

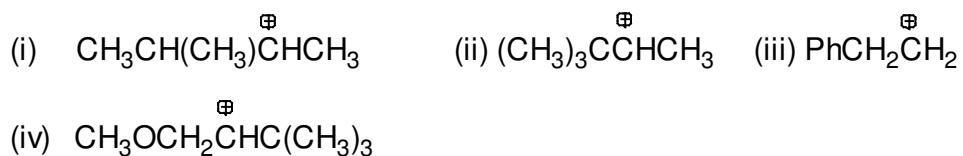
NATIONAL UNIVERSITY OF SCIENCE AND TECHNOLOGY
DEPARTMENT OF APPLIED CHEMISTRY
END OF SEMESTER EXAMINATIONS – DECEMBER 2005
ORGANIC CHEMISTRY I – SCH 1102
TIME –THREE HOURS (3)

INSTRUCTIONS TO CANDIDATES

Answer **ALL** questions from Section A and **ANY OTHER THREE** questions from Section B. Section A carries 40 marks and marks distribution within the Section is as indicated. Section B carries 60 marks. Each question in Section B carries 20 marks.

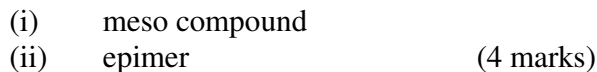
SECTION A

1. (a) Each of the following cations is capable of rearranging to a more stable cation. Limiting yourself to a single 1,2-shift, suggest a structure for the rearranged ion.

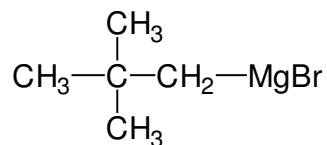


(4 marks)

- (b) With specific examples for each, define the following terms in your own words.



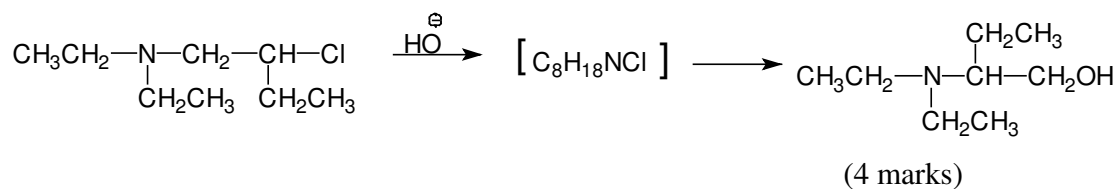
- (c) Treatment of neopentylmagnesium bromide 1 with iodine produces neopentyl iodine in good yield. Suggest a mechanism for this reaction.



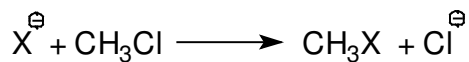
1

(4 marks)

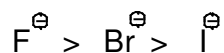
- (d) The reaction shown below is an interesting displacement, particularly because the skeleton of the product differs from that of the starting material. Given the information that the reaction proceeds *via* a water-soluble intermediate $\text{C}_8\text{H}_{18}\text{NCl}$, suggest a mechanism for this transformation.



- (e) The following reaction has been studied in the gas phase.



It is found that the following is the order of nucleophilicity for the various halides (X).



Explain this observation.

(4 marks)

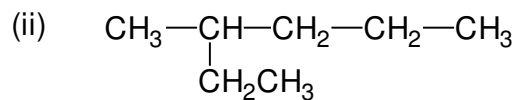
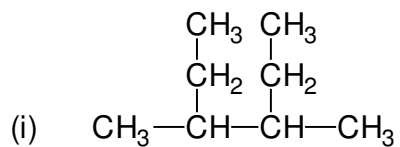
- (f) A potential energy diagram for rotation about the C₂-C₃ bond in butane is shown below.

- (i) At what position is the staggered-anti conformer?
 (ii) At what position is the eclipsed conformer?

(4 marks)

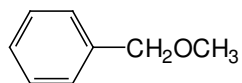
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- (g) Give the IUPAC name of each of the compounds shown below:

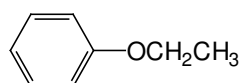


(4 marks)

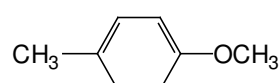
- (h) An unknown compound having the formula $\text{C}_8\text{H}_{10}\text{O}$ gave the proton NMR spectrum shown below. With brief explanations, give the structure of the compound from the list shown (1 – 4).



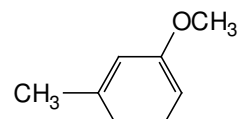
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2



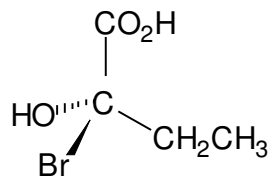
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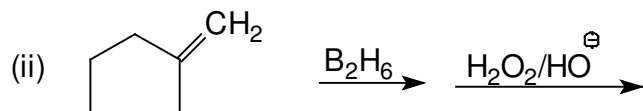
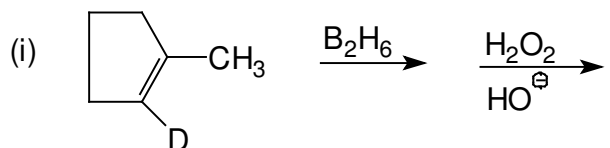
(4 marks)

- (i) Draw a Fisher projection of the compound shown below.



(4 marks)

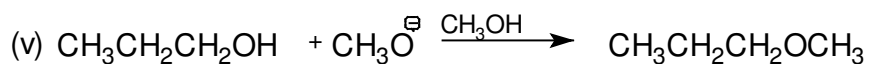
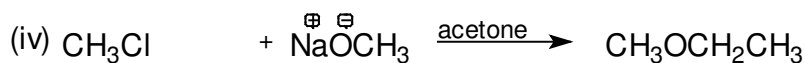
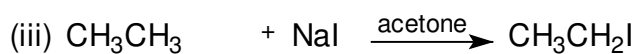
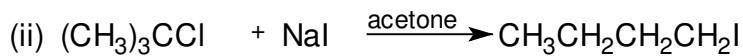
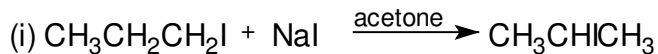
- (j) Give the major product for each of the following set of reactions:



(4 marks)

SECTION B

2. (a) Each of the following proposed synthesis contains an error. The desired products are correct. Identify the error and suggest a means of correcting it.



(2x5 marks)

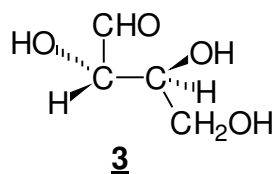
- (b) Draw the Fisher projection of threo-2-chloro-3-thiocyanatobutane (enantiomer of your choice). Transform this into the corresponding Newman projection. Using Newman projections, show the most stable

conformations of the compound and indicate the preferred one(s), noting that the steric factors are in the order $\text{CH}_3 > \text{SCN} > \text{Cl} > \text{H}$.

(10 marks)

3. (a) Transform the 3-D representation of compound 3 into each of the following projections:

- (i) Fischer
- (ii) Newman
- (iii) Sawhorse

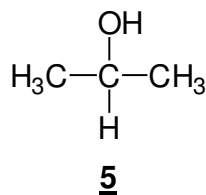
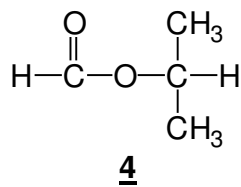


(9 marks)

- (b) Using the R/S notation, show how you could establish the absolute configuration of compound 3.
- (9 marks)
- (c) Using the Fischer projection you have drawn [a(i)], designate as D_sL_s the configuration of compound 3.

(2 marks)

4. (a) The spectrum shown below is of a mixture of isopropyl formate 4 and isopropanol 5. Assign the resonances in the spectrum of the mixture.



(5 marks)

5

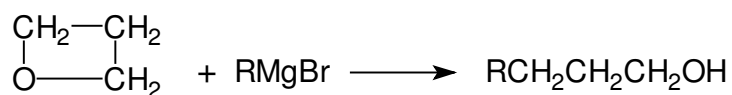
(b) (i) Draw all the optically active compounds with the formula $C_5H_{11}Cl$.
(4 marks)

(ii) Give the major product(s) of the reaction of each of the isomers in [b(i)] with:

- Alcoholic KOH
- Aqueous KOH
- Magnesium metal in diethyl ether.

(6 marks)

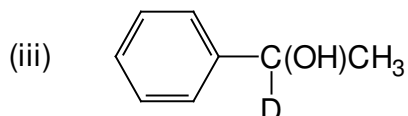
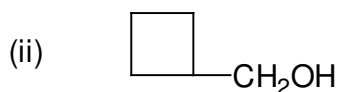
(c) Trimethylene oxide **6** reacts with Grignard reagents to give an alcohol with a carbon chain three atoms longer than the starting Grignard reagent. Give a mechanistic account of this reaction.



6

(5 marks)

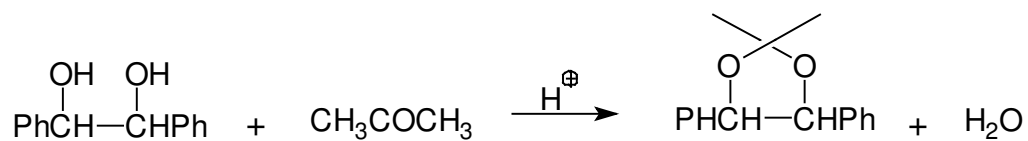
5. (a) For each of the compounds given below, give the Grignard reagent and starting material which will react to give each of the compounds.



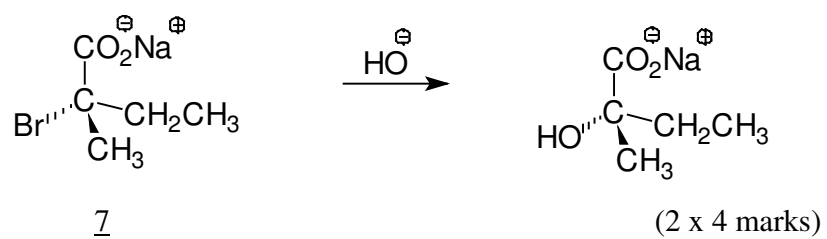
(12 marks)

(b) Explain each of the following observations:

(i) racemic hydrobenzoin reacts with acetone to form an acetal at a faster rate than meso-hydrobenzoin does.



- (ii) hydrolysis of the carboxylate 7 proceeds with retention of configuration and an enhancement in the rate of the reaction.



END OF QUESTION PAPER.