M.Sc. 2nd Semester Examination, 2014 CHEMISTRY

(Organic)

PAPER -CEM-202

Full Marks: 40

Time: 2 hours

Answer any five questions taking at least two from each Group where Q. No. 5 or 6 is compulsory

The figures in the right-hand margin indicate marks

GROUP - A

1. (a) Predict the products of the following reactions and indicate which one is faster and why?

$$[?] \stackrel{C_N}{\longleftarrow} OH$$

$$[?] \stackrel{H_5C_2O}{\longleftarrow} OC_2H_5$$

$$[?] OH$$

(Turn Over)

(b) Define "periselectivity" and 'site selectivity" and hence predict the products of the following reactions (attempt any two): $2 + (2 \times 2)$

$$(i) \bigcirc + \bigcirc \xrightarrow{\Delta} ?$$

$$(ii) \longrightarrow + CH_2 \stackrel{ZnI}{\sim} \longrightarrow ?$$

2. (a) What is secondary interaction in pericyclic reaction? Predict the product of the following reactions indicating frontier orbital interaction (F. O. I)in each case and indicate the stable product. $1 + (2 \times 2)$

$$(i) \implies + \implies ?$$

$$(ii) \bigcirc + \bigcirc + \bigcirc ?$$

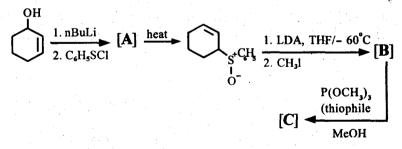
(b) The following reaction scheme gives the product as:

$$\underbrace{/N} + \epsilon tO_2C - C \equiv C - COO\epsilon t \xrightarrow{hv} [A] \xrightarrow{\Delta} [B]$$
Identify **A** and **B**

3. Predict the product(s) (any four, with plausible mechanism): 4×2

(a)
$$H_2C$$
 OH $\frac{\text{Ti(OiPr)}_4, \text{'BuOOH}}{\text{L(+) DET}}$

(b)



(Turn Over)

3

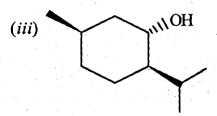
- 4. (a) What is AD-mix? Give an example of asymmetric transformation using AD-mix. 3
 - (b) Write the structures of [A] and [B] and explain their formation: 3+2

(Continued)

(ii)
$$CH_3 \xrightarrow{\text{CPh}_2^+} [A] \xrightarrow{\text{H}_3\text{O}^+} [B]$$

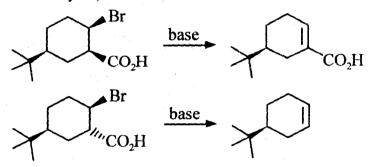
GROUP - B

- 5. (a) Draw the structures of most stable conformers for the given molecules: 1×4
 - (i) Meso-2, 3-butane-diol;
 - (ii) Cyclohexane-1,4-dione;

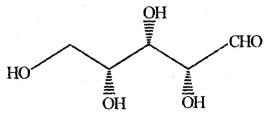


- (iv) cis-1-tertbutyl-2-methyl cyclohexane,
- (v) trans-1-tertbutyl-3-methyl cyclohexane.

(b) Account for the contrasting results in these two reactions (explain in terms of conformational analysis): 2 × 2

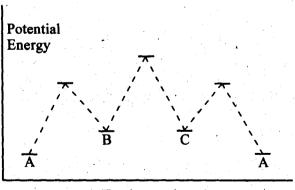


- 6. (a) How many chiral centers are there in 9, 10-dimethyl decalins? Write 3d structures of those conformers and show in them the gauche-butane interactions.
 - (b) How many chiral centers are there in the following compound? How many stereo isomers are possible? Assign the stereogenic centers as R or S?



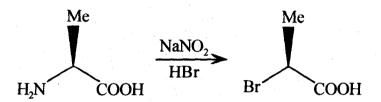
(Continued)

- 7. (a) The observed rotation of a 0.3 g of cholesterol in 15 ml of CHCl₃ contained in 10 cm long polarimeter tube is -0.78° . Calculate specific rotation of cholesterol. When (+)-cholesterol was mixed to the above (-)-cholesterol, the mixture had a specific rotation of -13° . What is the fraction of the (+)-cholesterol?
 - (b) The following is the energy profile drawing of 1,1-dibromo-2-methylpropane, draw the appropriate Newman conformations of A, B and C.



Torsion angle

(c) Account for the stereochemistry of the following reaction.



8. Synthesize the following (any four):

(Continued)

 4×2