

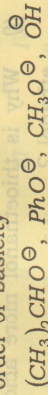
Full Marks : 60

Time : Three hours

**The figures in the margin indicate full marks for the questions.**

1. Answer the following questions : 1×7=7

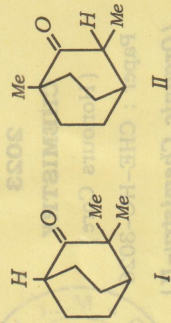
(a) Arrange the following in increasing order of basicity



(b) Draw the energy profile diagram of E1CB mechanism of  $\beta$ -elimination reaction.

Contd.

(c) Which one of the following bridged bicyclic compounds will exhibit Keto-Enol tautomerism.



(d) DMF and DMSO favours  $S_N2$  reaction although they are polar solvents. Explain.

(e) Potassium - *t* - butoxide is a widely used base in organic reactions but the corresponding sodium compound is unknown. Give reason.

(f) Why is thioethanol more acidic than ethanol ?

(g) Name the reagent that can be used to convert Cis - 2 - butene to racemic 2,3 - butanediol.

2. Answer the following questions : 2×4=8

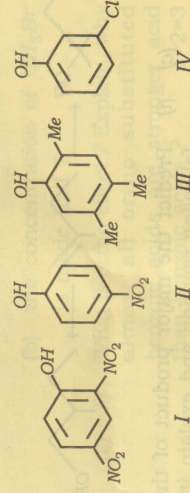
(a) Arrange the following compounds in increasing boiling point and give reason for your answer.

*n*-hexanol, *n*-butanol and *t*-butanol

(b) Between  $\text{CH}_3\text{CH}_2\text{CH}_2\text{Cl}$  and

$\text{CH}_3\text{OCH}_2\text{Cl}$ , which would react faster in  $S_N1$  solvolysis. Explain.

(c) The phenols shown have approximate  $pK_a$  value of 4, 7, 9 and 11. Suggest with explanation which  $pK_a$  value belong to which phenol :



(d) Arrange the following carboxylic acid derivatives in order of increasing reactivity towards hydrolysis reaction and justify your answer :

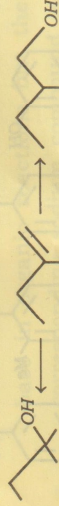
R - COOR', RCONH<sub>2</sub>, RCOCl

3. Answer **any three** questions : 5×3=15

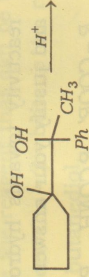
(a) Write the mechanism of Benzoin condensation. Explain why *p*-dimethylaminobenzaldehyde fails to undergo benzoin condensation but when mixed with benzaldehyde the condensation occurs. 3+2=5

(b) (i) Explain why alcohols are weaker acids than phenols but phenols are stronger nucleophiles. 2

(ii) Provide the required reagents and conditions for the following conversion :  $1\frac{1}{2} \times 2 = 3$



(c) (i) Predict the major product of the following reaction and explain its formation mechanistically. 3

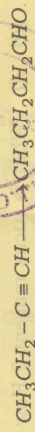


3 (Sem-3/CBSC) CHE HC 2/G 4

3 (Sem-3/CBSC) CHE HC 2/G 5

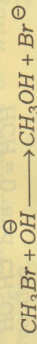
Contd.

(ii) How do you carry out the following conversion ? 2



(d) (i) Why are vinylic and aryl halides unreactive towards both  $S_N1$  and  $S_N2$  reactions ? 3

(ii) The rate equation of  $S_N2$  reaction



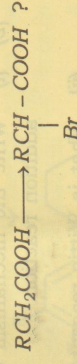
$$\text{Rate} = k[\text{CH}_3\text{Br}][\text{OH}^-]$$

What type of changes are expected in the rates of the reaction if

- (a) the concentration of each of the reactants is made double ?  
 (b) the concentration of  $\text{CH}_3\text{Br}$  is made half ?

(e) (i) What is ortho effect ? Explain, why almost all ortho substituted benzoic acids are stronger acid than benzoic acids ? 1+2=3

(ii) How can you convert : 2



4. Answer **any three** questions : 10×3=30

(a) (i) What is Lucas reagent ? How is it used to distinguish between 1°, 2° and 3° alcohols ? 1+2=3

(ii) Methyl chloromethyl ether is readily hydrolysed by water to  $\text{HCHO}$  and  $\text{CH}_3\text{OH}$  but

$\text{CH}_3\text{OCH}_2\text{CH}_2\text{Cl}$  does not. Explain. 2

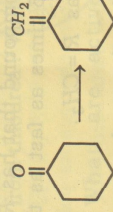
(iii) Picric acid liberates  $\text{CO}_2$  from aqueous  $\text{Na}_2\text{CO}_3$  but phenol does not. Explain. 2

(iv) Give the products of Reimann-Tiemann reaction on *p*-Cresol. Explain the reaction with mechanism. 3

(b) (i) Write the mechanism of Michael addition reaction. 3

(ii) What is Wittig reagent ? 1

(iii) How will you convert



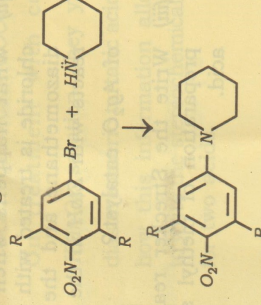
Write the mechanism of the reaction involved. 3

(iv) Write the significance of Wittig reaction. 2

(v) What do you mean by ylides ? 1

(c) (i) Both *o*- and *m*-bromo aniline give the same product on treatment with  $\text{NaNH}_2$  in liq.  $\text{NH}_3$ . Account for the observation with appropriate mechanism. 5

(ii) Write down the mechanism of the following reaction :



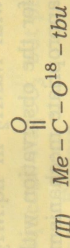
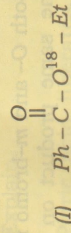
3 (Sem-3/CBSC) CHE HC 2/G 6

3 (Sem-3/CBSC) CHE HC 2/G 7

Contd.

Account for the fact that the compound that has  $R = H$  reacts 35 times as fast as the one that has  $R = CH_3$ . 3+2=5

- (d) (i) Give the mechanism of alkaline hydrolysis of the following ester in ordinary water ( $H_2O^{16}$ ) and indicate the distribution  $O^{18}$  is the products in each case. 4




- (ii) What happens when an acid chloride is treated with excess of diazomethane and the product reacts with  $EtOH$  in the presence of  $Ag_2O$  catalyst? 2

- (iii) Write the Strecker reaction for preparation of methyl sulphonic acid. 2

3 (Sem-3/CBCS) CHE HC 2/G 8

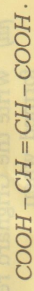
- (iv) How can  $CH_3CH_2SH$  be prepared from thiourea? Write the reactions. 2

- (e) (i) What are active methylene compounds? 1

- (ii) Convert EAA to  3

- (iii) 7-chloro cyclohepta-1, 3, 5-triene readily forms white  $AgCl$  ppt. When boiled with  $AgNO_3$  solution but 5-chlorocyclopenta-1, 3-diene does not give reason. 2

- (iv) Two dicarboxylic acids have the general formula



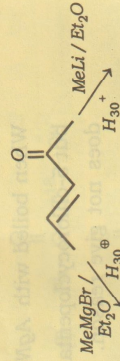
- On treatment with cold dil.  $KMnO_4$  solution, they yield two diastereomeric tartaric acids. Show how this information allows one to write the stereochemical formula for two acids. 4

3 (Sem-3/CBCS) CHE HC 2/G 9

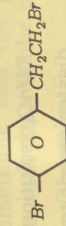
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- (i) When an alkyl halide is converted to a Grignard reagent then the carbon atom linked to halogen atom changes its polarity. Justify this statement with an example. 3

- (ii) Identify the product/products for the following reaction and offer explanation: 3



- (iii) Write the Grignard reagent that is formed when



- is treated with one mole of  $Mg$  in dry ether. 2

3 (Sem-3/CBCS) CHE HC 2/G 10

3 (Sem-3/CBCS) CHE HC 2/G 11

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