M.Sc. 2nd Semester Examination, 2011

CHEMISTRY

(*Organic*)

PAPER—CEM-202

Full Marks : 40

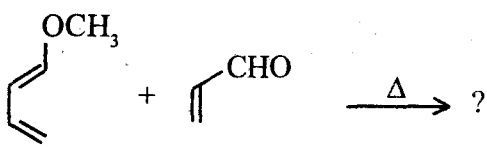
Time : 2 hours

Answer any **five** questions taking at least **two** from each Group where **Q. No. 6** or **Q. No. 7** is compulsory

The figures in the right-hand margin indicate marks

GROUP – A

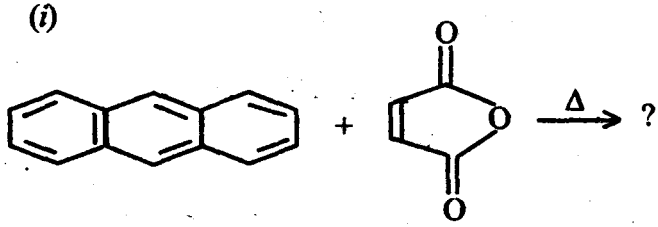
1. (*a*) Explain the term "Regioselectivity" in pericyclic reactions and hence predict the product of the following reaction indicating the lowest energy path; 1 + 2



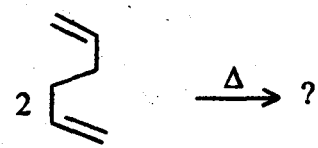
(*b*) What is Diels-Alder reaction of 'reverse electron demand' ? Explain by showing an example. 2

(*c*) Predict the product/s of the following reactions with proper justification in each case (attempt any *two*): $1\frac{1}{2} \times 2$

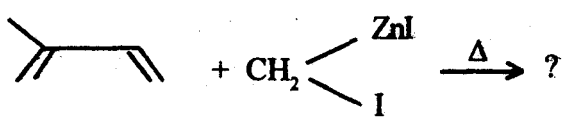
(*i*)



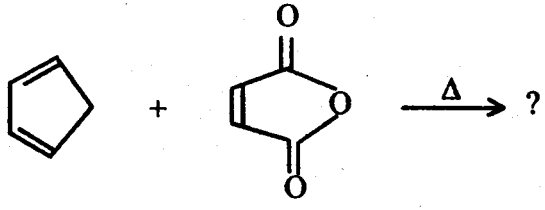
(*ii*)



(*iii*)

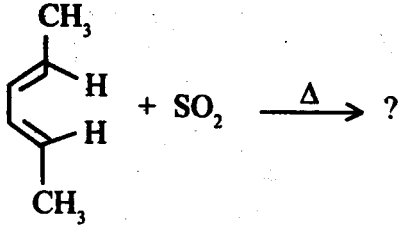


2. (*a*) What is secondary interaction ? Predict the product of the following reaction indicating Frontier orbital interaction (F.O.I.). 2

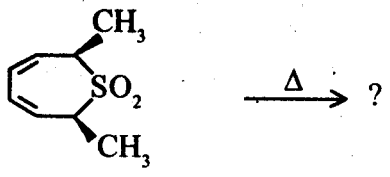


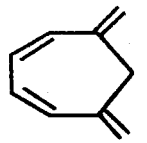
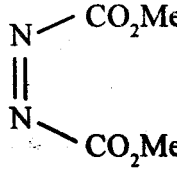
(*b*) Predict the product/s of the following reactions indicating Frontier orbital interaction in each case (attempt any *three*). 2 × 3

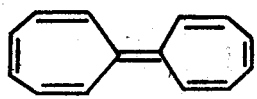
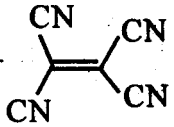
(*i*)



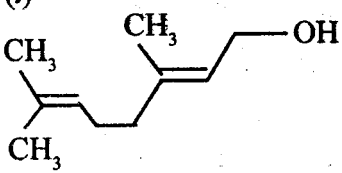
(*ii*)



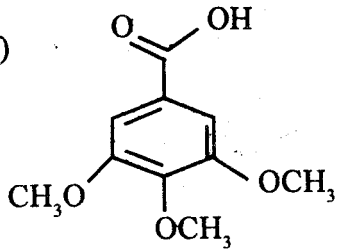
(*iii*)  +  $\xrightarrow{\Delta}$?

(*iv*)  +  $\xrightarrow{\Delta}$?

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

(*i*) 

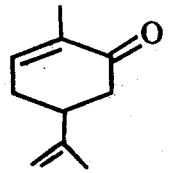
$\xrightarrow[\text{L(+) DET}]{\text{Ti (OiPr)}_4,\ {}^t\text{BuOOH}}$?

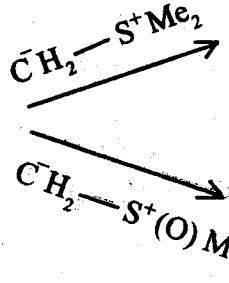
(*ii*) 

$\xrightarrow[{}^t\text{BuOH}]{\text{Na | liq. NH}_3}$?

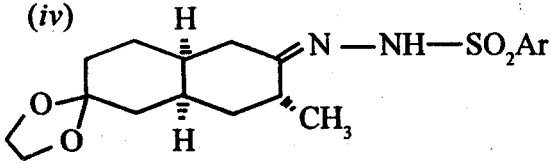
(*Continued*)

(*iii*)

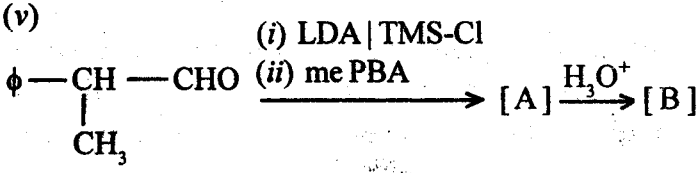



$\bar{C}H_2-S^+Me_2$
?
$\bar{C}H_2-S^+(O)Me_2$
?

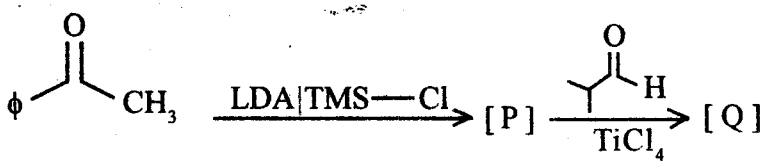
(*iv*)


H
N—NH—SO_2Ar
O
O
CH_3
H
(*i*) 2 CH_3 Li
(*ii*) CO_2
(*iii*) H_3O^+

(*v*)

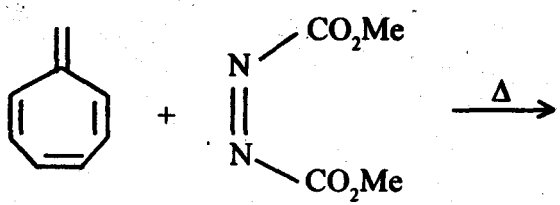

ϕ—CH—CHO
CH_3
(*i*) LDA | TMS-Cl
(*ii*) me PBA
[A]
H_3O^+
[B]

(*vi*)


O
ϕ
CH_3
LDA|TMS—Cl
[P]
O
H
$TiCl_4$
[Q]

4. (*a*) What is cheletrofic reactions ? Explain with examples and show mechanism of addition. 3

(*b*) Predict the product of the following reactions indicating F.O.I. 2



(*c*) Define 'site selectivity' and 'periselectivity' with examples indicating Frontier orbital interaction. 3

5. What is 'isoprene rule' ? Explain with example. A monoterpenoid $C_{10}H_{16}O$(A) on treating with hydroxylamine HCl forms oxime and reduces tollen's reagent compound A on reduction gives B $C_{10}H_{18}O$ (B) lent on oxidation with 1% $KMnO_4$/NaOH followed by CrO_3 oxidation : gives oxalic ā, laevulic ā and acetone. Further A on treating with aq. K_2CO_3 forms hepta-6-methyl-5-ene-2-one and acetaldehyde. Identify compound-A indicating reactions involved in the above steps. 2 + 6

GROUP – B

6. (*a*) Answer any *two*: $1\frac{1}{2} \times 2$

(*i*) Write a molecule having diastereotopic ligands and designate them. Explain by symmetry and substitution criteria.

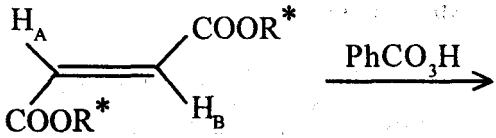
(*ii*) Write a biphenyl derivative having a prochiral axis with enantiotopic ligands. Designate the ligands and explain by symmetry and substitution criteria.

(*iii*) Write a Fischer projection formula of the meso diastereomer of 2, 4-dihydroxy-glutaric acid,

$HOOC-CHOH-CH_AH_B-CHOH-COOH.$

Explain why C3 is a prostereogenic but proachirotopic center, by substitution criterion, and hence designate H_A and H_B.

(*b*) Write down the product of the following reaction :



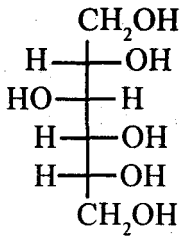
R^* is a chiral ligand

Comment on the ^1H NMR signals of H_A and H_B of both the starting material and the product/s. Explain in terms of their topicity as revealed by their symmetry criterion. 3

(*c*) Predict the product/s of the following reaction with plausible mechanism, and name the predominant product, if any. 2

(*S*)-PhCMe(OH)COPh $\xrightarrow{\text{LiMe}}$

7. (*a*) Comment on the topicity of the CH_2OH groups of **D**-glucitol (**A**) by application of its symmetry and selective oxidation criteria. 2



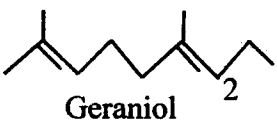
D-Glucitol (**A**)

(*b*) Indicate the plausible mechanism of the following reactions, and name the predominant product. $2\frac{1}{2} \times 2$

(*i*) (*R*)-PhCO.CO.O.CHClMe $\xrightarrow[(ii)\ H_3O]{(i)\ EtMgBr}$

Assign the π-face undergoing predominant product and the pref/parf nomenclature to the predominant product.

(*ii*)



Geraniol

$\xrightarrow[Ti\ (i\text{-}PrO^-)_4\ (0{\cdot}5\ eq.)]{t\text{-}BuOOH/CH_2Cl_2\ (2eq.)}$

TS *not needed* (+)-Diethyl tartarate

(–20 °C)

Name the reaction and the face undergoing ~95·5 % epoxidation; find the enantiomeric excess in this case.

(*c*) Give an example of the buttressing effect in the biphenyl system. 1

Or

Define asymmetric synthesis. 1

8. (*a*) "Ephedrine undergoes two different types of C—N bond fission." Justify the observation citing the examples of Hoffmann exhaustive methylation and hydramine fission of ephedrine. Explain the mechanisms of the two reactions. 4

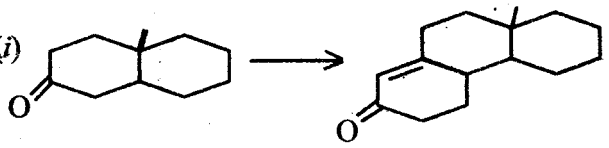
(*b*) Discuss the sequence of degradation reactions to establish the absolute configuration of the only asymmetric center present in (-)nicotine. 4

9. (*a*) Elaborate a synthesis of (+)coniine using (+)norephedrine as chiral auxiliary. 4

(*b*) "Joining of nicotinic acid with N-methylpyrrilinium cation leads to final stages of nicotine biosynthesis." Identify the biogenetic steps and describe the results of related biosynthetic experiments. 4

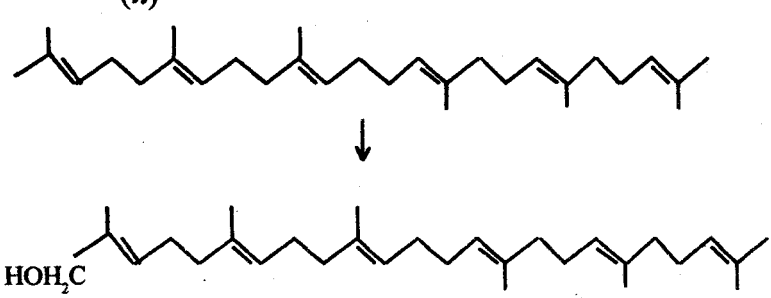
10. (*a*) Carry out the following transformation (any *two* with plausible mechanism): 2 × 2

(*i*)

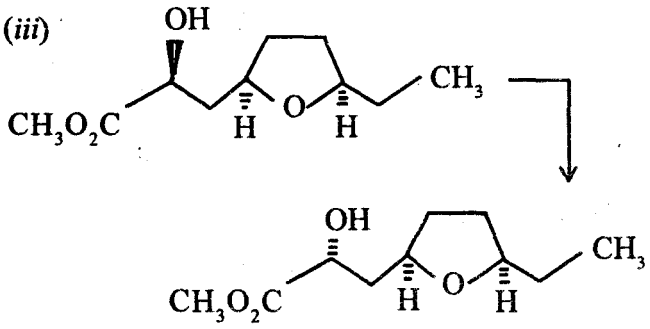


(*Continued*)

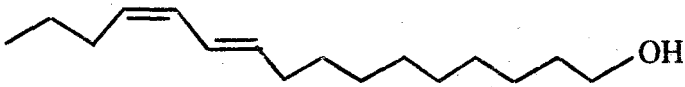
(*ii*)



(*iii*)



(*b*) Synthesize Bombykol from simple precursors. 4



(Bombykol)