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UG/II/CHEM/H/III/17 (Old)

2017

CHEMISTRY

[ Honours ]

PAPER — III (Gr.-A + B)

Full Marks : 90

Time : 4 hours

*The figures in the right hand margin indicate marks*

[ OLD SYLLABUS ]

GROUP — A

( Organic )

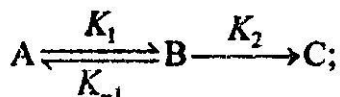
Group — A (a)

Answer any one question : 15 × 1

1. (a) What is called 'captodative radical'? Give example. 2

( Turn Over )

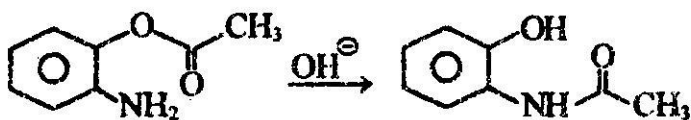
(b) In a reaction sequence



C has a lower free energy than A and  $K_2 \gg K_{-1} \gg K_1$ . Draw an energy profile diagram. 3

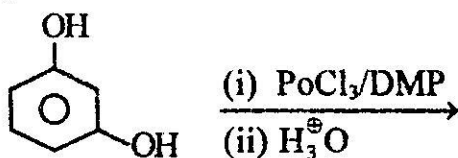
- (c) Benzyl Chloride is only very slowly decomposed by water or by dil. alkali than acetyl chloride. Give reason. 2
- (d) Explain why  $\alpha, \beta$  unsaturated ketone does not undergo epoxydation with  $H_2O_2$  in acid medium. 2
- (e) Acetylene is less reactive towards bromine addition than ethylene. Explain. 2
- (f) Ethyl vinyl ether is hydrolysed more readily than diethyl ether by dilute mineral acid – Explain. 2
- (g) Acetals are stable towards alkali hydrolysis but susceptible to acid hydrolysis – Explain. 2

2. (a) When either of ortho or meta or para xylene is treated with HCl and anh.  $\text{AlCl}_3$ , the same equilibrium mixture of all these isomers with meta xylene predominates – Explain. 2
- (b) A crossed Cannizzaro reaction involving formaldehyde is a good synthetic tool. Why? 2
- (c) After standing in aq. acid (R)-2 butanol is found to have lost its optical activity. Explain this fact? 2
- (d) Give a comparison using energy profile diagram of mechanistic possibilities of  $\text{E}_1$ ,  $\text{E}_2$  and  $\text{E}_1\text{CB}$  Eliminations. 3
- (e) Give the mechanism of the reaction : 2



- (f) What is meant by ipso substitution? Give an example. 2

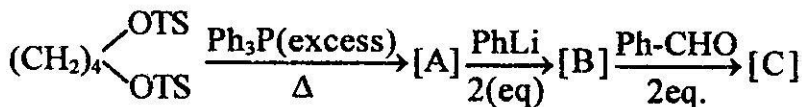
- (g) Identify the product of the following reaction with plausible mechanism : 2



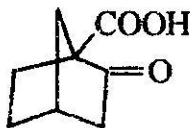
GROUP – A (b)

Answer any two questions : 10 × 2

3. (a) Write the structures of A, B and C : 3

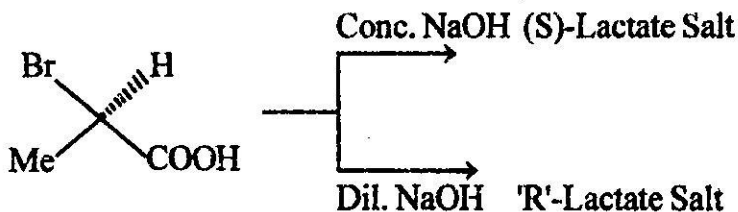


- (b) Bring out the mechanistic similarity between the Dakin reaction and cumene to phenol process. 2
- (c) Write the mechanism of decarboxylation of  $\beta$ -keto acid  $\text{Me COCH}_2 \text{COOH}$  and hence explain the following stability order  $\text{Me COCH}_2 \text{COOH} < \text{CF}_3 \text{COCH}_2 \text{COOH} < 3$

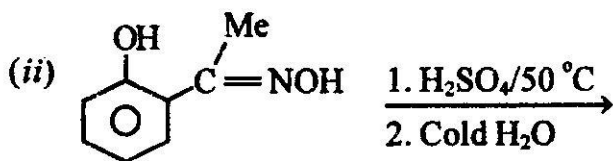
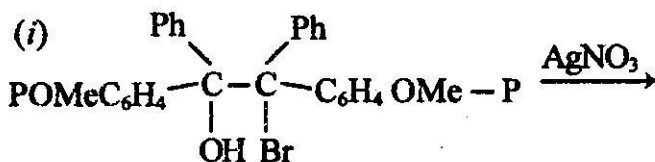


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(d) Account for the following observations : 2



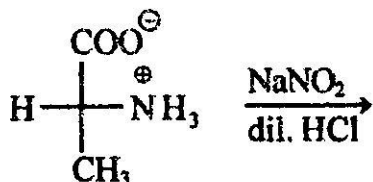
4. (a) Predict the products of the following reaction with plausible mechanism : 2 × 2



(b) Reactions of ethylene with (i) HI in ethanol  
(ii) HCl in ethanol, furnish different products.  
*Explain.* 2

( 6 )

- (c) Write the product of the following reaction with mechanism : 2



- (d) Draw the energy profile diagram for the sulphonation of naphthalene. Account for the fact that at 40 °C, the main product is naphthalene-1-sulphonic acid, while at 160 °C, the main product is naphthalene-2-sulphonic acid. 2

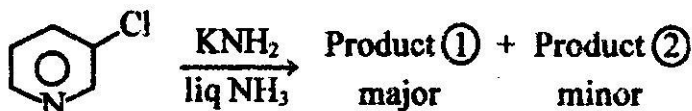
5. (a) Give the structures of all possible alkenes that could form in the following reaction. Indicate the major product and explain the formation. 3



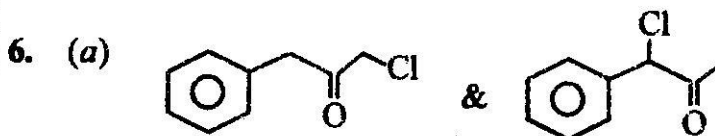
- (b) Convert the following transformation in one step, give mechanism : 2



- (c) Write down the products of the following reaction and indicate major and minor product with mechanism : 3



- (d) Convert : 2

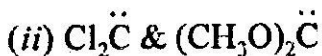
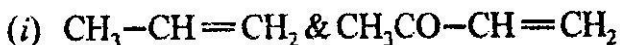


both the two isomer give the same product in presence of MeOH/NaOMe. 3

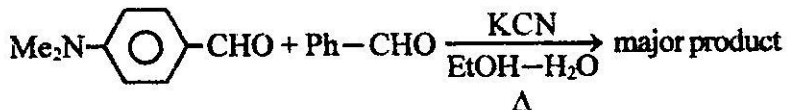
- (b) Provide the required reagents and conditions for the conversions of the following reaction scheme, give mechanism : 3



(c) Choose the best pair with respect to reactivity between the olefins (A) and carbenes (B). Give reason. 2



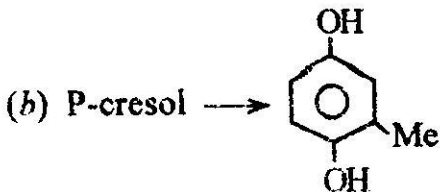
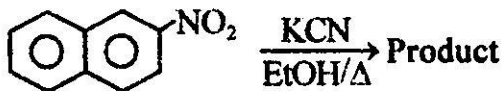
(d) Write down the products of the following reaction and give the plausible mechanism : 2



GROUP - A (c)

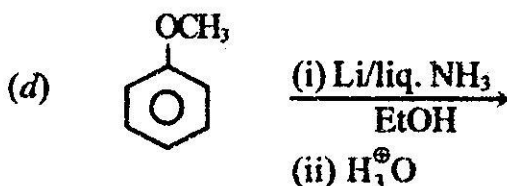
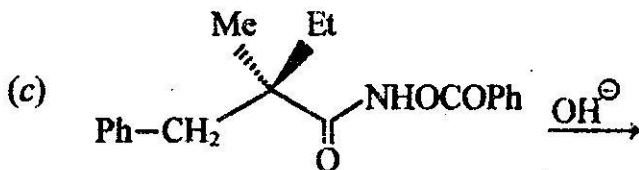
7. Answer the following questions (any five) : 2 × 5

(a) Write down the product with mechanism :



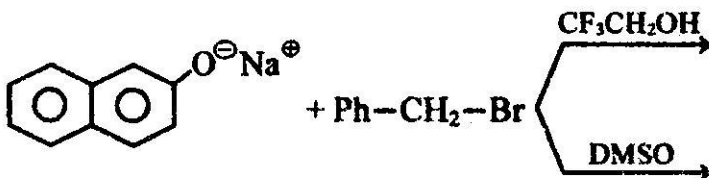


( 9 )



(e) Convert cis-2-butene to trans-2-butene.

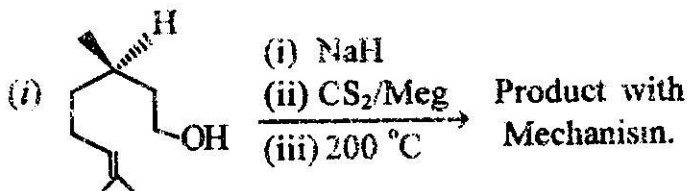
(f) Write down the products :



(g) Why  $R_2CHCO_2Et$  cannot undergo claisen condensation under normal condition but it occurs in presence of Ph-Li. Explain.

(h) Convert  $CH_3CHO$  to  $CH_3CDO$ .

( 10 )



GROUP -- B

( *Inorganic* )

GROUP -- B (a)

Answer any one question : 15 × 1

8. (a) State the major postulates of Sommerfeld's modification of Bohr's theory and hence explain how this model can be used to explain the hyperfine splitting of spectral lines under high resolution. 2 + 3
- (b) Discuss the criteria of a redox indicator. Show the mechanism of a redox indicator known to you. 2 + 3
- (c) Calculate the density of a nucleus of atomic oxygen, assuming the radius of its nucleus

to be  $10^{-15}$  m. Compare it with that of iridium ( $22.61 \text{ g cm}^{-3}$ ) and elucidate the significance of the result. 3

(d) Neutron rich radio nuclides are  $\beta$  active – explain. 2

9. (a) What is radial wave function and radial probability function? Draw qualitatively the radial probability function curve for 3s, 3p and 3d orbitals and comment on the sequence of ionisation energy of those orbital electrons.

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

(b) Can Fe(III) be estimated iodometrically with high accuracy? 3

Given,

$$E^{\circ}_{\text{Fe}^{3+}/\text{Fe}^{2+}} = 0.77 \text{ V}$$

$$E^{\circ}_{\text{I}_2/\text{I}^-} = 0.54 \text{ V at } 25^{\circ}\text{C.}$$

(c) Calculate the volume of  $\text{KMnO}_4$  (0.016 M) required to react with 20 ml oxalic acid (0.1 M). 3

- (d) Dithionic acid is not considered as a member of polythionic acid – justify. 2

GROUP – B (b)

Answer any two questions : 10 × 2

10. (a) Show the possible steps involved in the synthesis of  $^{12}\text{C}$ ,  $^{14}\text{C}$  and  $^{16}\text{O}$  through nuclear fusion of protons. 3

- (b) Calculate the 1st ionisation potential and 1st resonance potential for H atom in ev unit. 2 + 2

Given,

$$\text{Mass of electron} = 9.1 \times 10^{-28} \text{ g}$$

$$\text{Charge of electron} = 4.8 \times 10^{-10} \text{ eso}$$

- (c) How does  $\text{XeF}_4$  and  $\text{XeF}_6$  react with water ?

Give chemical equations.  $1\frac{1}{2} + 1\frac{1}{2}$

11. (a) Disproporsonation and comporsonation reactions are actually redox reactions – justify with suitable examples. 3

(b) In the fission reaction the particle cannot in the reactants and products remain invariant. Then what is the source of the fission energy? 2

(c) How many millilitres of radon (Rn) under standard conditions of temperature and pressure are in equilibrium with 1.0 g radium (Ra)? Given 3

$$t_{\frac{1}{2}} \text{ for Ra} = 1590 \text{ yrs}$$

$$t_{\frac{1}{2}} \text{ for Rn} = 3.82 \text{ days.}$$

(d) Write the product of the reaction and predict the geometry of the product formed. 2



12. (a) Write down the possible arrangement of electrons in  $p^3$  configuration and identify the arrangement with maximum exchange energy. 3

(b) Compare and contrast the chemistry of  $\text{H}_2\text{O}_2$  with hydrazine and ozone. 3 + 3

(c) Predict the structure of  $\text{XeF}_8^{2-}$  ion. 1

13. (a) Write notes on (any two) : 4 x 2

(i) Poly thiazyl

(ii) Pseudohalogens

(iii) Oxyacids of sulphur.

(b) Balance by ion electron method : 2



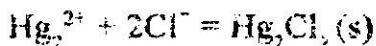
GROUP – B (c)

14. Answer any five questions : 2 x 5

(a) An  $\alpha$ -ray irradiated Al-foil on acid treatment produces active hydrogen gas – why ?

(b) Two H–F bonds in  $\text{HF}_2^-$  ion are equivalent – explain.

(c) Construct the cell where the following reaction takes place :



- (d) liq.  $\text{BrF}_3$  and liq.  $\text{AsF}_3$  are both poor conductor of electricity but a liquid mixture of the two is a much better conductor. — Explain.
- (e) What happens when  $\text{NaClO}_3$  is heated with oxalic acid in aqueous solution.
- (f) Two S atoms in  $\text{S}_2\text{O}_3^{2-}$  are not equivalent — justify.
- (g) Chlorine forms many oxyacids but fluorine has practically no tendency to form such compounds.
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