This question paper contains 8 printed pages]

HPAS (Main)—2016

CHEMISTRY

Paper II

Time : 3 *Hours* *Maximum Marks :* 100

Note :— Attempt *five* questions in all. Question No. **1** is compulsory. *All* parts of a question must be answered in continuation at one place.

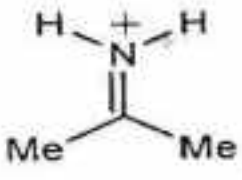
1. Answer the following with suitable explanation :

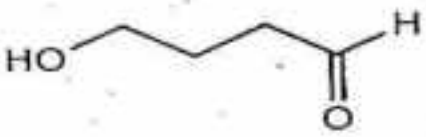
   (*a*) Compound (A) is highly unstable and it get converted to a compound whose IR, ^{1}H NMR and ^{13}C NMR data is given below : IR : 3200-3400 (no peak of carbonyl stretching); ^{1}H NMR : 1.11 (s, 6H), 1.46 (s, 3H), 2.0 (brs, 1H), 1.8 (s, 2H), 3.67 (s, 2H); ^{13}C NMR; 23, 24, 29, 56, 75, 95 (no peak for carbonyl). Identify the product and propose suitable mechanism for its formation. 8

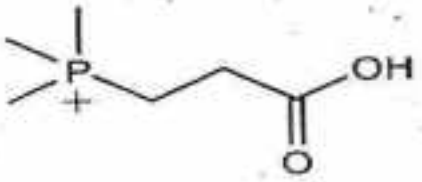
P.T.O.

A

(*b*) Each of the following electrophiles could react with nucleophile at (at least) two different atoms. Identify these atoms in the following compounds and identify the product when a nucleophilic (Nu) reacts at each center in the following compounds. Draw suitable mechanism for each case. 8







(*c*) What factors affect the crystallinity of PET ? 4

2. Attempt *all* of the following :

(*a*) How many non-equivalent hydrogens and carbons are present in N, N-dimethylacetamide at room temperature and high temperature. Give proper justification to your answer. 7

(*b*) Explain briefly, giving one common example as to how FMO method, PMO method and correlation diagrams can be used for analyzing a pericyclic reaction. 7

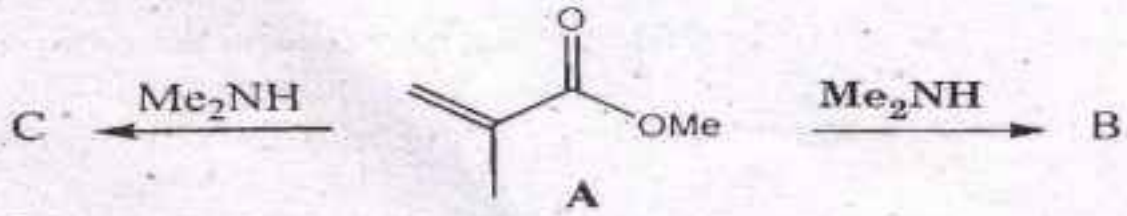
(*c*) Why Z, Z-2, 6-octadiene is not the product of pyrolysis of trans-3, 4-dimethylcyclohexadiene ? 6

3. Answer the following :

(*a*) How will you differentiate ethylbenzene and *n*-butylnenzene by mass spectrometry. 6

(*b*) Explain why the bond angle of H-C-H in the singlet and the triplet carbenes are different ? 6

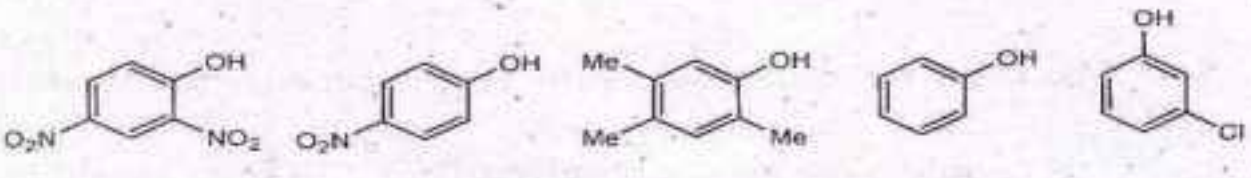
(*c*) Addition of dimethylamine to the unsaturated ester (A) could give either product B or C. Draw suitable mechanism for the formation of B and C and show how you would distinguish them spectroscopically ? 8



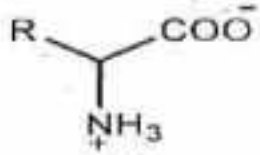
4. Explain the following :

(*a*) Explain why dichlorocarbene inserts in allylic and benzylic C-H bonds and not in non-allylic primary and secondary C-H bonds ? 6

(*b*) Phenols shown below have approximate pKa value of 4, 7, 9, 10 and 11. Suggest with explanation which pKa value belongs to which of the phenols. 8



(*c*) In the preparation of ester of amino acids (A) it is necessary to keep the ester as its HCl salt. What would happen if the ester is neutralized ? 6

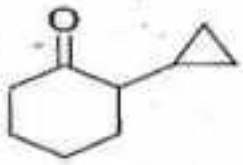


(A)

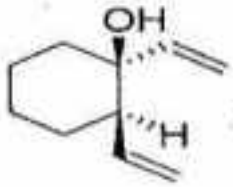
5. Answer all of the following :

(*a*) Explain why [4+2] cycloaddition is photochemically forbidden. 5

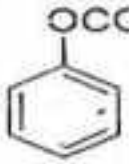
(*b*) Write the products of the following reactions and propose suitable mechanism for their formation : 9

(i) 

$\xrightarrow[C_6H_6]{h\nu}$ A + B

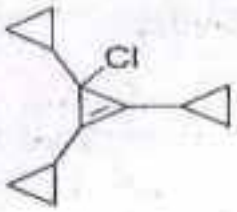
(ii) 

$\xrightarrow{\text{heat}}$

(iii) 

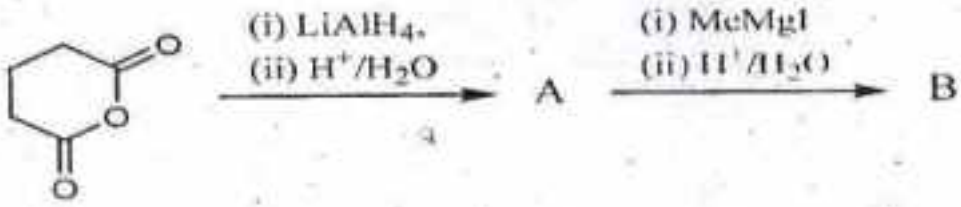
$\xrightarrow[EtOH]{h\nu}$ A + B + C

(*c*) Which species, Cl^- or Cl^+ is formed when the compound shown below ionizes ? Give a suitable reason to support your answer. 6

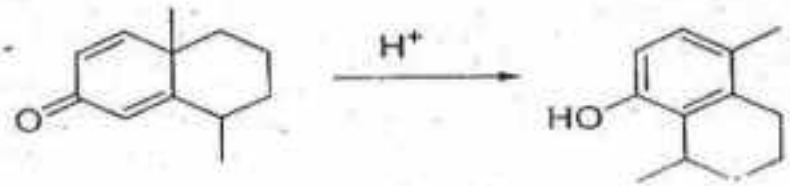


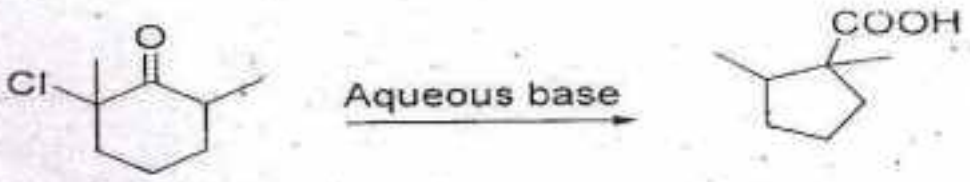
6. Answer *all* of the following :

(*a*) Identify the products in the following reaction and propose suitable mechanism. 8



(*b*) Write the name and mechanism of the following transformations : 8





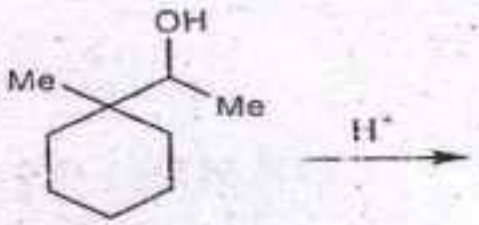
(*c*) Reaction between PhCl and NaOH at 300°C proceeds by a dual mechanism, what are those mechanisms and how will you demonstrates it experimentally ? 4

7. Attempt *all* of the following :

(*a*) Explain stereoselective, stereospecific and regioselective reactions with the help of suitable examples. 7

(*b*) Draw the structures of the products formed from the *syn* hydroxylation of *cis*-2-butene and trans-2-butene in the perspective formula (wedge line structure). Discuss the chirality of the proudcts. 7

(*c*) Identify the product in the following reaction and propose suitable mechanism for its formation. 6



8. Attempt *all* of the following :

(*a*) Explain why the solvolysis of 4-chlorobutanol is much faster than the solvolysis of 3-chlorobutanol in water. 7

(*b*) List the problems associated with lead and cadmium based pigments. How can these problems be resolved ? 7

(*c*) Cyclobutylamine on reaction with nitrous acid gives two products, identify the products and propose suitable mechanism for their formation. 6