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THE OPEN UNIVERSITY OF SRI LANKA
B.Sc. Degree Programme
and Stand Alone Courses in Science - 2013/2014
CMU2221/CME4221 - Organic Chemistry I
CONTINUOUS ASSESSMENT TEST II

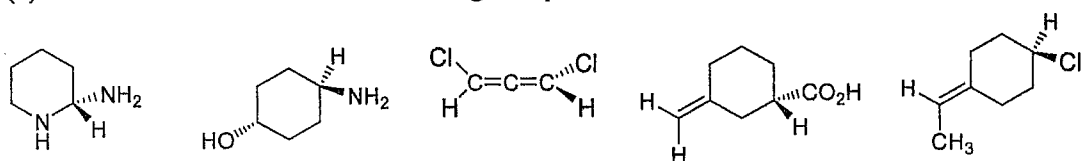
Ques No.	Max.	Marks
1	50	
2	50	
Total	100	

Thursday 21st August 2014

4.00 p.m. – 5.00 p.m.

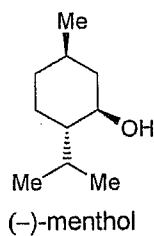
ANSWER ALL QUESTIONS

1. (a) State whether each of the following compounds are chiral or achiral.

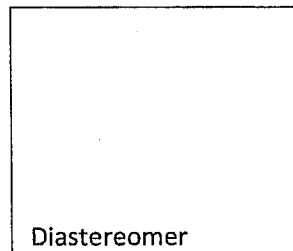
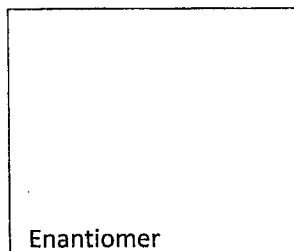


(10 marks)

(b) Consider the structure of (-)-menthol given below.



(-)-menthol



- How many stereocenters are there in this molecule?
- Label them as p, q, r etc.
- How many stereoisomers are possible for this compound?
- Enantiomer of (-)-menthol is (+)-menthol. Draw structure of (+)-menthol *in the box above*.
- Draw structure of any **ONE** diastereomer of (-)-menthol *in the box above*.
- $[\alpha]_D$ value of (-)-menthol is -49° . What is the $[\alpha]_D$ value of (+)-menthol?
- What is the $[\alpha]_D$ value of racemic mixture of menthol?
- $[\alpha]_D$ of a sample of containing (-)-menthol and small amount of (+)-menthol was found to be -39.2° .

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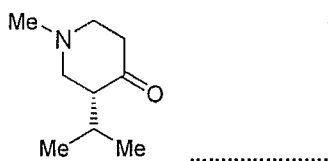
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Calculate the enantiomeric excess (ee) of (–)-menthol.

Calculate the percentage of (–)-menthol in the sample.

(30 marks)

- (c) Determine the configuration of stereocenter of the following compound as *R* or *S* showing the priorities of the groups attached to it according to Cahn-Ingold-Prelog rules. *If priorities of the groups are not shown marks will not be awarded.*



(10 Marks)

2. (a) Categorize the following solvents using any one of the terms; polar protic, non-polar protic, polar aprotic and nonpolar aprotic.

- (i) Acetic acid ($\text{CH}_3\text{CO}_2\text{H}$)
- (ii) Acetonitrile (MeCN)
- (iii) Diethylether (Et_2O)
- (iv) Methanol (MeOH)
- (v) Dichloromethane (CH_2Cl_2)

(10 Marks)

- (b) Consider the anions, CH_3O^- and CH_3S^- . Which of them show;

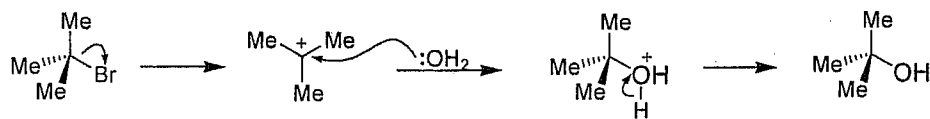
- (i) Higher basicity
- (ii) Higher nucleophilicity in DMSO
- (iii) Higher nucleophilicity in MeOH

(12 Marks)

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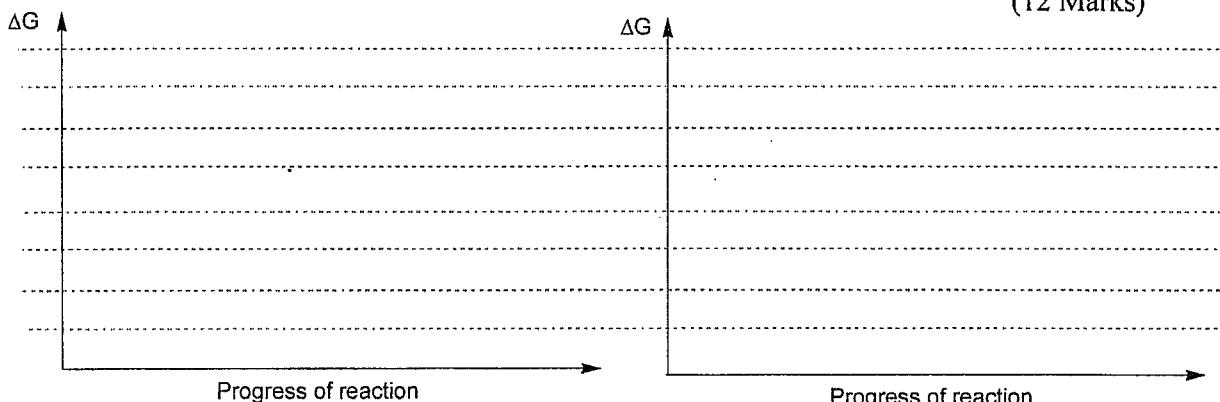
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Given below is the mechanism of the solvolysis of 2-bromo-2-methylpropane in water.



(c) Draw the completely labeled energy diagram for the above reaction (*diagram A*).

(12 Marks)



(A) Energy diagram for solvolysis in water

(B) Energy diagram for solvolysis in ethanol

(d) Giving reasons state what happens to the rate of the reaction if the solvolysis of 2-bromo-2-methylpropane is carried out in ethanol.

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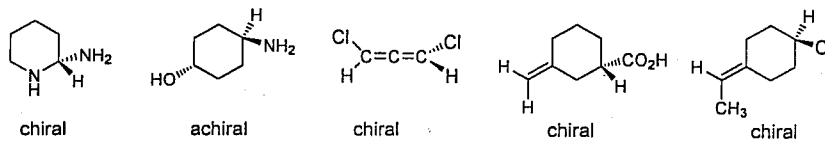
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(12 Marks)

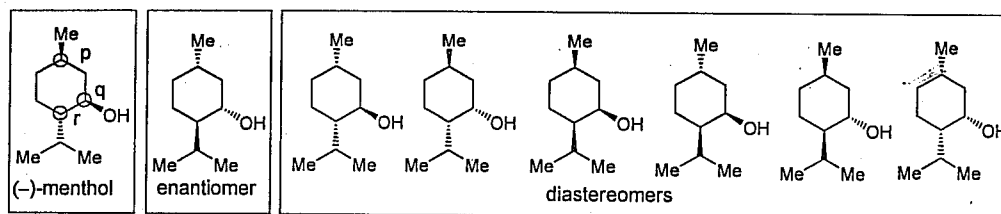
(e) Draw the labeled energy diagram to show the changes you have explained in (d) next to the diagram you have drawn previously (*see above*) (*diagram B*).

(04 Marks)

1. (a)



(b)



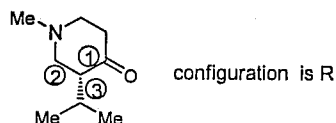
- (i) 03 (iii) $2^n = 2^3 = 8$ (vi) $[\alpha]_D$ value of (+)-menthol = $+49^\circ$
 (vii) $[\alpha]_D$ value of racemic mixture of menthol = 0°
 (viii)

$$\text{percent optical purity} = \text{enantiomeric excess (ee)} = \frac{|\alpha|_D \text{ of the sample}}{|\alpha|_D \text{ of (-) menthol}} \times 100$$

$$= \frac{-39.2}{-49} \times 100 = 80\%$$

Amount of racemic mixture = $(100 - 80)\% = 20\%$
 Therefore 10% of the racemic mixture is (-)-menthol.
 Hence % of (-)-menthol in the mixture = $(80+10)\% = 90\%$

(c)



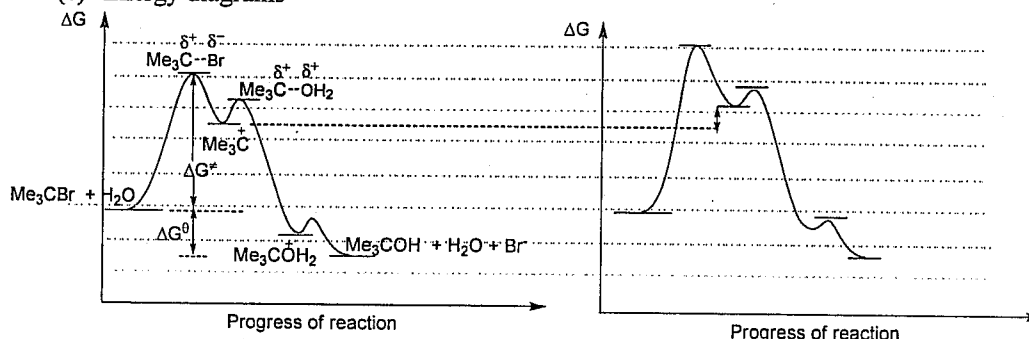
2. (a) Solvent properties

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|--|------------------|
| (i) Acetic acid ($\text{CH}_3\text{CO}_2\text{H}$) | non-polar protic |
| (ii) Acetonitrile (MeCN) | polar aprotic |
| (iii) Diethylether (Et_2O) | nonpolar aprotic |
| (iv) Methanol (MeOH) | polar protic |
| (v) Dichloromethane (CH_2Cl_2) | nonpolar aprotic |

(b) Comparison of anions, CH_3O^- and CH_3S^-

- | | |
|--------------------------------------|---------------------------|
| (i) Higher basicity | : CH_3O^- |
| (ii) Higher nucleophilicity in DMSO | : CH_3O^- |
| (iii) Higher nucleophilicity in MeOH | : CH_3S^- |

(c) Energy diagrams



(A) Energy diagram for solvolysis in water

(B) Energy diagram for solvolysis in ethanol

- (d) Ethanol is less polar solvent than water and solvation of carbocation by ethanol is lesser than that by water. Therefore carbocation is less stabilized in ethanol and ΔG of rate determining step is increased. Hence the reaction rate is lowered.