NATIONAL UNIVERSITY OF SCIENCE AND TECHNOLOGY
DEPARTMENT OF APPLIED CHEMISTRY
END OF FIRST SEMESTER EXAMINATIONS – DECEMBER 2004
ORGANIC CHEMISTRY I – SCH 1102
TIME: 3 HOURS

INSTRUCTIONS TO CANDIDATES

This paper consists of two sections viz Section A and Section B. Answer **all questions** in Section A and **three questions** from Section B. Section A carries 40 marks and Section B 60 marks. Mark distribution within questions is as indicated.

SECTION A

1. (a) Draw and classify as (i) E/Z and (ii) cis/trans the isomers of 2-bromobut-2-ene. (4 marks)

(b) Draw and designate in the most appropriate convention the enantiomers of 2-hydroxypropionic acid. (4 marks)

(c) (i) Construct/draw the 3-D representation of 2-methyl-butanoic acid. (enantiomer of your choice).

(ii) Convert the 3-D representation you have drawn in (c) (i) into a Fischer project. (4 marks)

(d) With specific examples for each, define the following terms:

(i) Chiral Centre

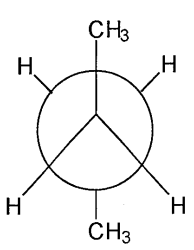
(ii) meso compound

(4 marks)

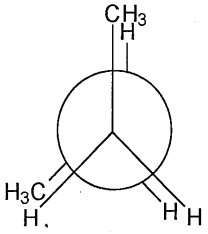
(e) Each of the following ions are capable of rearranging to a more stable carbonium ion. Limiting yourself to a 1,2-shift, give the structure in each case for the rearranged ion.

(i) $PhCH_2\overset{\oplus}{C}H_2$ (ii) $(CH_3)_3C\overset{\oplus}{C}HCH_3$ (4 marks)

(f) Using the conformers numbered 1 to 6 shown below, arrange these in decreasing conformational energy order:



1



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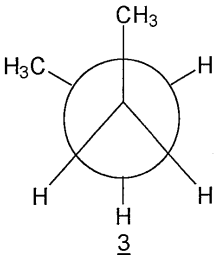

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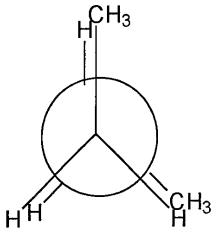

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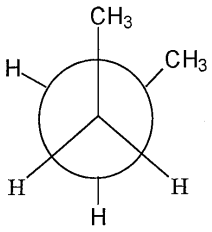

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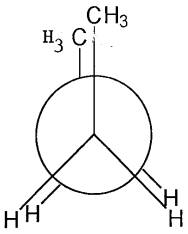

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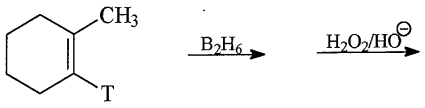
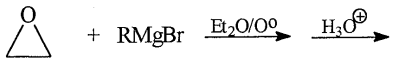
(4 marks)

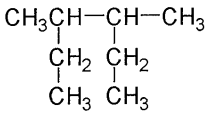
(g) Give the major product for each of the following sets of reactions:

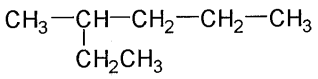
(i) 

(ii) 

(4 marks)

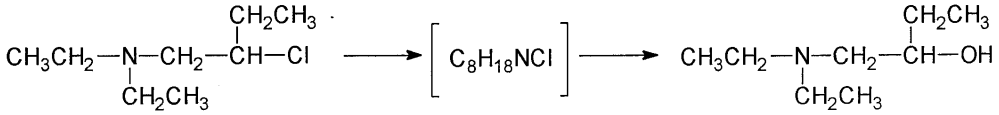
(h) Give the IUPAC name of each of the following compounds:

(i) 

(ii) 

(4 marks)

(i) Mechanistically, account for the following transformation given that the intermediate is water-soluble.



(4 marks)

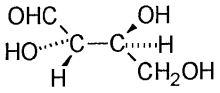
(j) For each of the compounds given below, give the Grignard reagent and starting material which would react to give:

(i) ethanol
(ii) 2-methylbutan-2-ol

(4 marks)

SECTION B

2. (a) Transform the 3-D representation of compound 1 into each of the following projections:



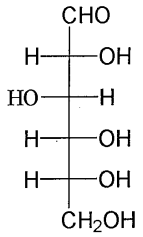
1

(i) Newman
(ii) Sawhorse
(iii) Fischer (3x3 marks)

2. (b) Designate as D or L the relative configuration of compound 1. (2 marks)

(c) Show how you could establish the absolute configuration of compound 1 in the R/S convention. (5 marks)

(d) Give one example of each of the following stereoisomers of compound 2.



2

(i) diastereoisomer
(ii) C_2 epimer (5 marks)

3. (a) Two sugars have been obtained with the empirical formula $C_4H_8O_4$ and have the molecular structure:

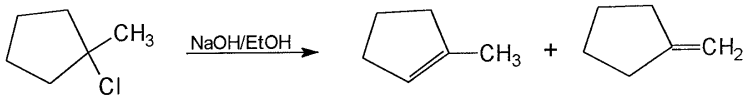
$HOCH_2CH(OH)CH(OH)CHO$

One sugar, A has an $[\alpha]_D$ of +30.5°. The other sugar B has an $[\alpha]_D$ of 13.2°.

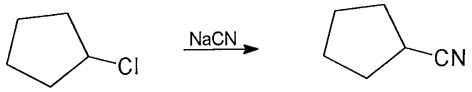
What type of isomers are the pair A and B? (2 marks)

(b) Mechanistically account for each of the following transformations:

(i)



(ii)

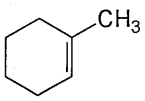


(2x2½ marks)

3. (c) Give the major product for each of the following reactions:

(i) $CH_3CH_2CH_2CH_2CH_2MgBr + HCHO \xrightarrow[(ii)H_3O^{\oplus}]{(i)Et_2O/O^{\circ}}$

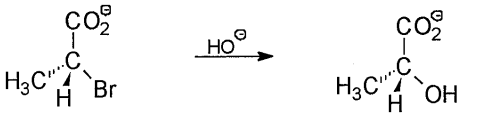
(ii) $CH_3CH{=}CH_2 \xrightarrow{HBr}$

(iii)  $\xrightarrow{H_2SO_4/\Delta}$

(iv) $CH_3CH_2CH(CH_3)Br \xrightarrow{NaOH}$

4x2½ marks)

(d) Mechanistically account for the following observation; which proceeds with retention of configuration.



(3 marks)

4. (a) Three products are obtained by the solvolysis of t-butylbromide 3 in ethanol-water (80:20v/v).

(i) Give a detailed mechanistic account for the formation of each product and;

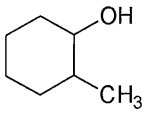
(ii) Classify each mechanism in terms of reaction types.

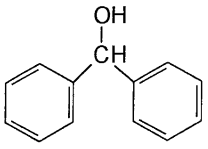
$(CH_3)_3CBr \xrightarrow{EtOH/H_2O} (CH_3)_3COH^{+} \quad (CH_3)_3COCH_2CH_3^{+} \quad (CH_3)_2C{=}CH_2$

3 58% 29% 13%

(9 marks)

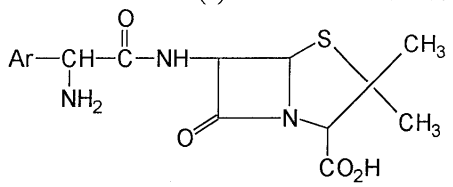
(b) Briefly show how you could prepare each of the following compounds:

(i)  starting from 2-methylcyclohexene and any other reagents of your choice.

(ii)  starting from benzaldehyde and any other reagent of your choice.

(8 marks)

4. (c) Mark with an asterisk(*) the chiral centres of compound 4 shown below:



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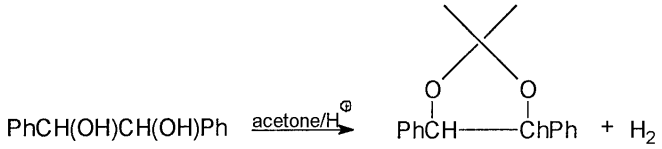
(3 marks)

5. Explain each of the following observations:

(i) Racemic hydrobenzoin 5 reacts with acetone to form an acetal at a faster rate than meso-hydrobenzoin.



5

(6 marks)

(ii) Bromination of 2-butene in acetic acid gives a dibromo-addition adduct only. However, bromination of phenylethene under the same conditions gives 6 and 7.

6 7

(7 marks)

(iii) The reaction of (S)-2-chlorobutane with NaOH gives optically active butanol of opposite configuration to that of the original substance.

(7 marks)

End of question Paper!!!