PG/IS/CH-1102/10

M.Sc. 1st Semester Examination, 2010

CHEMISTRY

(*Organic*)

PAPER—CH-1102

Full Marks : 40

Time : 2 hours

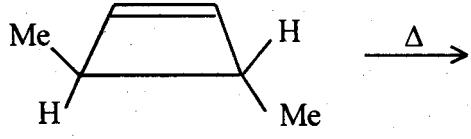
Answer any **five** questions taking at least **two** from each Group where **Q. No. 6** is compulsory

The figures in the right-hand margin indicate marks

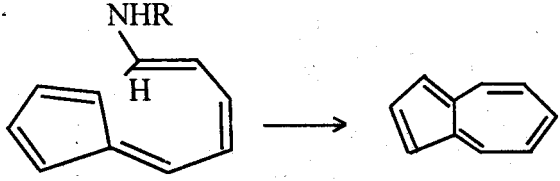
GROUP—A

1. (*a*) Explain suprafacial and antafacial addition and migration respectively in cycloaddition and sigmatropic reactions with reference to frontier orbital interaction (F.O.I) with example. 4

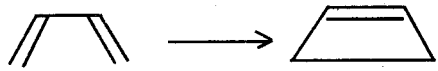
(*b*) Explain in what way the following ring opening reaction takes place and predict the preferred product. 2



(*c*) Explain the mechanism of the following transportation indicating F.O.I : 2



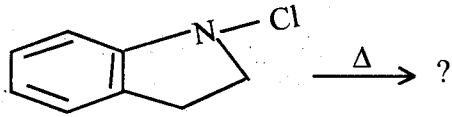
2. (*a*) Draw the correlation diagram of the following conversions :



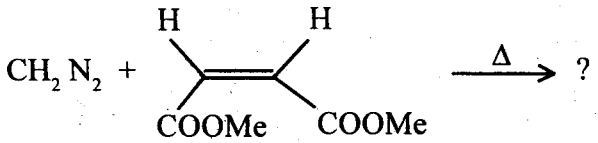
and indicate the symmetry allowed path in thermal reaction. 4

(*b*) Predict the product/s of the following reactions indicating frontier orbital interactions (attempt any *two*): 2 x 2

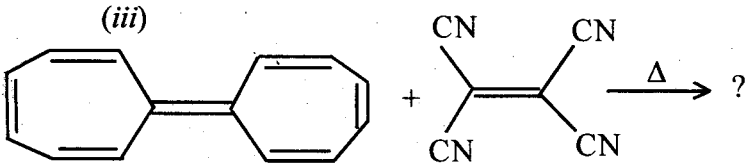
(*i*)



(*ii*)



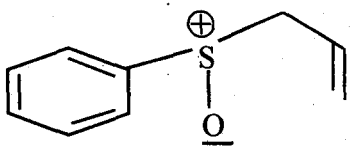
(*iii*)



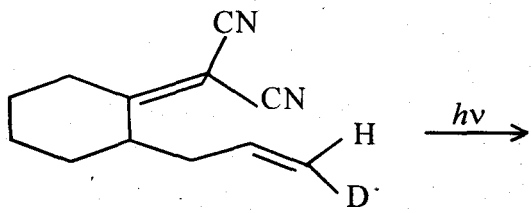
3. (*a*) Write down the Woodward-Hoffmann selection rules for *H* and *C*-migration in sigmatropic reactions. 4

(*b*) Predict the product of the following reactions indicating F.O.I in each case (attempt any *two*) : 2 x 2

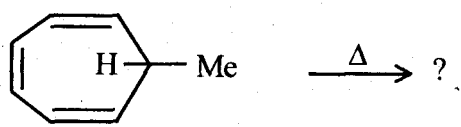
(*i*)



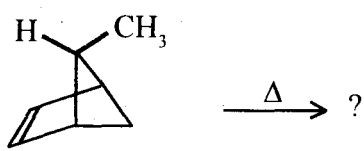
(*ii*)



(*iii*)

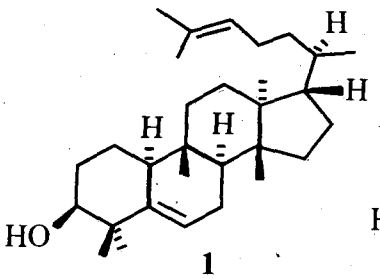


(*iv*)

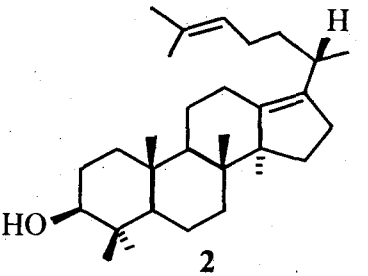


4. (*a*) Predict the possible (*i*) bicyclic and (*ii*) tricyclic products by acid catalyzed transformation of squalene epoxide (with plausible mechanism) : 2 + 2

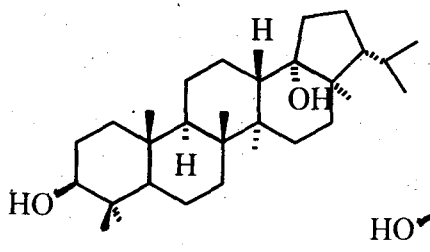
(*b*) Synthesize Boeticol **1**, dammara-13(17), 24-dien-3-ol **2**, 3, 18-neohopanediol **3**, β-amyrin **4**, from squalene epoxide (any *two*, with plausible mechanism) : 2 x 2



1



2



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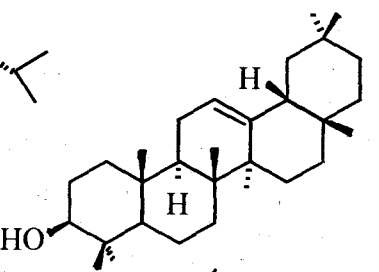
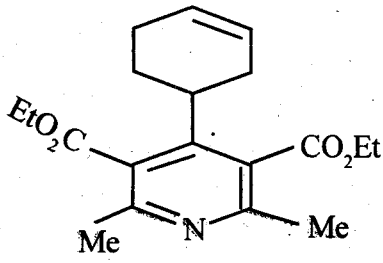


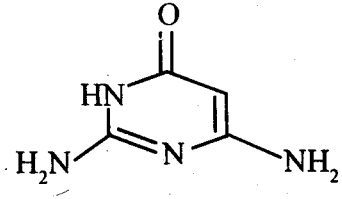
4

5. (*a*) Carry out the following synthesis using retrosynthetic analysis (any *two*): 2 x 2

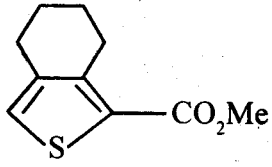
(*i*)



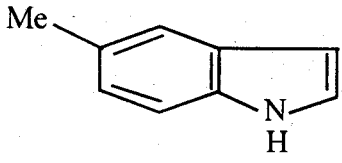
(*ii*)



(*iii*)

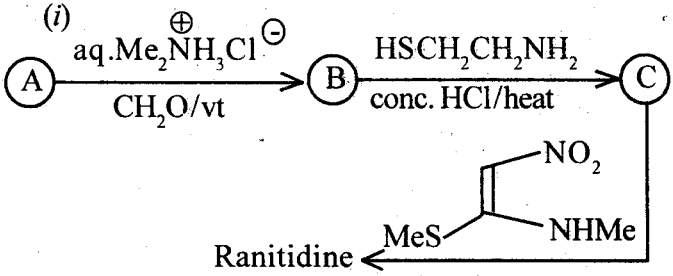


(*iv*)

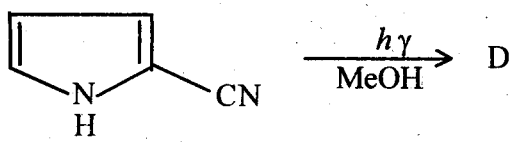


(*b*) Identify A, B, C and D of the following reactions : 4

(*i*)



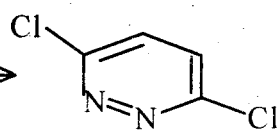
(*ii*)



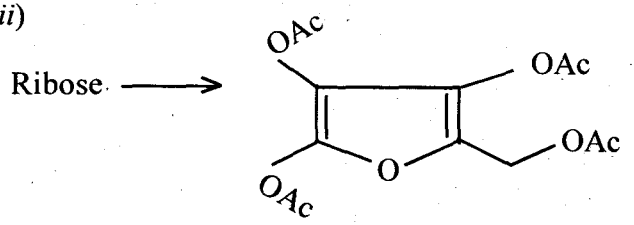
GROUP – B

6. (*a*) Carry out the following transformations (any *two*) : 2 x 2

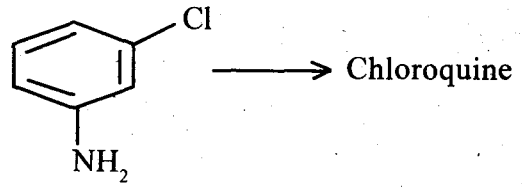
(*i*) Maleic anhydride ⟶



(*ii*)

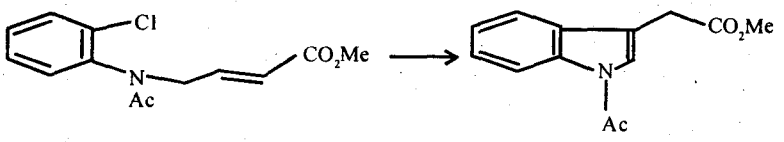


(*iii*)

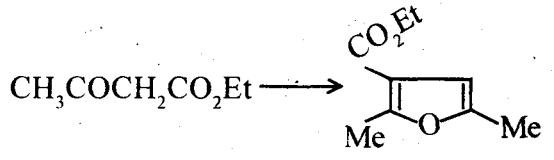


(*b*) Use suitable reagents : $1\frac{1}{2} \times 2$

(*i*)



(*ii*)



(*Continued*)

(*c*) Draw the structure of octaethyl porphyrin. 1

7. (*a*) Identify the following statements as *true* or *false* with justifications. Answer any *three* : 3

(*i*) A molecule may have a chirotopic but nonstereogenic center. Explain with an example.

(*ii*) The two forms of *cis*-1, 2-dimethyl-cyclohexane are configurational isomers.

(*iii*) The molecule $BrCH_2Cl$ is chiral in 2-dimension and prochiral in 3-dimension.

(*iv*) The symmetry point group of the skew-boat form of cyclohexane is $\mathbf{D}_2$.

(*v*) The molecule $C_{ab}=C=C_{aa}$ possesses a prochiral axis.

(*b*) Answer any *two* of the following : $2\frac{1}{2}\times 2$

(*i*) Write all possible Fischer projection formulae of (*S*)-2-phenylbutane and specify its (**D**, **L**)-nomenclature.

(*ii*) Draw the chair conformations and the corresponding Newman projection formulae of *trans*-1, 2-dimethylcyclohexane and hence show the signs of the torsion angles along the C1—C2 bond inside the ring of each conformer.

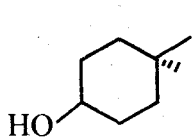
(*iii*) Indicate the plausible mechanism of the following reaction leading to the product/s.

$$\underset{\text{threo, active isomer}}{\text{MeCH(OTs).CHPhMe}} \xrightarrow{\text{gl. AcOH}}$$

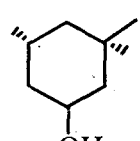
Comment on the optical activity of the product/s.

8. Answer any *four* of the following : 2 x 4

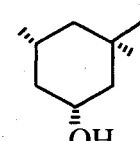
(*a*) Compare the relative rates of CrO_3 oxidation of the following compounds by considering their conformers :



(*i*)



(*ii*)



(*iii*)

(*b*) Indicate by (*R*, *S*)-notation the absolute configuration of each diastereomer of CHA_3, where A = CHPhMe.

(*c*) Correctly write down the 3-dimensional structure of the following compounds :

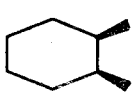
(*i*) (*R*)-$CH_2SH.C(Me)Cl.\ COOMe$

(*ii*) (*S*)-2′, 3, 6-Trimethoxy-2, 6′-dinitrobiphenyl

(*d*) Write down the product(s) of the following reaction showing plausible mechanism

$$\underset{\text{Pref diastereomer (any enantiomer)}}{\text{PhCOCH Br CH(COOH)Ph}} \xrightarrow{\text{Py, }\Delta}$$

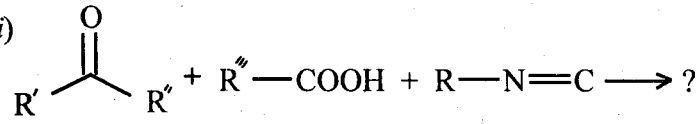
(*e*) Complete the following sequence of reactions, showing rational mechanism :



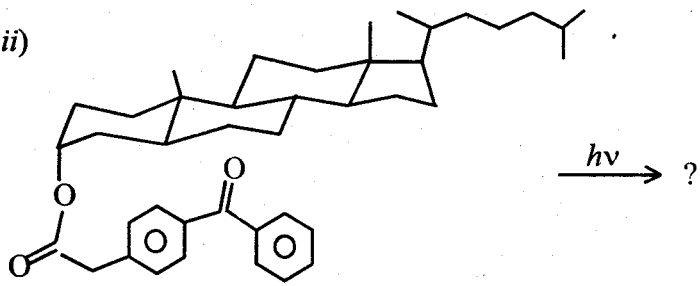
$$\xrightarrow{\text{gl. AcOH}} (\mathbf{A}) \xrightarrow{\text{conc. HCl}} (\mathbf{B})$$

9. Predict the products with plausible mechanism (any *four*) : 2 x 4

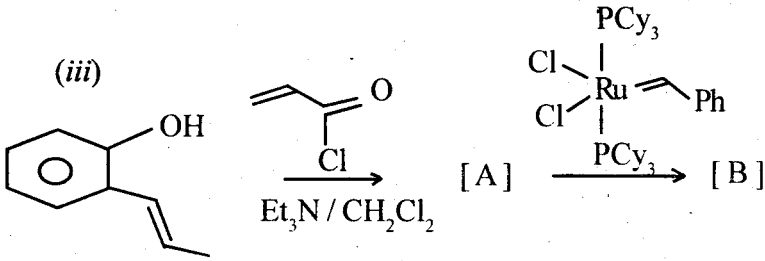
(*i*)



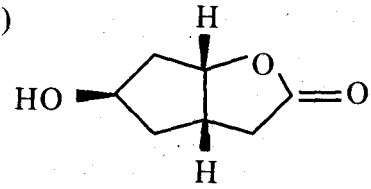
(*ii*)



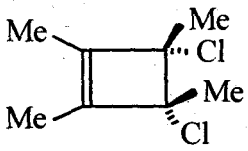
(*iii*)

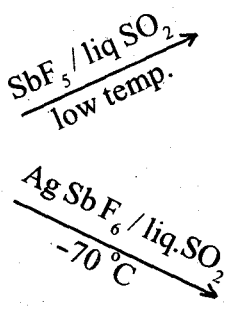


(*iv*)



(*v*)





10. (*a*) (*i*) Explain briefly the equation which determines vicinal coupling constants in aliphatic systems.

(*ii*) Name two ways by which the chemical shifts and coupling constants of ^{1}H-nmr signals can be determined. 4

(*b*) Identify the functional groups from the following data ?

(*i*) IR : 1745 Cm^{-1}
^1H-NMR : δ 3·5 (3 H, S)

(*ii*) DBE = 4, ^1H - NMR : δ 6·7 (2 H, d, J = 7 Hz), δ 7·2 (2H, d, J = 7 Hz). 4