PG/I/CHEM/II/07

2007

CHEMLSTRY

PAPER-II

Full Marks : 75

Time **3 hours**

Answer any **five questions taking at least two** from each Group including **at least one** from Q. **Nos. 6 to 8**

The figures in the right hand margin indicate marks

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

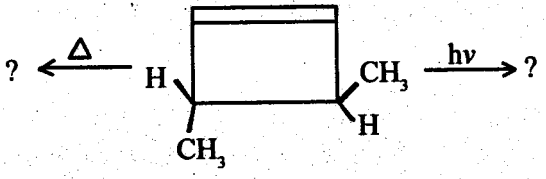
Illustrate the answers wherever necessary

Write the **answers Questions** of each Group **in separate books**

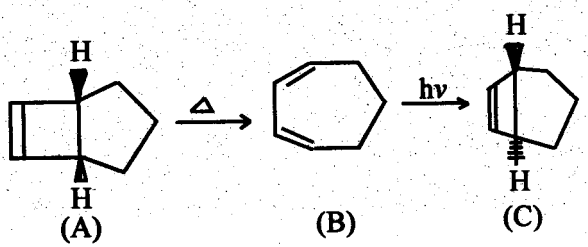
GROUP–A

1. (a) **Draw correlation diagram** for the **butadiene r cyclobutene interconversion under photochemical condition. Indicate symmetry allowed path for this conversion.**

(b) In what pathway the following ring opening reaction takes place? Indicate the most favourable path in each reaction, 3



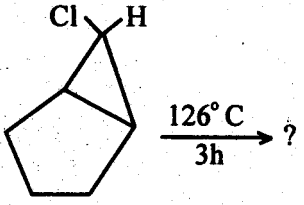
(c) The following transformation gives the product as follows: 4+1



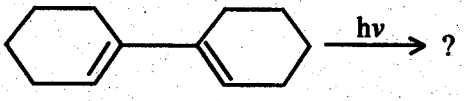
Explain, whether A -4 11 and B -' C follow Woodward Hoffmann Rule and reverse reaction C -+ B is. at all possible. Indicate mechanism and show frontier. orbital interactions for each steps whenever necessary. Comment on `principle of microscopic reversibility' for the above transformation.

(d) Predict the product (s) of the following reactions showing frontier orbital interactions (attempt any two) : 11 x 2 = 22

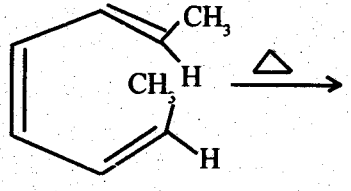
(*i*)



(*ii*)

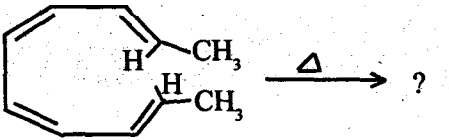


(*iii*)

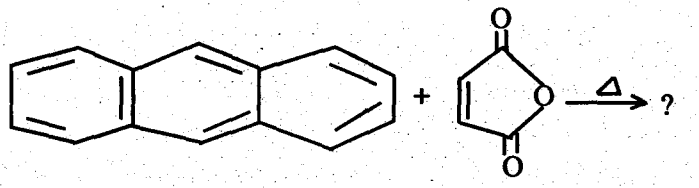


(a) **Define `Site Selectivity' and `periselectivity'. Predict the product (s) of the following reactions with proper reasoning** ***(any three) :*** **6,**

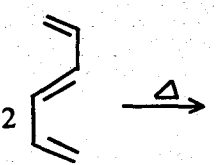
(i)



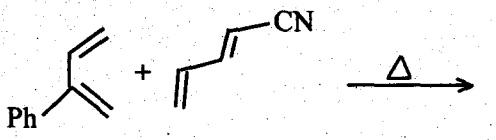
(*ii*)



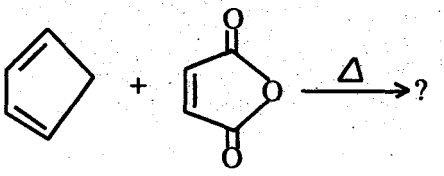
(*iii*)



(*iv*)



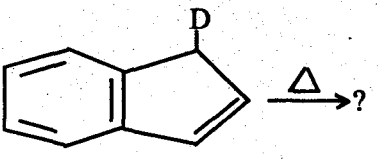
(b) Indicate whether exo or endo product will be preferred in the following reaction: 3



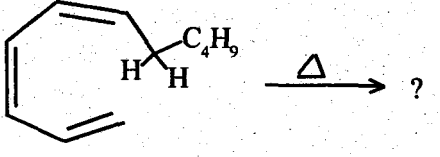
Show Frontier orbital **interactions and rationalise** on the basis of secondary **interactions.**

(c) Predict the product (s) of the following **reactions indicating** frontier orbital **interactions where necessary (attempt** any *three) :* 2x3

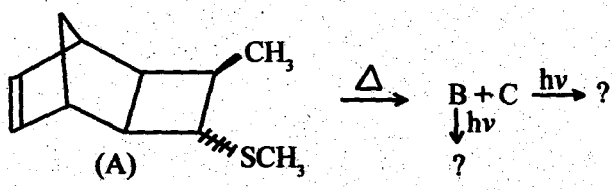
(*i*)



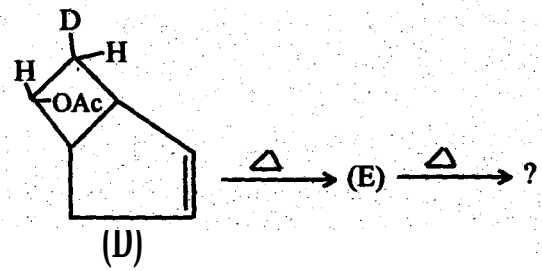
(*ii*)



(*iii*)



(*iv*)

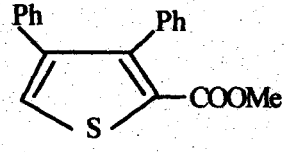


3 **(a) Outline syntheses of the following compounds** from readily **available materials** *(any four) :*

$2\frac{1}{2} \times 4$

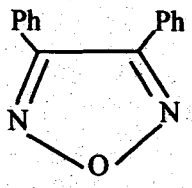
(*i*) **Octaethylporphyrin**

(*ii*)

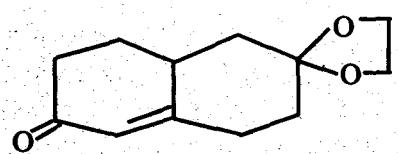


U d) **Rantidine**

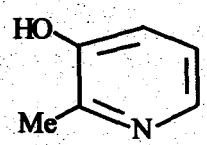
(*iv*)



(*v*)

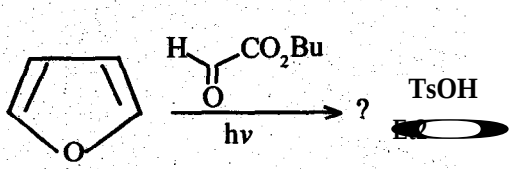


(*vi*)



(b) Predict the products (s) of the following reaction: 5

(*i*)

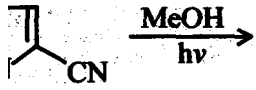


Ph

+CH-C-CO,Me

s

(iii)



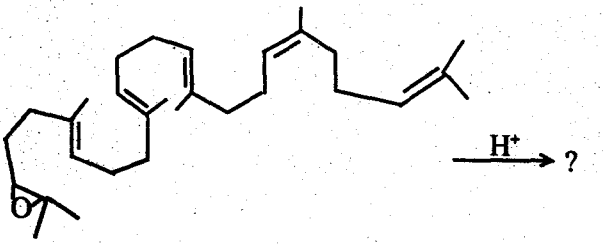
TOSNIIC

CH3-CH= CH-CO-CH3 TOS HC ?

rt

4. Predict the product**(s)** **and suggest a plausible** mechanism *(any five) :* *3x5*

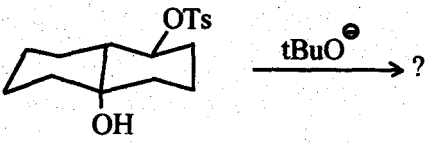
(a)


H+
?

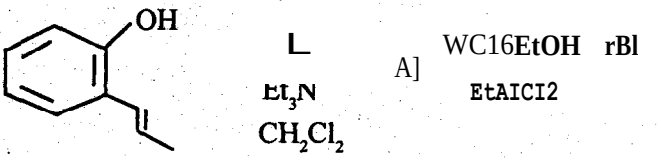
(b)


O O
R'-C-R + R OH+R-N=C--'?

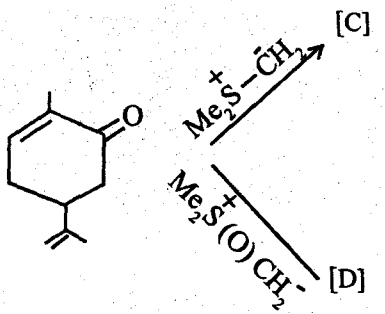
(c)


OTs
tBuO
?
OH

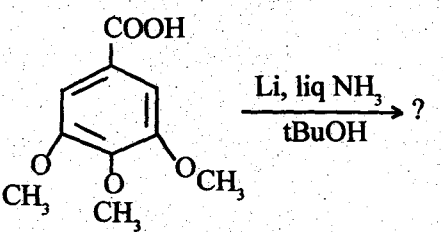
(d)


OH
Cl, 0
L
Et3N
CH2Cl2
A]
WC16EtOH rBl
EtAICI2

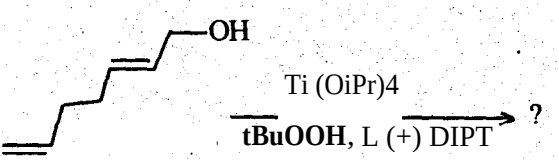
(*e*)


O
$Me_2S^+-\bar{C}H_2$
[C]
$Me_2S^+(O)\,CH_2^-$
[D]

(*f*)


COOH
O
CH_3
O
CH_3
O
CH_3
Li, liq NH_3
tBuOH
?

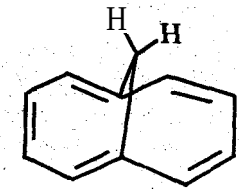
(*g*)


OH
Ti (OiPr)4
tBuOOH, L (+) DIPT
?

5. (*a*) Answer any *two* of the following:

(*i* How would you account for the fact that the protons of acetylene resonate at a higher field (82.-80) than those of ethylene (55-80) , although sp carbon of acetylene is more electronegative than sp2 carbon of ethylene ? 4

(ii) Indicate the multiplicity of the methylene **protons of an ethoxyl function** (O CH2-CH3) **Give reason** for your **answer**. How many types of non equivalent **protons are** there in CH3-CH=CH2? How would you expect the methylene **protons** of compound **1 to resonate and** why ? **4**



(iii) Compound A,C8H8andB,C12H18are both characterized by 'H-NMR spectra which consist of only one singlet signal at 8 0.9 and 2.2, respectively, while the 'H NMR spectrum of compound C, C8 H6,

shows two signals at S 3.**08 (s) and 7.3 (m) in the ratio** of 1.5 **. Identify the compounds** A, Band C.

1+11+i 1
2 2

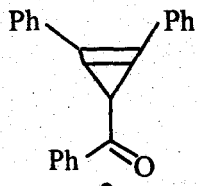
(b) **Answer** any *two* **of the following :**

(i) What are the energy units a and P? Give the mathematical expressions of the n MOs of benzene obtained by the linear combination of the six 2 p orbitals (LCAO). **standing perpendicular** to the **planar a skeleton of benzene**. Show **that due to 'conjugation benzene is stabilized by an amount of energy equal to 2'A**.

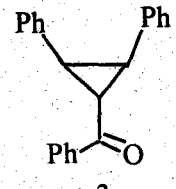
1+1+1 1

(9) Account for the fact that the base-catalyzed **ionization of compound 2 is 6000 times** slower than that of 3. What change of proton chemical shifts would you observe, if an aromatic compound is converted to **an antiaromatic** compound by the **addition of two electrons** (**by reaction with** KH/THF) and why.

2 i 1
2

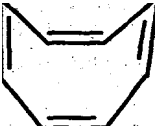


2



3

tiff) **What is homoaromaticity ? Indicate the product (X) obtained in the following reaction.**



SbCljconc..HCI
CH,NO2

X

Give 'H-NMR spectral- evidence for the structure of X indicating the nature of the compound and its relative ground state stability compound to 4 and tropylium cation.

1t1+11.
2

GROUP - B

6. Answer (a) and any *four* of the rest :

(a) Write whether the following **statements are** *True* or *False ;* **explain or** justify **with a suitable example**. Attempt any *three :* 3

(i) A molecule **may have an achirotopic but stereogenic center.**

(ii) A center **in a molecule** may be prochiral **but not-prostereogenic.**

(iii.) The molecule Cth=C= C= C=Cal, **possesses a chiral axis.**

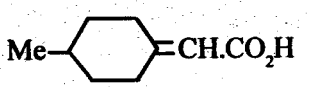
U O The ^ C (2) - H's **of n-pentane are homotopic.**

(b) Write down all possible. **Fischer projection** formulae of (K)-PhCHl1VIe **and give its D, L-nomenclature.** **3**

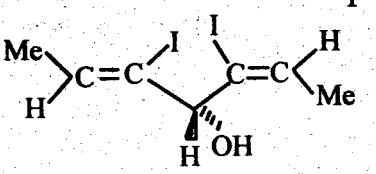
(c) Indicate by (R, ' S)-notation `the absolute configuration of .the diastereomers of HC'A2 B **where A CHBrMe and B = -CHOHPh. Comment on the stereogenicity and chirotopicity** of C' in **each diastereomer.** **3**

(d) The **two diastereomers** of 1,2-**dibromocyclo-hexane display dipole moments 3·09D and 2.11 D. Identify them with proper justification and comment on their optical** activity. 3

(e), (i) Write down the correct **3-dimensional structure** ofthe (S)-enantiomer **of 1; name it.** **1**



1



2

(ii) Give the *R,* S-descriptor for 2 according to the new convention of Prelog. Explain briefly. Designate it according to the old C1P convention. 2

(f) Assign the topicity of HA and H. in the following **compounds** (**3 to 6**), and give their **configurational descriptors**, wherever **applicable**. **Comment on** their L**H NMR signals.** Attempt any *three:*

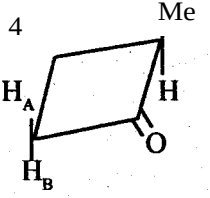
(R)-MeCH1 CHAHBMe

3

5

CHAHB= C =CHMe

4



6

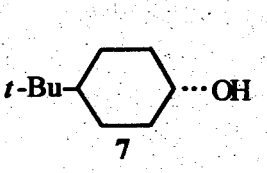
7. Answer (a) and any *three* of the rest :

(a) Draw the chair conformations and the corresponding Newman projection formulae of the two conformers of cis-1, 2-dimethylcyclo-hexane and hence show the sign in the ring across C (1)-C(2) bond in each conformer. How can you ascertain the sign of such torsion angles without drawing the Newman projection formulae?

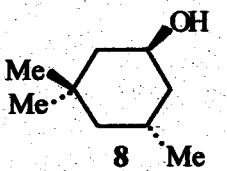
(b) (i) **Give examples of two allenes one having C. point group and another having C2 point group. Explain.** 2

(ii) **Draw a potential energy diagram of 6, 6'-dichloro**-2, 2'-dimethylbiphenyl. **Indicate the preferred pathway of thermal racemization.** 2

(c) The relative **rates** of Cr03 oxidation of **compounds 7 and 8 are 1 and 63** respectively. Draw their **conformations and explain with a potential energy diagram** (**qualitative**) 4

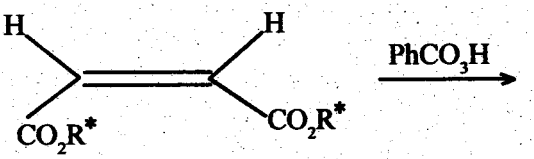


7



8

(d) Write down the : products of the following reaction and comment on the 'H NMR signals of HA and H. for **the starting material and the product/s, explaining in terms of topic relationship in each case.** 4



R* is a chiral ligand.

(e) Assign the configurational description of any face of the following ketone 9. Applying both Cram and Felkin models write down the products, indicating the predominant one. **4**

(R)-EtCOCHBrMe $\xrightarrow[\text{(ii) H3O}]{\text{(i) PhMgBr}}$ **9**

8. Indicate the plausible **mechanisms** of the following **reactions leading to the products**. **Answer any** *five:* 3x5

(a) 1, 2-dibromocyclohexane $\xrightarrow{\text{To}}$

(*cis* and *trans* isomers separately)

Comment on the reaction rates.

(b) McCH (OTs).CHPh. Me $\xrightarrow{\text{gl AcOII}}$

threo, **active isomer**

Comment on the optical activity of the **product/s.**

(c) Ph C(OH)Ar. CHNH2Me NaN02/H -

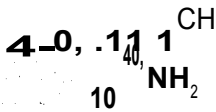
Parf diastereomer (any enantiomer).

(*d*) (*i*)

rti NaNO2/HCl

9 -

(*ii*)



NaNO2/HC1

Name compounds 9 and 10

(e) PhCOCHBr. CH(.CO2H) Ph $\xrightarrow{\text{Py, A}}$

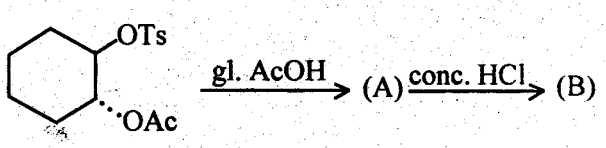
pref isomer
(any enantiomer).

(f) (R)- t-Bu CHMe OCOCOMe $\xrightarrow[\text{OH30+}]{\text{O PhMgBr}}$

(Apply Prelog's **rule)**

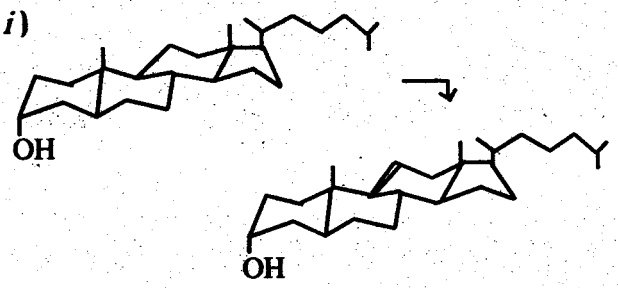
Label the face **undergoing** predominant attack and the resulting new chiral centre.

(*g*)

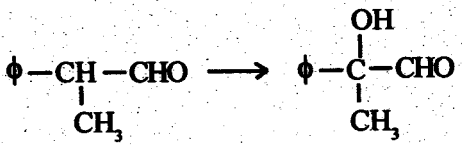


9. (a) Carry out **the following transformations** (any *three)* 3 **C**

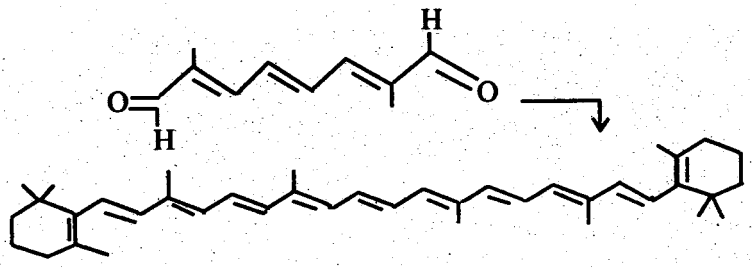
(*i*)



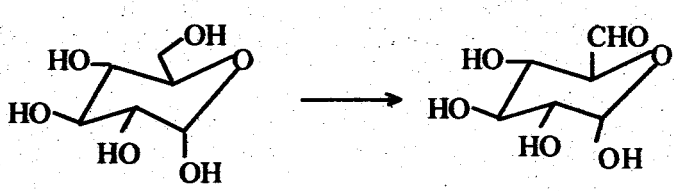
(*ii*)



(*iii*)

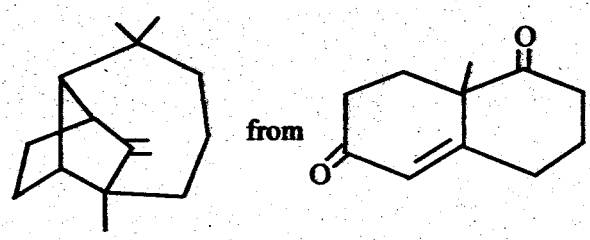


(*iv*)

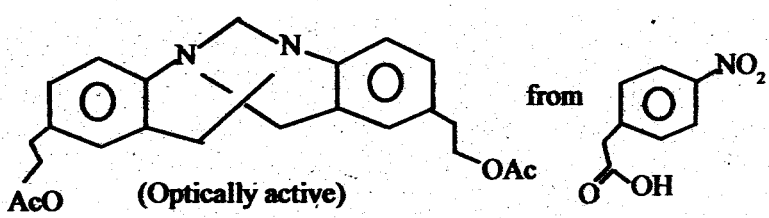


(*b*) Synthesize the following (any *one*): 6

(*i*)



(*ii*)



10. (a) What happens when ephedrine is boiled with conc. HCl ? Discuss the mechanism. Indicate the structural feature present in ephedrine which is responsible for this reaction to occur: 1+2+1

(b Show that suitable chemical modification of pyridine ring in nicotine makes it vulnerable to oxidative degradation keeping N-methyl pyrrolidine ring intact. 4

(c) Outline the steps involved for the enantiospecific synthesis of ® confine. 7

Or

A monoterpenoid, C, off 160 (A) on treating with semicarbazide hydrochloride forms semicarbazone and on reaction with silver nitrate (ammonical) * reduces to silver. Compound (A) on reduction gives C 1 0H, 8O (B) but on oxidation with 1% KMnO4/NaOH followed by chromic and oxidation yields oxalic acid, Laevulic acid and acetone. Further (A), on treating with aqueous K2C03 forms hepta-6-methyl-5-ene-2-one and acetaldehyde. Identify compound (A) indicating reactions involved in the above steps. What are the possible isomers of (A) ? Distinguish them by chemical method. 7