M.Sc. 1st Semester Examination, 2011

CHEMISTRY

(*Organic*)

PAPER—CEM-102

Full Marks : 40

Time : 2 hours

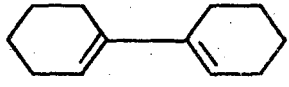
Answer any **five** questions taking at least **two** from each Group where **Q. No. 6** is compulsory

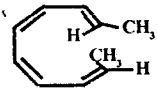
The figures in the right-hand margin indicate marks

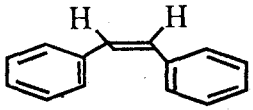
GROUP – A

1. (*a*) What are the characteristic features of pericyclic reactions ? State Woodward-Hoffman rules for electrocyclic ring closure reactions. 4

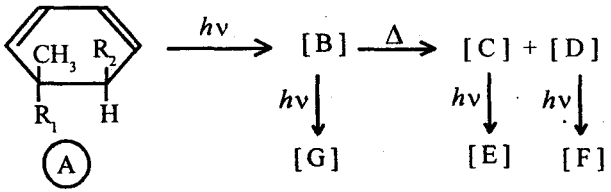
(*b*) Predict the product/s of the following reactions indicating Frontier orbital interaction in each case (F.O.I) (attempt any *two*) : 2 × 2

(*i*)  ?

(*ii*) 

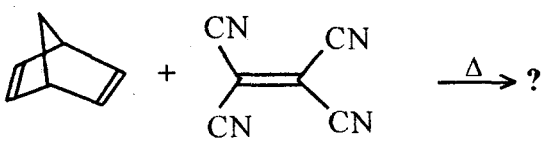
(*iii*) 

2. Complete the following reactions sequence indicating F.O.I. : 8



Identify the compounds B, C, D, E, F and G.

3. Write Woodward-Hoffmann selection rules for cycloaddition reaction and hence predict the product/s of the following reaction (any *three*) indicating F.O.I. $2 + 3 \times 2$

(*i*) 

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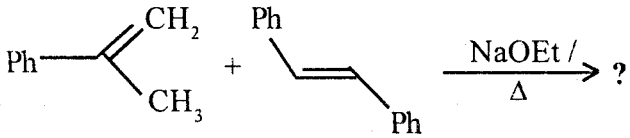
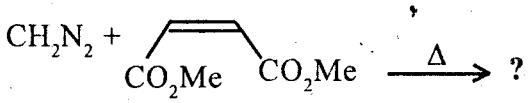
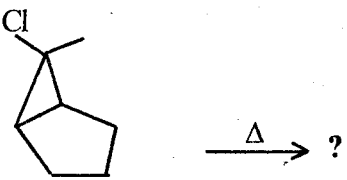
(*ii*)



(*iii*)



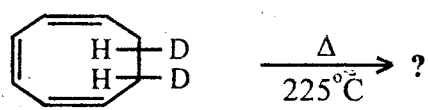
(*iv*)



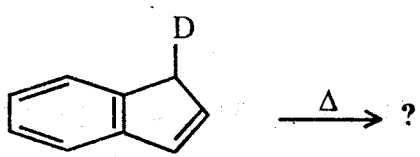
4. (*a*) What is *i, g* sigmatropic shift. Explain with examples. 2

(*b*) Predict the product of the following with F.O.I. : 6

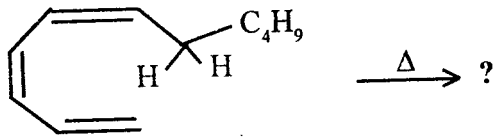
(*i*)



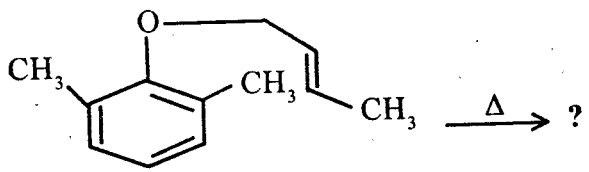
(*ii*)



(*iii*)

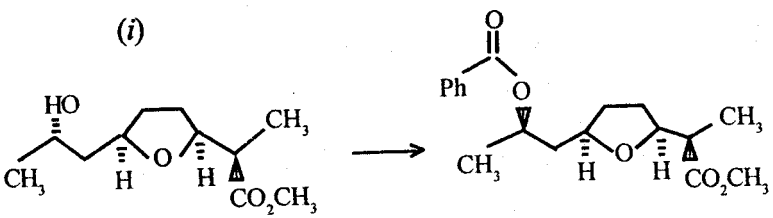


(*iv*)



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

(*i*)



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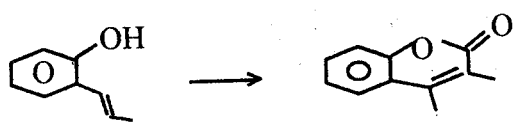

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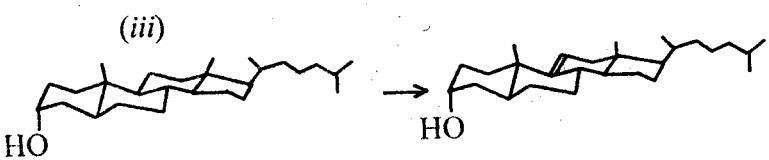
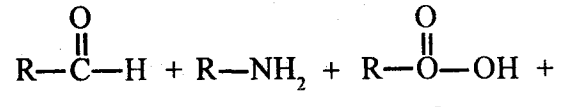
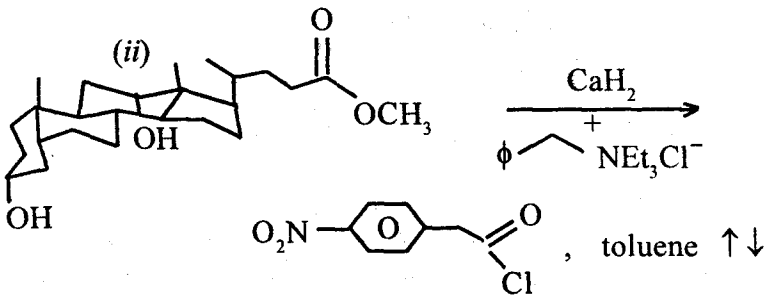
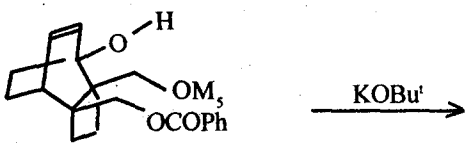


(*Continued*)

(*b*) Predict the products (any *two* with plausible mechanism): 2 × 2

(*i*) 

(*ii*) 

(*iii*) 

GROUP – B

Q. No. 6 is compulsory

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

(*i*) *trans*-1, 2-Diphenylcyclohexane is optically inactive.

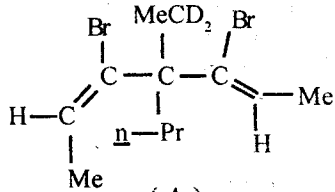
(*ii*) The two conformations of *trans*-1-methyl-3-ethyl cyclohexanes are conformational diastereomers.

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

(*iv*) Methane is a pro-pro-pro-chiral molecule in 3-dimensions.

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

(*i*) Give the R, S-descriptor for the following compound (A) according to the new CIP convention. Explain briefly. Designate it according to the old CIP convention.

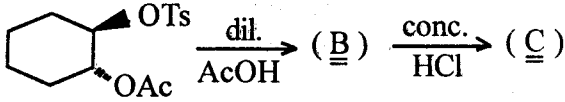


(A)

(*ii*) Write all possible Fischer projection formulae of (S)-PhCHBrEt and give its D, L-nomenclature.

(*Continued*)

(*iii*) Complete the following sequence of reactions. Showing rational mechanism.



7. (*a*) Draw the chair conformations of *cis*-1, 2-dimethyl -cyclohexane and show the signs of the torsion angles the C1—C2 bond inside the ring of each conformer; state the empirical rule that you are applying. 2

(*b*) Indicate plausible mechanism of the following reactions leading to the products. Stereoelectronic effect. Attempt any *three* : 2 × 3

(*i*) PhCOCHBrCH(COOH)Ph $\xrightarrow{Py\ ,\ \Delta}$ Parf diastereomer
(take any enantiomer)

(*ii*) $PhC(OH).Ar\ CHNH_2\ Me \xrightarrow{NaNO_2/HCl}$

Ar = p-anisyl

Indicate the major product.

Parf diastereomer

(any enantiomer)

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

threo, active isomer

Comment on the optical activity of the product.

(*iv*) 1, 2-Dibromo-cyclohexane $\xrightarrow{I^{\ominus}}$

(*cis* and *trans* isomers separately)

Comment on the reaction rates.

8. Attempt any *four* : 2×4

(*a*) Indicate by (R, S)-notation the absolute configuration of each diastereomer of CHA_2B where A = CHPhMe and B = CHBrMe.

(*b*) Give examples of two allenes, one having C_s point group and another having C_1 point group. Explain.

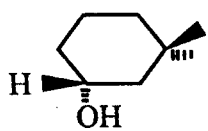
PG/

(*c*) Write down the three-dimentional structures of

(*i*) (S)-*trans*-cyclo-octene and

(*ii*) (R)-4-methylcyclohexanone oxime.

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



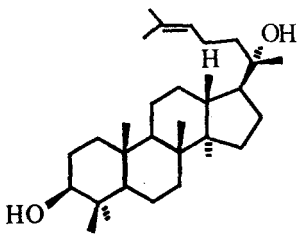
and

(*e*) The two isomers of 1, 2-dibromocyclohexane exhibit dipole moments 2·11 D and 3·12 D, characterize the isomers and comment on their optical activity.

9. Predict the possible (*i*) monocyclic, (*ii*) bicyclic and (*iii*) tricyclic products by acid catalyzed transformation of squalene epoxide (with plausible mechanism) : 2 + 3 + 3

10. Synthesize (20S) dammarene-diol **1**, butyrospermeol **2**, baccharis oxide **3**, lupeol **4**, germanicol **5**, β-amyrin **6**,

isobauerenol 7 from squalene epoxide (any *four*, with plausible mechanism) : 2 × 4



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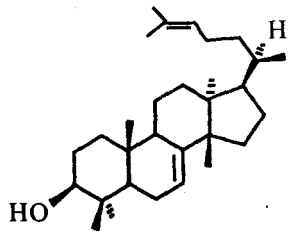

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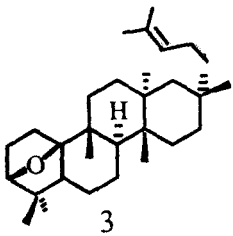

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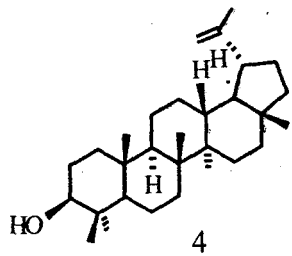

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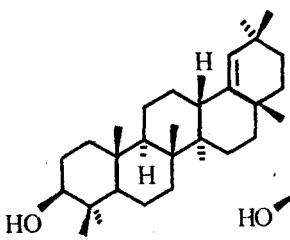

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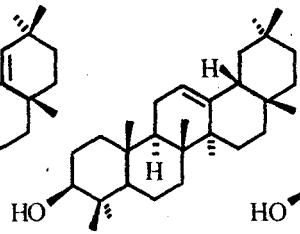

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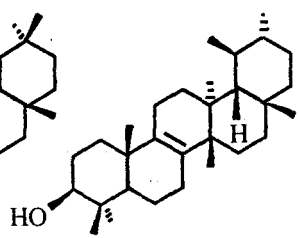

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