chiral. The ^{13}C NMR spectra of **A**, **B** and **F** comprised 4 separate signals, and **C**, **D** and **E** only 2 signals.

What are **A** to **F**? Show the detailed mechanism (use curly arrows) for the conversion of **E** to **F**.

THE END