THE UNIVERSITY OF CALGARY

FACULTY OF SCIENCE

MIDTERM EXAMINATION

CHEMISTRY 353

February 16th, 1999 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***.

* Due to our participation in a research study you will be allowed **3 hours**

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.

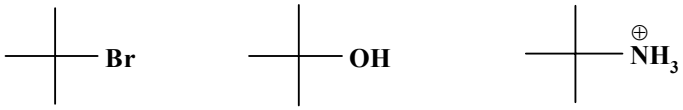
Use the following code to indicate your answers.

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 in polar, protic solvents of the following:

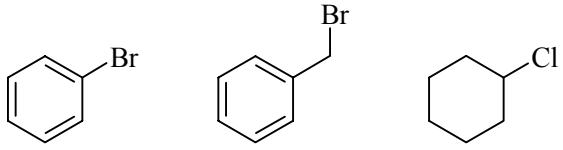
H_2O	HO^-	HS^-
(i)	(ii)	(iii)

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



(i) (ii) (iii)

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

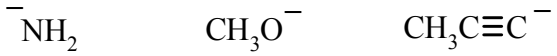


(i) (ii) (iii)

Use the following code to indicate your answers.

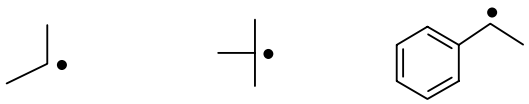
A.	i > ii > iii	D.	ii > iii > i
B.	i > iii > ii	E.	iii > i> ii
C.	ii > i > iii	AB.	iii > ii > I

4. The relative basicity of the following species:



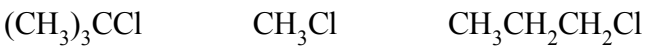
(i) (ii) (iii)

5. The relative stability of the following radicals:



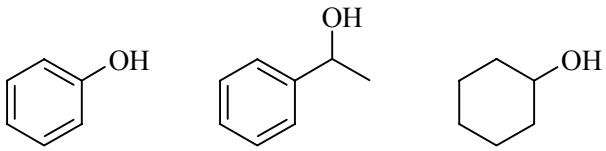
(i) (ii) (iii)

6. The relative reactivity towards NaCN in DMSO of the following:



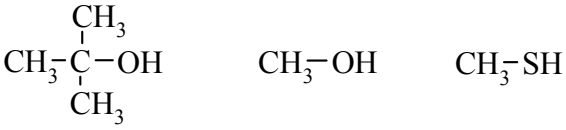
(i) (ii) (iii)

7. The rate of dehydration of the following alcohols with H_2SO_4 / heat:



(i) (ii) (iii)

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

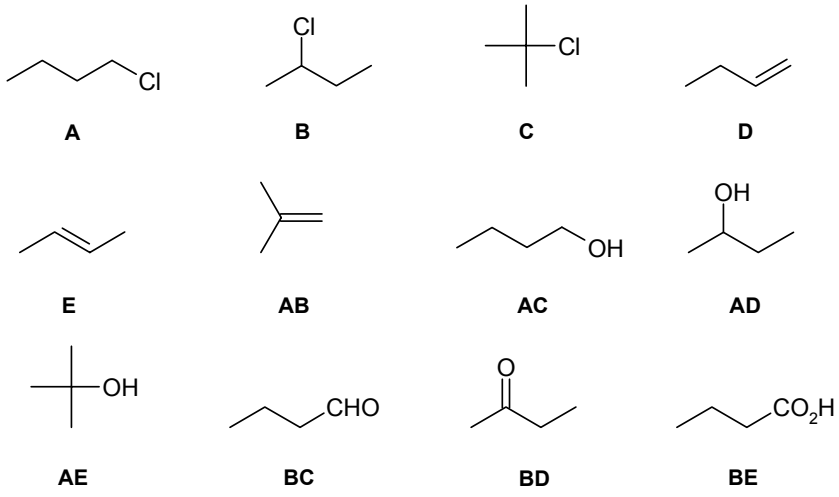


(i) (ii) (iii)

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:



9. Compound **9** was found to react very slowly with $AgNO_3$ / ethanol / water but rapidly with NaI / acetone.

10. Compound **10** gave a colourless solution when tested with bromine in chloroform. Compound **10** was obtained from an alcohol by dehydration. That same alcohol when oxidised gave **BD**.

11. Compound **11** 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.

12. Compound **12** gave a precipitate when tested with 2,4-DNP. Compound **12** was produced by reacting aqueous chromic acid with an alcohol (this alcohol only reacted at a moderate rate with the Lucas reagent).

13. Compound **13** reacts very slowly with NaI / acetone but rapidly with $AgNO_3$ / ethanol / water. Compound **13** was produced when **AE** was treated with the Lucas reagent.

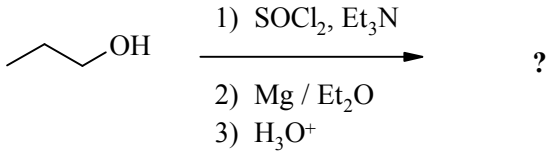
14. Compound **14** was obtained when **AC** was heated with aqueous chromic acid solution. Compound **14** gave a clear red solution when tested with 2,4-DNP.

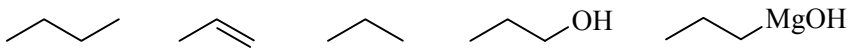
PART 3: PRODUCTS OF SYNTHESIS

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

For each of questions 15- 20 select the major product given the reaction conditions indicated by selecting from the list of compounds provided.

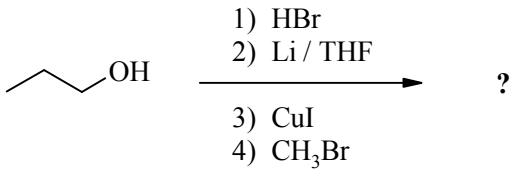
15.

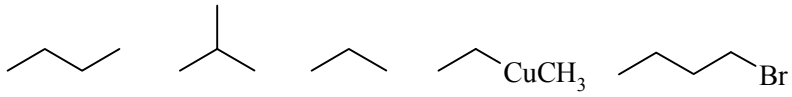




A. B. C. D. E.

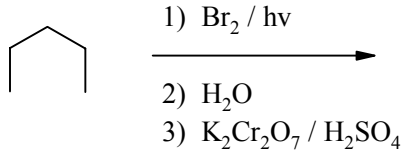
16.

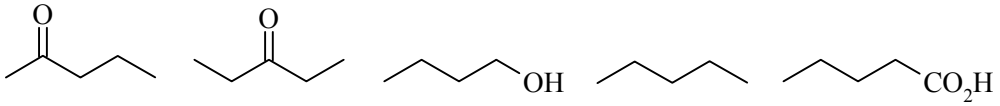




A. B. C. D. E.

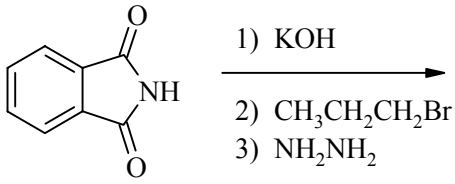
17.

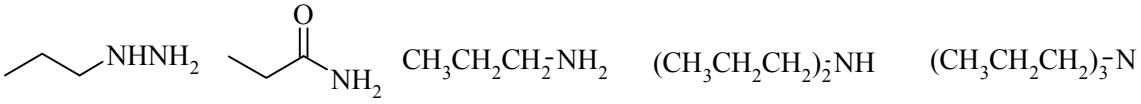




A. B. C. D. E.

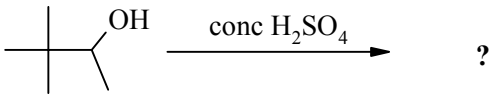
18.

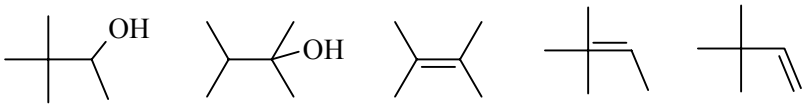




A. B. C. D. E.

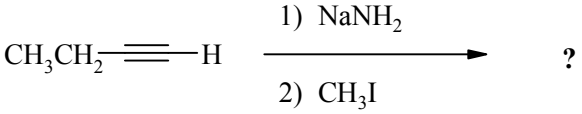
19.

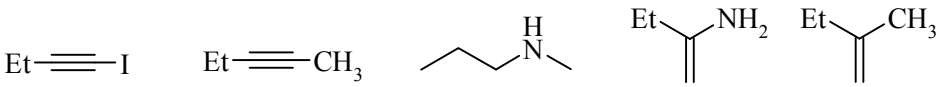




A. B. C. D. E.

20.





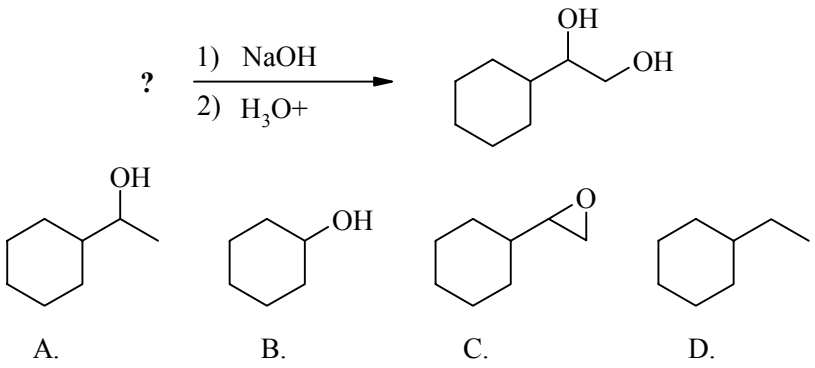
A. B. C. D. E.

PART 4: STARTING MATERIALS

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

For each of questions 21-26, choose from the lists provided the appropriate starting material that would give the product shown under the reaction conditions indicated:

21.



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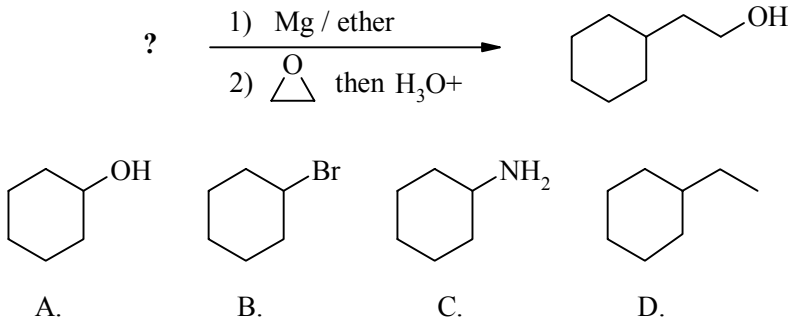
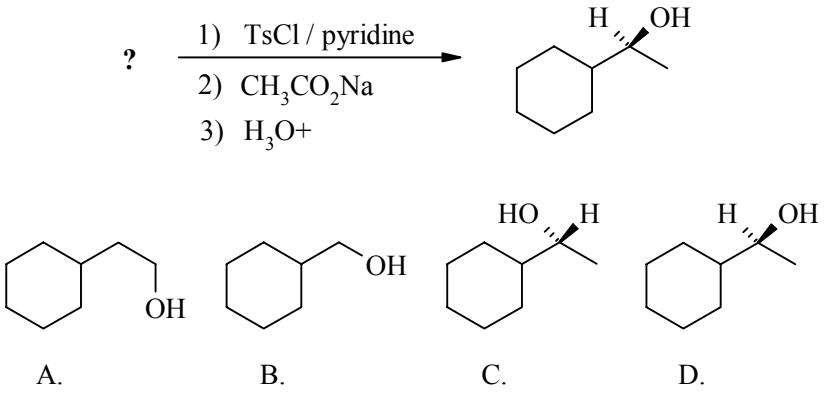
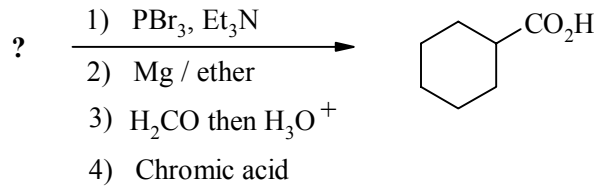
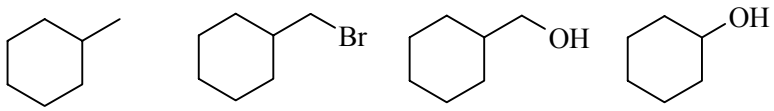


23.



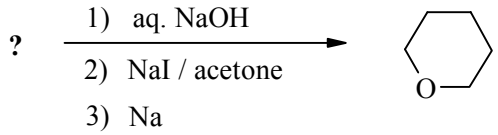
24.

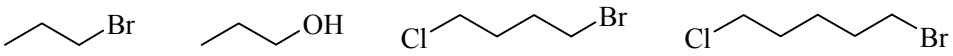




A. B. C. D.

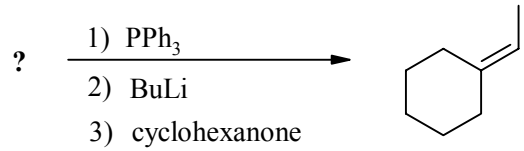
25.





A. B. C. D.

26.



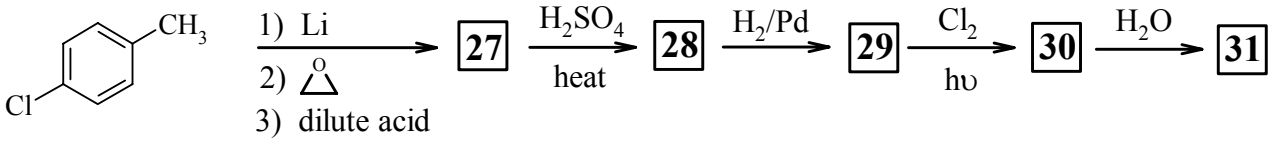
CH_3Br CH_3CH_3 CH_3CH_2OH CH_3CH_2Br

A. B. C. D.

10% PART 5: APPLIED SPECTROSCOPY

ANSWER ALL OF THE QUESTIONS 27 - 31.

A novice organic chemist was carrying out the synthesis shown but managed to mix up all the ^{1}H-NMR spectra ! For each of the **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.

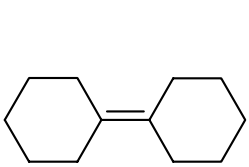
HOPE TO FIX AS TIME ALLOWS.

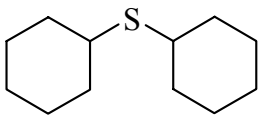
PART 6: SYNTHESIS

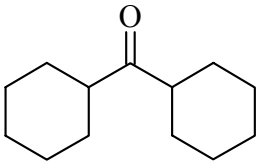
12% Using any of the starting materials shown, design efficient syntheses of any **THREE (3)** of the following molecules.

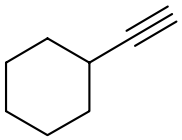
WRITE YOUR ANSWERS ON THE PAGE PROVIDED.

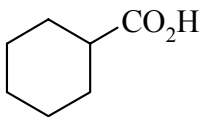
DO NOT SHOW MECHANISMS.

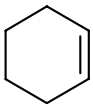


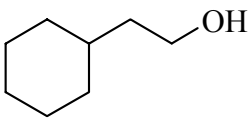




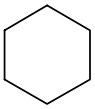








Allowed Starting Materials:



solvents
inorganic reagents
PPh_3
Any C_1 or C_2 compounds
p-toluenesulfonyl chloride (TsCl)

PART 7 : STRUCTURE DETERMINATION

14% **WRITE YOUR ANSWER ON PAGE PROVIDED**

Compound **A**, C_5H_{10}, decolourised Br_2 in chloroform and was achiral. When **A** was treated with Br_2 / H_2O, a mixture of two isomeric compounds **B** and **C**, $C_5H_{11}OBr$, were isolated. On closer examination, it was found that **B** and **C** were constitutional isomers and both existed as RS / SR pairs of enantiomers. Oxidation of **B** gave a methyl ketone.

On treatment of a mixture of **B** and **C** with K_2CO_3, and single compound **D**, $C_5H_{10}O$, was obtained as a pair of enantiomers (configurations RR and SS). **D** was then reacted with $LiAlH_4$ in ether (a source of hydride, H^-), followed by a dilute acid work-up, and two isomeric compounds **E** (minor) and **F** (major) , $C_5H_{12}O$ were generated. **E** was chiral and **F** was achiral. Both **E** and **F** reacted moderately quickly with the Lucas Reagent ($HCl/ZnCl_2$). The H-nmr of **F** was fairly simple, showing 4 separate signals: δ 3.7 ppm, quintet, 1H; δ 2.6 ppm, br. singlet, 1H (exchangeable with D_2O), δ 1.85 ppm, quintet, 4H; δ 0.9 ppm, triplet, 6H. When **F** was reacted with $K_2Cr_2O_7$ / H_2SO_4, the orange solution turned green, and an achiral compound **G** $C_5H_{10}O$ was isolated. **G** gave an orange solid when reacted with 2,4-DNP. The H-nmr of **G** was δ 2.44 ppm, quartet, 2H; δ 1.06 ppm, triplet, 3H.

On treating **F** with H_2SO_4 / heat, the original material **A** and a small amount of a diastereomer of **A** were obtained. In an independent synthesis, **F** was prepared by reacting ethylmagnesium bromide with propanal followed by a dilute acid work-up.

What are the structures of **A** to **G** ?

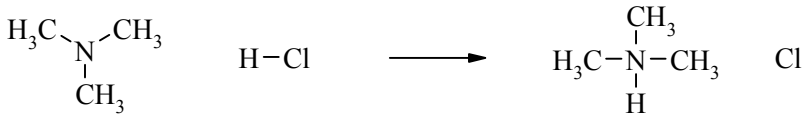
Given the stereochemical information provided, describe the stereochemistry for the addition reaction that converts **A** into **B**.

PART 8: MECHANISMS

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

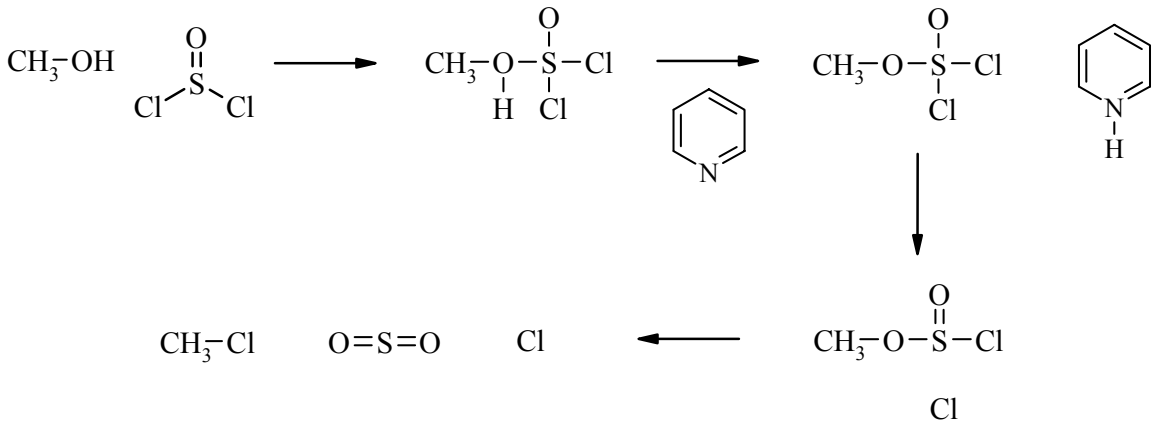
DRAW in **ALL** of the curly arrows, lone pairs, and any required charges to complete the mechanisms for the following reaction schemes. **ALL** the required bonds have been shown.

32.



33.

34.



35.