Total Pages—18 **PG/IS/CHEM/CH 1102/09**

2008

CHEMISTRY

(*Organic*)

PAPER—CH-1102

Full Marks : 40

Time : 2 hours

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

The figures in the right-hand margin indicate marks

Candidates are required to give their answers in their own words as far as practicable

Write the answers to question of each Group in separate books

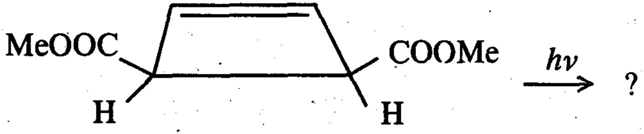
GROUP—A

1. (*a*) Draw correlation diagram for the following interconversion,

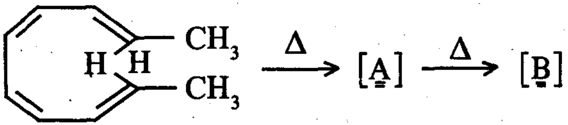
Cyclobutene $\rightleftharpoons$ butadiene

under thermal condition. Indicate symmetry allowed path for the reaction.

(*b*) Predict the easiest path of opening ring for the following reaction under photochemical condition ;



(*c*) Identify 'A' and 'B' of the following reaction sequence and explain indicating F. O. I (frontier orbital interaction) :

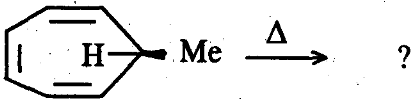


4 + 2 + 2

2. (*a*) '1, 3-H migration is difficult to occur but 1, 3-Carbon migration occurs with inversion of configuration under thermal condition.' Justify the statement showing frontier orbitals.

(*b*) Predict the product(s) of the following reactions showing F. O. I., (attempt any *two*):

(*i*)



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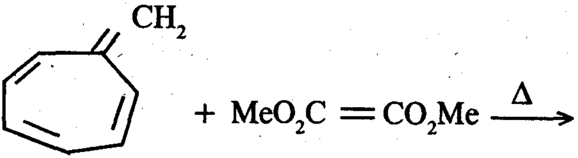

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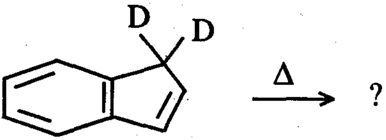
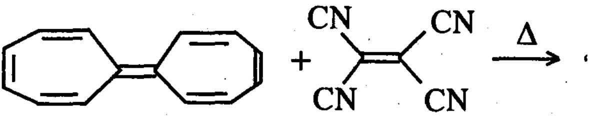
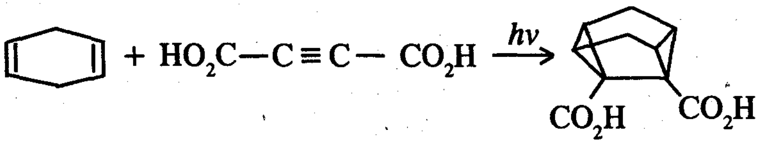


(*iv*)

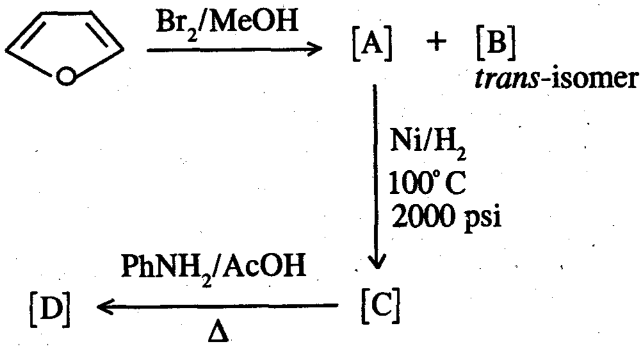


(*c*) Explain the following conversion with mechanism indicating F. O. I.



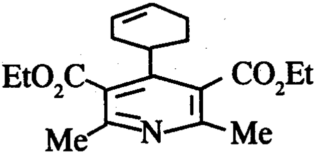
$1 + 2 + (1\frac{1}{2} \times 2) + 2$

3. (*a*) Identify [A], [C] and [D], where [A] and [B] are geometrical isomers.

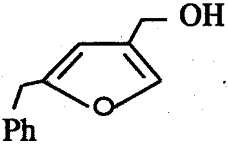


(*b*) Outline the synthesis of any *one* of the following compounds showing retro-synthetic analysis:

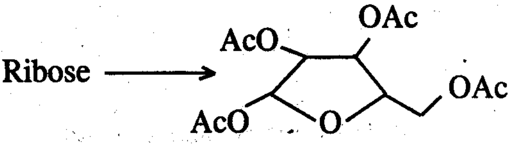
(*i*)



(*ii*)

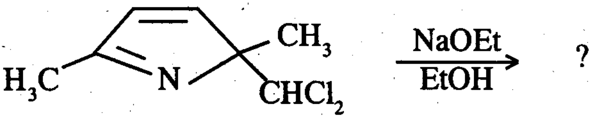


(*c*) Carry out the following transformation:



(*d*) Why does nucleophilic attack take place at 1-position not at 3-position of isoquinoline?

(*e*) Predict the product(s) and suggest plausible mechanism of the following reaction :



$$1\frac{1}{2}+2\frac{1}{2}+1\frac{1}{2}+1+1\frac{1}{2}$$

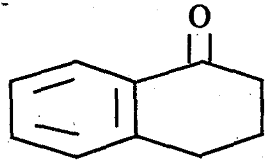
4. (*a*) (*i*) Why only the minor isotope of carbon $\left({}^{13}C_6\right)$ is used in NMR spectroscopy, while its most abundant isotope $\left({}^{12}C_6\right)$ is unsuitable for this purpose?

(*ii*) Why is TMS chosen as the reference compound in ^{1}H-NMR?

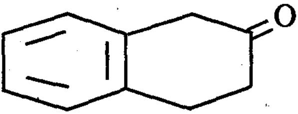
(*iii*) How many signals would you expect for the following compound in its ^{1}HNMR spectrum? Explain your answer $CH_3—CH(Cl)—CH_2Cl$.

(*b*) Why does an aldehydic proton resonate at a low field of about δ 10·0?

(*c*) Show how the following pair of isomeric compounds are distinguished from their ^1H–NMR spectral data. Give only distinguishing features.



and

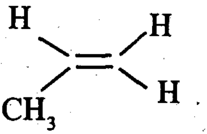


$(1 + 1\frac{1}{2} + 1) + 2\frac{1}{2} + 2$

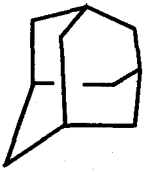
Or

(*c*) How many different type of non-equivalent protons are there in each of the following compounds: 2

(*i*)

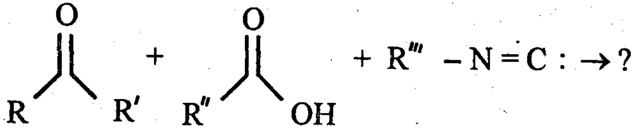


(*ii*)



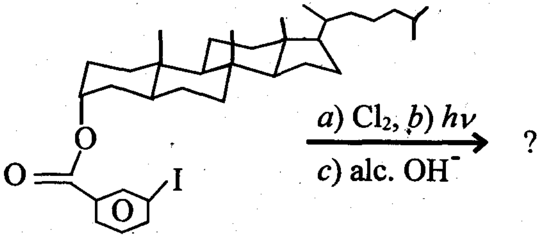
5. Predict the product(s) and suggest plausible mechanism (any *four*) of the following reactions : 2 × 4

(*i*)

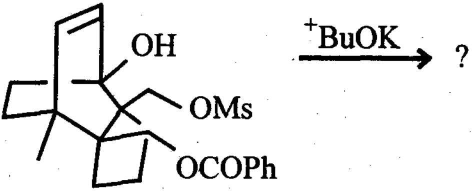


$RCOR' + R''COOH + R''' - \dot{N} = C : \rightarrow ?$

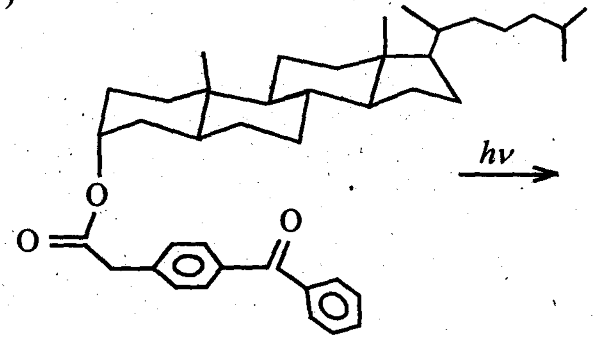
(*ii*)



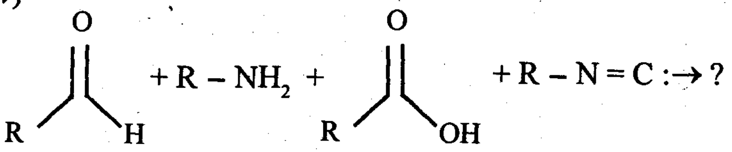
(*iii*)



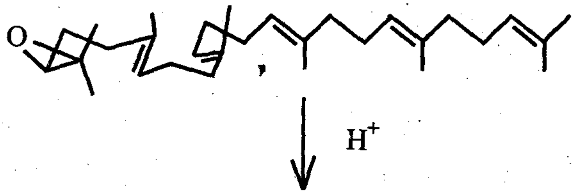
(*iv*)



(*v*)

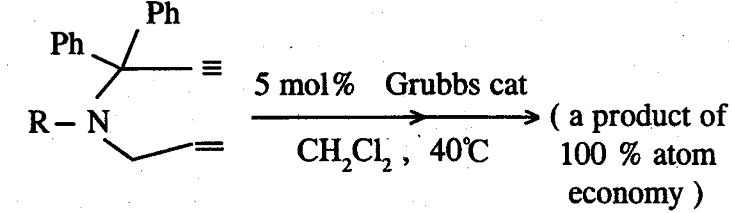


(*vi*)



Possible Bicyclic Products.

(*vii*)



GROUP—B

6. Answer (*a*) and any *two* from (*b*) to (*e*): 2+3×2

(*a*) Write whether the following statements are *true* or *false* with justification. Attempt any *two* :

(*i*) The molecule $C_{ab} = C = C = C_{ab}$ possesses a chiral axis.

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

(*iii*) *trans*-1, 2-Dichlorocyclohexane is optically inactive.

(*iv*) The four methylene protons of *n*-butane are homotopic and appear as a four proton quartet.

(*b*) Write all possible Fischer projection formulae of ($\underline{R}$)-z-bromobutane and give its ($\underline{\underline{D}}$, $\underline{\underline{L}}$) -nomenclature.

(*c*) Indicate by ($\underline{R}$, $\underline{S}$)-notation the absolute configuration of each diastereomer of CHA_3, where, A = CH(Br)Me.

(*d*) Write down the correct 3-dimensional structure of ($\underline{R}$) -1, 3-Dimethyl-1, 3-Diphenylallene and delineate its point group.

(*e*) Complete the following reaction by application of Felkin model

$$(\underline{S})\text{-MeCOCHBr Et} \xrightarrow[(ii)\,H_3O^+]{(i)\,\text{PhLi}} (\underline{\underline{A}}) + (\underline{\underline{B}}).$$

Or

Answer (*a*) and any *two* from (*b*) to (*d*): $2 + 3 \times 2$

(*a*) Attempt any *two* of the following:

(*i*) Write a molecule having diastereotopic faces; designate any chosen face.

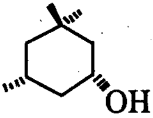
(*ii*) Correctly write down the structure of ($\underline{R}$)-2′,3,6–Trimethoxy–2,6′–dinitrobiphenyl

(*iii*) Delineate the symmetry elements of the twist form of cyclohexane and hence name its point group.

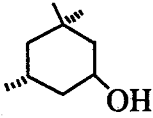
(*b*) Draw the chair conformations and the corresponding Newman projection formulae of *trans*–1, 2–dimethylcyclohexane and hence show the signs of the torsion angles along the C1–C2 bond inside the ring of each conformer.

(*c*) Compare the relative rates of CrO_3 oxidation of the following compounds:

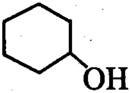
(*i*)



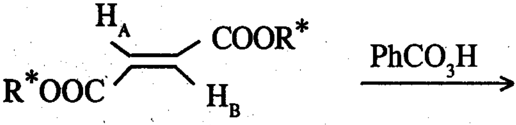
(*ii*)



(*iii*)



(*d*) Write down the product/s of the following reaction:



(R^* is a chiral ligand)

Comment on the ^{1}H NMR signals of H_A and H_B for both the starting material and the products, explaining in terms of the topic relationship as revealed by symmetry criteria.

7. Indicate the plausible mechanisms of the following reactions leading to the products. Name the predominant product, if any. Indicate the stereoelectronic and steric effects, whenever applicable.

Attempt (*a*) and any *two* from (*b*) to (*e*):

$3+2\frac{1}{2}\times 2$

(*a*) (*i*) (R̲)-PhCOCO.O. CH(Me)-Et $\xrightarrow[(ii)\ H_3O^+]{(i)\ \text{EtMgBr}}$

Assign the π–face undergoing predominant attack and give pref/parf nomenclature to the predominant product.

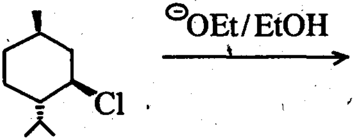
Or

(*ii*) MeCH(OTs) CHPhMe $\xrightarrow{\text{gl.AcOH}}$

Active threo–isomer (any enantiomer)

Comment on the opt. activity of the product/s.

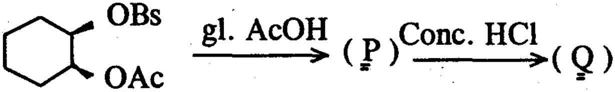
(*b*)



(*c*) PhCO CHBr CH $(CO_2H)Ph \xrightarrow{Py\ ,\ \Delta}$

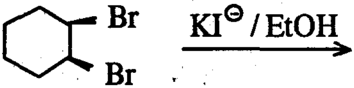
Parf diastereomer (any enantiomer)

(*d*)



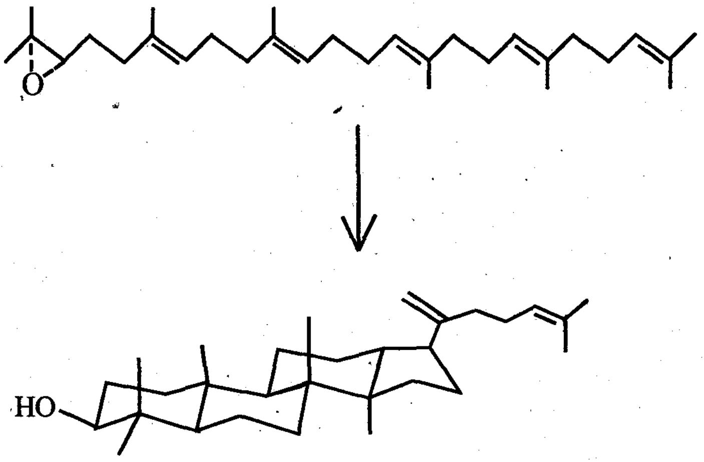
(*e*) (*i*)

(*ii*)

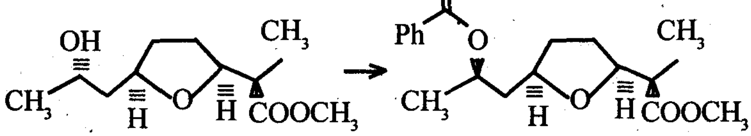


8. Carry out the following transformation (any *four*, with mechanism) : 2 × 4

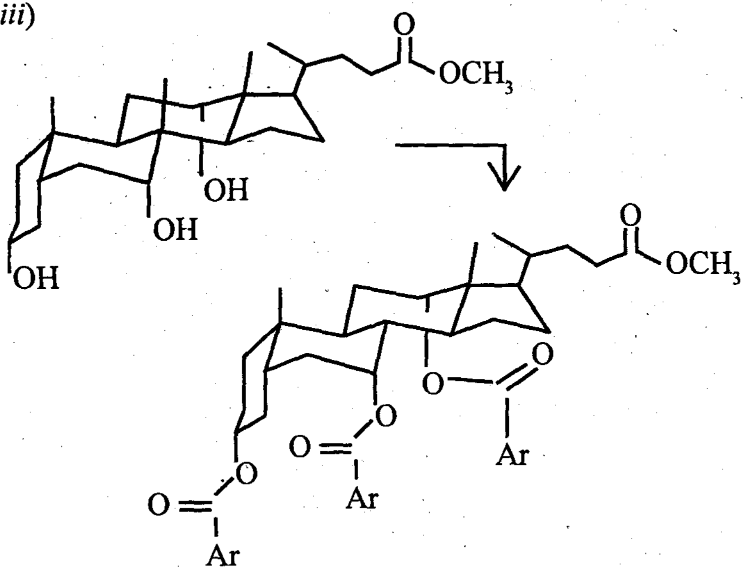
(*i*)



(*ii*)



(*iii*)



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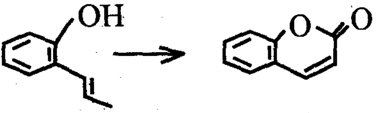
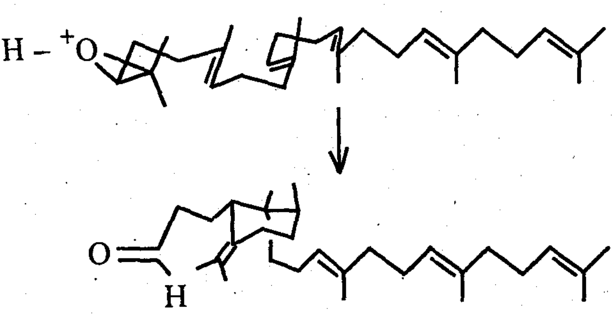


(*v*)



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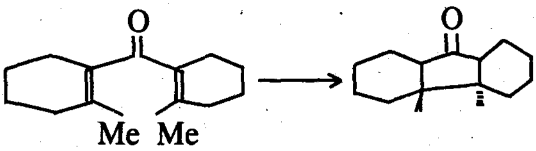

9. Define the term homoaromaticity. How [18] annulene is synthesised ? What happens when [18] annulene is treated with potassium in THF at low temperature ? What changes would you observe in the chemical shifts of the protons of the above product from that of [18] annulene ? Is porphyrin aromatic ? What is spherical aromaticity ?

1 + 2 + 1 + 2 + 1 + 1
