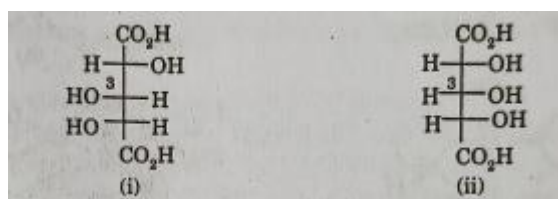
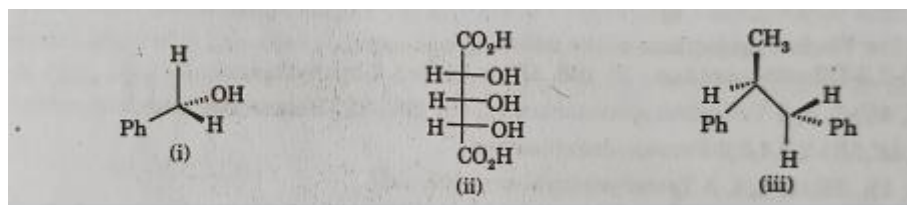


**Stereochemistry-II**

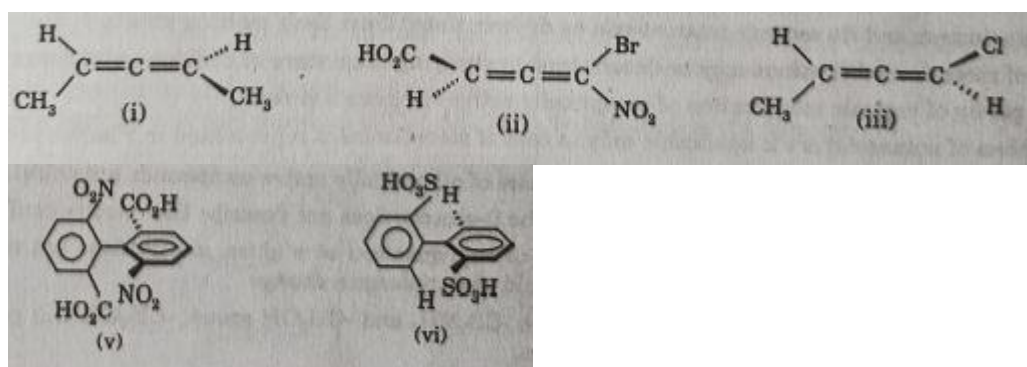
1. Draw the potential energy diagram of (i) 2,3-Dimethylbutane (ii) 2,3-Butane diol for rotation around  $C_2 - C_3$  bond showing the conformers. Indicate their relative stability.
2. Draw the potential energy diagram for the conformations of 1,2-Dichloroethane. How the % composition of the conformer changes with the change of medium from non polar to polar?
3. Draw the staggered conformations of 1-Chlorobutane for rotation about  $C_1 - C_2$  bond and  $C_2 - C_3$  bond. Comment on their relative stability.
4. Draw the possible staggered conformations of meso- and active form of 2,3-Dibromobutane. Give the composition of the conformational equilibrium with proper reasons.
5. Comment on the Chirotopicity and Stereogenicity of the C-3 centre of the following compounds:



6. Identify pro-R and pro-S hydrogen atoms in the following molecules:

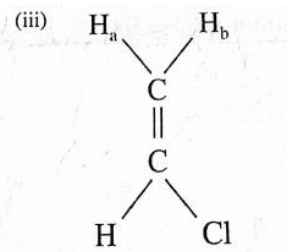
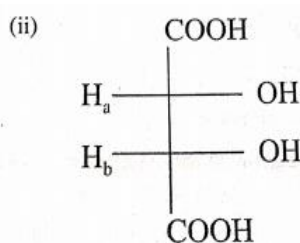
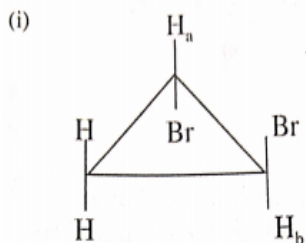


7. Find out the absolute configuration of the following compounds:



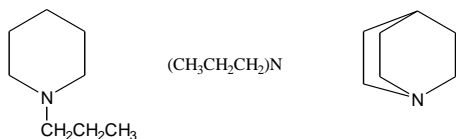
8. Draw the energy profile diagram of the conformations of 6,6'-dinitrodiphenic acid through the rotation of two rings about the  $C-C$  bond joining the two rings.
9. Predict the configurations of the products when –  
(i) Bromine is added to  $R_e-R_e$  and  $S_i-S_i$  faces of fumaric acid.

- (ii)  $\text{CH}_3\text{CHO}$  is treated with  $\text{PhMgBr}$  where nucleophilic attack occurs from the  $S_1$  face.  
 (iii)  $R$ -3-Hydroxybutanal is treated with  $\text{CH}_3\text{MgBr}$  where nucleophilic attack occurs from the  $R_e$  face.
10. Identify  $H_a$  and  $H_b$  in each of the following structures as homotopic, enantiotopic or diastereotopic ligands.

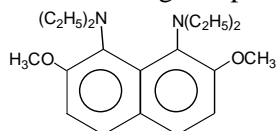


### General Treatment of Reaction Mechanism-III

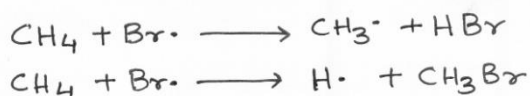
1. Explain the relative order of reactivity of the following amines with  $\text{Me}_3\text{B}$ . (2)



2. The following compound is a strong base. Explain. (2)

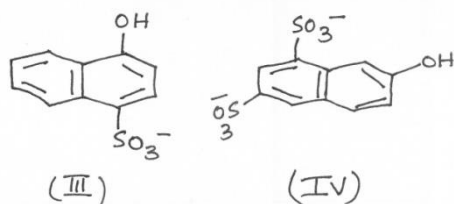


3. In the reaction of bromine free-radical with methane, justify which pathway out of the following two possibilities will be more favourable? (2)

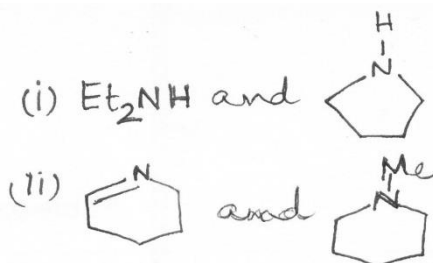


4. Compare the acidity of  $p$ -chlorophenol and  $p$ -fluorophenol (2)  
 5. Give the mechanism of bromination of benzene with  $\text{Br}_2/\text{FeBr}_3$  (cat.). Indicate the rate-determining step. Draw the energy profile diagram of the reaction with proper labelling. (4)  
 6. Arrange, with reasons, the following compounds in increasing order of basicity: (i) in aqueous solution and (ii) in chlorobenzene –  $n$ -butylamine, di- $n$ -butylamine and tri- $n$ -butyl amine (2+2)  
 7. Arrange the following, with reasons, as indicated below:  
 (i)  $\text{I}^-$ ,  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$  (in the increasing order of nucleophilicity in aqueous solution)  
 (ii)  $\text{OH}^-$ ,  $\text{OC}_2\text{H}_5^-$ ,  $(\text{CH}_3)_3\text{CO}^-$ ,  $\text{CH}_3\text{COO}^-$  (in the increasing order of basic character) (2+2)  
 8. Chloride ion in  $\text{Bu}_4\text{N}^+\text{Cl}^-$  in acetone is a better nucleophile than that in  $\text{LiCl}$  in the same solvent. Explain. (2)

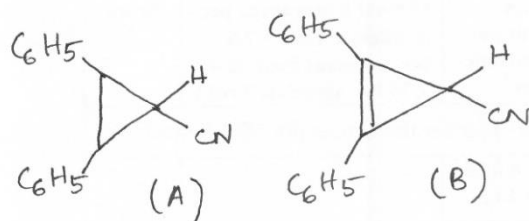
9. Which one is a better nucleophile of the following pair of oxyanions  $\text{OH}^-$  and  $\text{HOO}^-$ ? Explain. Discuss the role of the above anions in the hydrolysis of  $\text{RCN}$  to  $\text{RCONH}_2$  when hydrogen peroxide is added to the alkaline aqueous-ethanolic solution of  $\text{RCN}$ . (3)
10. The diazo-coupling reaction of (III) shows no isotope effect, while coupling of (IV) gives a  $K_H/K_D$  ratio of 6.55. Explain. (2)



11. Discuss the mechanism of sulphonation of benzene which shows moderate primary isotope effect. Elaborate your answer with the help of the energy profile diagram of the reaction. (5)
12. Arrange the following compounds in order of their increasing acid strength: (4)
- (i) Benzoic acid, (ii) 2-hydroxybenzoic acid, (iii) 4-hydroxybenzoic acid, (iv) 2,6-dihydroxybenzoic acid
13. Justify the observation that the rate of bromination of acetone is independent of the concentration of bromine under acid catalysed as well as base catalysed conditions. Give a supportive energy profile diagram. (5)
14. Explain the following observations: (1.5 each)
- (i) Cyclopentadiene is more acidic than cycloheptatriene
- (ii) Tropylium bromide gives a precipitate with silver nitrate solution.
15. What will happen when p-chloronitrobenzene is treated with  $\text{NaOEt}$  in  $\text{EtOH}$ ? Explain the course of the reaction sequence with suitable energy profile diagram. (4)
16. Between sodium chloride and sodium bromide in dimethylsulphoxide solution, chloride ion behaves as a better nucleophile than bromide ion. Explain. (2)
17. Predict with proper reasoning which member in each of the following pairs behaves as a better base towards  $\text{BMe}_3$  (3)



18. The cyclopropane (A) loses its proton in hydrogen exchange reaction 10,000 times faster than the cyclopropene (B) – explain. (2)

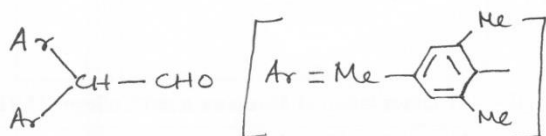


19. Write down the structures of all the possible tautomers of acetylacetone. Justify their relative stabilities. Write down the **s-cis** and **s-trans** forms of the possible tautomers. (4)
20. 2,6-Di-*t*-butylpyridine is a specific proton scavenger. Explain. (1)
21. 18-crown-6 ether greatly increases the rates of reaction where  $\text{KCN}$  is used as the source of cyanide ion. Account for the empirical observation. (1)
22. What is meant by nucleofugality? Explain with suitable examples. (2)

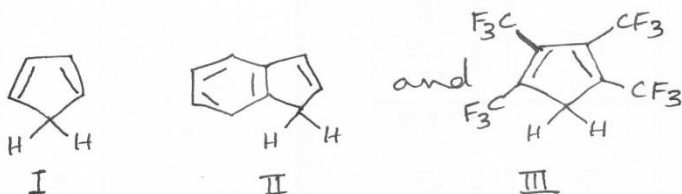
23. Give an example of a reaction which involves nucleophilic catalysis. Explain (2)
24. What do you mean by primary and secondary isotope effects? Indicate the pertinent one in connection with establishing the rate-limiting step in the chromic acid oxidation of isopropyl alcohol. (4)
25. Salicylic acid is a stronger acid than benzoic acid, whereas p-hydroxybenzoic acid is a weaker acid than benzoic acid – Explain. (2)
26. Arrange the following compounds in increasing order of acid strength and explain: (3)  
 (i) 4-nitrophenol, (ii) 2,6-dimethyl-1,4-nitrophenol, (iii) 3,5-dimethyl-4-nitrophenol
27. 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. (4)
28. In an investigation of mechanism of solvolysis (in 80% ethanol) of 2-chloro-2-methylbutane, the following results were obtained for the solvolysis of (i)  $\text{Me}_2\text{C}(\text{Cl})\text{CD}_2\text{Me}$  ( $K_H/K_D = 1.41$ ); (ii)  $(\text{CD}_3)_2\text{C}(\text{Cl})\text{CH}_2\text{Me}$  ( $K_H/K_D = 1.78$ ). Provide a mechanistic rationalisation of the above observations mentioning the nature of the isotope effect.
29. In the reaction given below, the order of reactivity of halide ion is  $\text{I}^- > \text{Br}^- > \text{Cl}^-$ , when the reagent is  $\text{LiX}$ , whereas this order of reactivity is reversed when the reagent is  $(n\text{-C}_4\text{H}_9)_4\text{N}^+\text{X}^-$ . Explain the observations. (3)



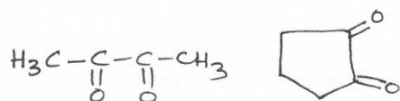
30. The following compound exists mainly in the enol form (~95%). Explain. (2)



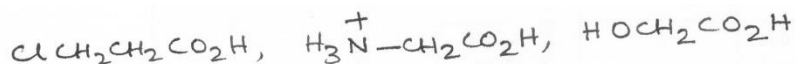
31. Arrange the following compounds in order of increasing pKa values: (3)



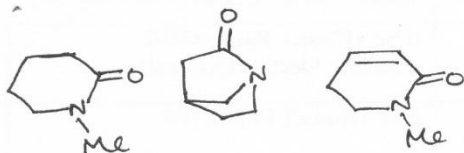
32. Compare the base strengths of ethylamine, guanidine and ethanamidine [ $\text{CH}_3\text{C}(=\text{NH})\text{NH}_2$ ]. (2)
33. The addition of chlorine (1 mol.) to 1,3-butadiene at 25°C produces 60% 3,4-dichloro-1-butene and 40% 1,4-dichloro-2-butene. At 200°C, the yields are 30% and 70% respectively. Explain these observations with an energy profile diagram. (4)
34. Give one example of trapping of intermediate in elucidation of reaction mechanism. (3)
35. Give the mechanism of oxidation of isopropyl alcohol with potassium dichromate and sulphuric acid indicating the rate determining step of the reaction. Give a kinetic evidence in favour of the mechanism. (3)
36. Compare the nucleophilicities and basicities of  $\text{tBuO}^-$  and  $\text{EtO}^-$ . (2)
37. Which one of the following diketones has higher enol content? (2)



38. Arrange the following acids in increasing order of their pKa values and justify. (2)



39. Arrange the following amides in increasing order of basicity. Give reasons. (2)



40. Arrange the following compounds in order of increasing acid strength and give reason for your answer. (3)

2-hydroxybenzoic acid, 4-hydroxybenzoic acid, 2,6-dihydroxybenzoic acid

41. Give the mechanism of nitration of chlorobenzene with mixed acid. Explain the directive influence of chlorine in the above reaction. Draw the energy profile diagram of the reaction. (4)

42. Show how deuterium labelling may be used to verify the mechanism of Cannizzaro reaction. (3)

43. Explain what is meant by primary kinetic isotope effect. Give the mechanism of oxidation of isopropyl alcohol with chromium (IV) oxide in glacial acetic acid. Indicate whether primary kinetic isotope effect is operative here. Cite a labelling experiment and its result, in favour of your answer. (4)

44. Explain why guanidine is a strong monoacidic base. (2)

45. Enol contents of acetylacetone in hexane and water are 92% and 15% respectively. Explain. (2)

46. Compare the basicities of N,N-dimethylaniline, 2,N,N-trimethylaniline and 2,6,N,N-tetramethylaniline. In aqueous medium. (2)

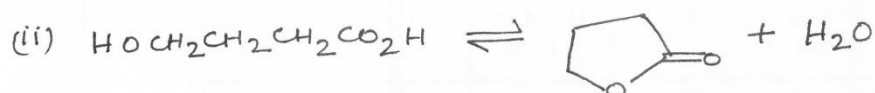
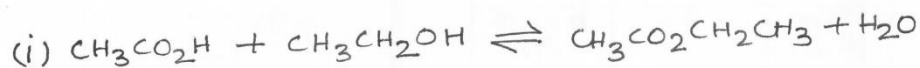
47. Write the structure of 18-crown-6 and its role in the reaction of  $\text{CH}_3(\text{CH}_2)_6\text{CH}_2\text{Br}$  with KF in warm benzene. (2)

48. Compare the basicity of methylamine, dimethylamine and trimethylamine in chlorobenzene (non-aqueous) and aqueous media. (3)

49. Arrange the following halide ions in increasing order of nucleophilicity in (i) ethanol and (ii) DMSO.  $\text{F}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$  and  $\text{I}^-$ . Explain. (3)

50. Guanidine is a much stronger base than urea. Explain (2)

51. Which of the following two reactions conducted at same temperature is expected to have larger values of equilibrium constant and why? (2)

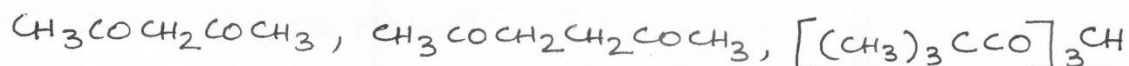


52. Compare the strengths of 4-nitroaniline and 2,3,5,6-tetramethyl-4-nitroaniline. (2)

53. Compare the base strength of N,N-dimethylaniline and 1,8-bis(diethylamino)-2,7-dimethoxynaphthalene. (2)

54. What do you mean by the term 'crown ether'? Write the structure of 15-crown-5 and its choice for one ion of the series  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$  (2)

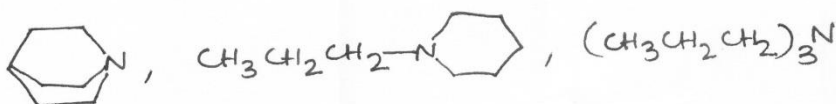
55. Arrange the following compounds in the increasing order of enol content. Justify your answer. (3)



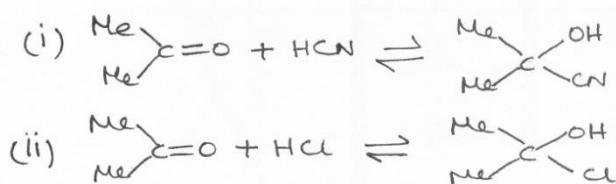
56. Explain the following: (2)

$\text{pK}_1$  (malonic acid)  $\ll$   $\text{pK}_a$  (acetic acid)  $\ll$   $\text{pK}_2$  (malonic acid)

57. Predict the increasing order of the equilibrium constants of the reaction of following bases with  $\text{Me}_3\text{B}$  and explain your answer. (3)

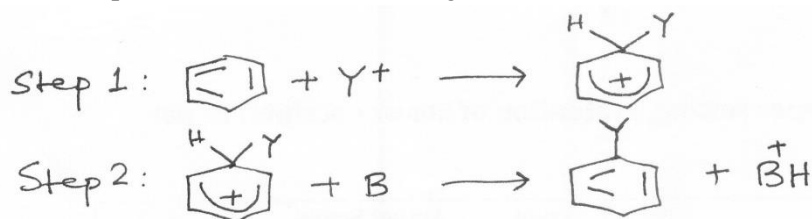


58. Estimate  $\Delta H^\circ$  for the following reactions and hence explain which one is thermodynamically more favourable: (2)



[Given, bond energy (Kcal/mol): H-Cl 103; C-Cl 84; H-CN 130; C-CN 122]

59. A two-step reaction with  $K_H/K_D \sim 7$  is given below:

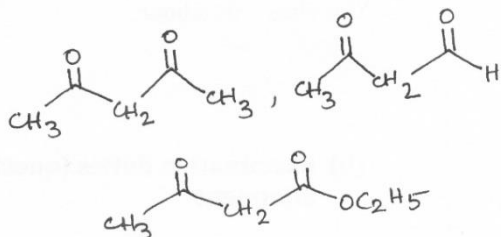


Draw and explain the energy profile for the reaction showing the transition state(s) and the intermediate. Indicate the 'rate determining step' also. (3)

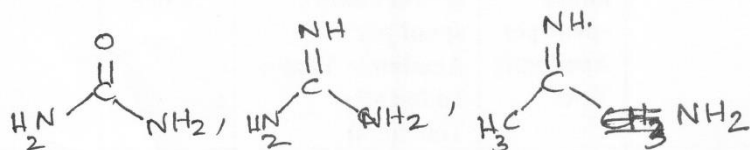
60. What is meant by valence tautomerism? Give an example. (2)

61. State and explain which of  $\text{CH}_3\text{COCH}_2\text{COCH}_3$  and  $\text{CH}_3\text{COCH}(\text{Ph})\text{COCH}_3$  has got higher enol content in tetrahydrofuran. (2)

62. Arrange the following dicarbonyls in order of their increasing  $\text{pK}_a$  values and justify your answer. (2)



63. Compare the base strengths of: (2)



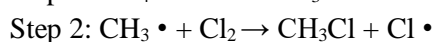
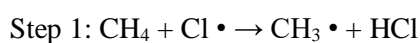
64. Give one example each of thermodynamically controlled and kinetically controlled reaction. Explain your answer with the help of energy profile diagrams. (4)

65. Write the structures of keto and stable enol forms of 2,4-pentanedione. What are the factors that stabilise these enol forms? Explain that enol content of this dicarbonyl compound is 92% in n-hexane and 15% in water. (3)

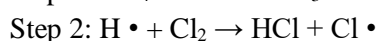
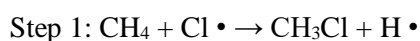
66. Compare the acidities of o-methoxyphenol, p-methoxyphenol and m-methoxyphenol. (2)

67. Using the bond energies given, explain which of the following two sequences for the propagation steps of chlorination of methane is more likely. (3)

Sequence-I



Sequence-II



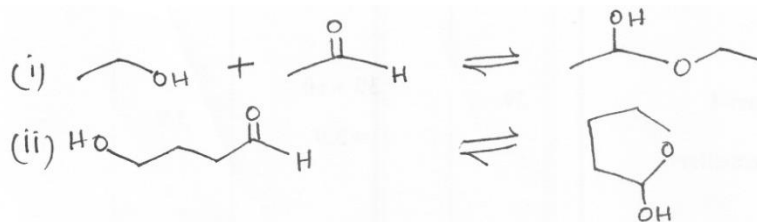
[Bond energies for  $\text{H}_3\text{C}-\text{H} = 105 \text{ Kcal/mol}$ ,  $\text{H}_3\text{C}-\text{Cl} = 85 \text{ Kcal/mol}$ ,  $\text{H}-\text{Cl} = 103 \text{ Kcal/mol}$  and  $\text{Cl}-\text{Cl} = 58 \text{ Kcal/mol}$  respectively]

68. Why does a small amount of oxygen slow down the reaction between methane and chlorine in the presence of diffused sunlight? (1)
69. What is meant by  $\sigma$  and  $\pi$ -complex in aromatic electrophilic substitution? Draw the energy profile diagram of an aromatic electrophilic substitution passing through  $\pi$  and  $\sigma$ -complex. (4)
70. Compare the enol content of diacetyl and cyclopenta-1,2-dione under identical external conditions and justify. (2)
71. Give an example of valence bond tautomerism and explain. (1)
72. Explain with mechanism the rate(s) of nitration of benzene and pentadeuteronitrobenzene under similar reaction conditions. (2)
73. Chlorination ( $\text{Cl}_2/h\nu$ ,  $25^\circ\text{C}$ ) of isobutane produces 1-chloro-2-methylpropane and 2-chloro-2-methylpropane in the ratio 64:36 but bromination ( $\text{Br}_2/h\nu$ ,  $127^\circ\text{C}$ ) furnishes 1-bromo-2-methylpropane and 2-bromo-2-methylpropane in the ratio 1:99. Explain the greater selectivity of bromination reaction. (3)
74. Reaction rate of  $\text{CH}_3\text{I}$  with  $\text{NaN}_3$  increases several fold with change of solvent from methanol to DMP – Explain. (2)
75. Describe with suitable examples how unimolecular and bimolecular solvolytic reactions can be distinguished on the basis of isotope effects and salt effects. (3)
76. Which one is more nucleophilic and why? (2)  
(i)  $\text{RO}^-$  and  $\text{RCOO}^-$  (ii)  $\text{NH}_3$  and  $\text{H}_2\text{O}$
77. Hydrolysis of methyl bromide takes place at a much faster rate in presence of sodium iodide. Explain with energy profile diagram. (2.5)
78. The rate expression for the acid catalysed dehydration of alcohol is,  $\text{rate} = k [\text{ROH}][\text{H}^+]$   
(i) Write a three step mechanism that is consistent with the rate expression taking  $\text{CH}_3\text{CHOHCH}_3$  as substrate.  
(ii) Explain how this mechanism is consistent with the rate expression.  
(iii) Classify this elimination reaction. (1.5+1.5+1)
79. 1,3-butadiene was allowed to react with chlorine at  $-15^\circ\text{C}$  and  $200^\circ\text{C}$  separately. Write down the product(s) formed and explain with mechanism, giving energy profile diagram. (3)
80. Compare the basicities and nucleophilicities of  $\text{NH}_3$ ,  $\text{NH}_2\text{NH}_2$  and  $\text{NH}_2\text{OH}$ . Give reasons. (3)
81.  $\text{CH}_3\text{CHClCH}_3$  and  $\text{CD}_3\text{CHClCD}_3$ , show kinetic isotope effect during (i) substitution reaction using  $\text{CH}_3\text{COOAg}/\text{CH}_3\text{COOH}$  and (ii) elimination reaction using  $\text{NaOMe}/\text{DMSO}$ .  
Indicate the primary/secondary nature of the kinetic isotope effect in the above reactions explaining the variation of rates. (4)
82. Which one of the following has higher enol content? Give reasons for your answer. (2)



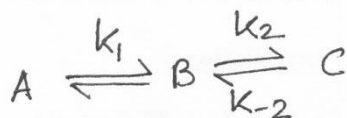
83. How will you prove whether a reaction is intramolecular or intermolecular? (2)
84. Two probable reaction paths for conversion of  $\text{CH}_3\text{COCl}$  to  $\text{CH}_3\text{COOEt}$  are as follows:  
(i)  $\text{CH}_3\text{COCl} + \text{Et}_3\text{N} \rightarrow [\text{Et}_3\text{NH}^+]\text{Cl}^- + \text{CH}_2=\text{C}=\text{O} \rightarrow (\text{EtOH}) \rightarrow \text{CH}_3\text{COOEt}$   
(ii)  $\text{CH}_3\text{COCl} + \text{Et}_3\text{N} \rightarrow [\text{CH}_3\text{CONEt}_3^+]\text{Cl}^- \rightarrow (\text{EtOH}) \rightarrow \text{CH}_3\text{COOEt} + [\text{Et}_3\text{NH}^+]\text{Cl}^-$   
Outline the mechanism of the above paths. How will you establish the appropriate pathway using  $\text{EtOD}$ ? (4)
85.  $\text{Me}_3\text{CH}$  on chlorination using  $\text{Cl}_2$  in diffused sunlight gives primary halide as major monosubstituted product while bromination by heating with  $\text{Br}_2$  produces tertiary halide as major. Justify this observation. (3)
86. Which of one of the following is more acidic and why? p-nitrophenol and p-methoxyphenol. (2)

87. In which case would the equilibrium be more favourable to R.H.S. and why? (2)



88. Addition of HBr to 1,3-butadiene yields two products and the product composition depends on the reaction temperature. Write the structure of the products and account for the observations with suitable energy profile diagrams. (3)

89. Draw a reaction coordinate diagram for the following reaction in which 'C' is the most stable and 'B' the least stable, and the transition state going from 'A' to 'B' is more stable than the transition state going from 'B' to 'C':

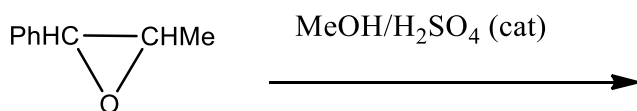


- How many transition states are there?
- Which is faster step in forward reaction?
- Which is the rate determining step in the forward direction? (3)

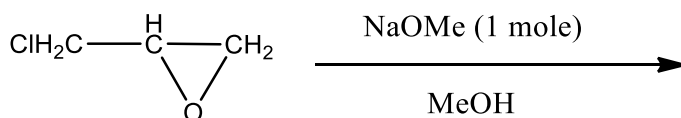
90. Arrange the following compounds, giving reasons, in order of decreasing acidity – propanoic acid, propenoic acid and propynoic acid. (2)

### Substitution and Elimination Reactions

- Explain the stereochemistry of the product with suitable mechanism when threo diastereomer of PhCHMeCHMeOTs is treated with acetic acid in presence sodium acetate.
- The  $S_N$  reaction of EtSCH<sub>2</sub>CH<sub>2</sub>Cl with ethanol proceeds at a rate of many fold faster than the similar reaction of EtOCH<sub>2</sub>CH<sub>2</sub>Cl, Explain
- Explain with plausible mechanistic justification what will happen in the following reaction:

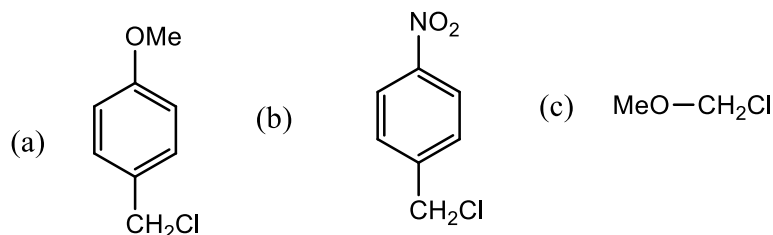


- Between NaCl and NaBr in DMSO solution, Cl<sup>-</sup> ion behaves as a better nucleophile than Br<sup>-</sup>. Explain.
- Explain the lack of reactivity of  $\alpha$ -halocarbonyl compounds in  $S_N1$  reactions. How will you synthesize di-tert-butyl ether?
- Predict the product and give the mechanism

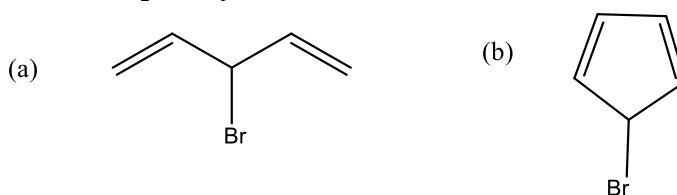




7. Write down the product of the following reaction and give the mechanism
- (S)-1-phenylethanol is allowed to react separately with thionyl chloride in the presence and absence of pyridine
  - Erythro-3-bromo-2-butanol is heated with hydrogen bromide. Explain the stereochemical course of the reaction in each case.
8. Predict the major product of the reaction of  $\alpha,\alpha$ -dimethyl chloride with thiophenoxide in ethanol-Explain
9. Which  $S_N1$  or  $S_N2$  is favourable for reaction with each of the following substrate-Explain



10. Which one of the following two bromo compounds would undergo silver ion assisted hydrolysis at a faster rate- Explain your answer

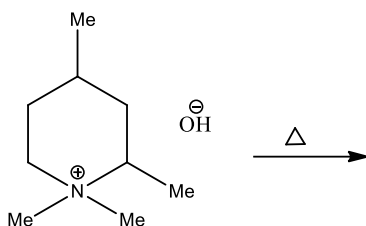


11. When  $\text{PhCH}_2\text{Br}$  is added to the suspension of  $\text{KF}$  in Benzene no reaction occurs. However when a catalytic amount of 18-crown-6 ether is added,  $\text{PhCH}_2\text{F}$  can be isolated in high yields. If  $\text{LiF}$  is substituted for  $\text{KF}$  there is no reaction even in presence of crown ether. Explain these observations.
12. Describe with suitable examples how unimolecular and bimolecular solvolytic reactions can be distinguished on the basis of isotope effects and salt effects.
13. Reaction rate of  $\text{CH}_3\text{I}$  with  $\text{NaN}_3$  increases several fold with change of solvent from methanol to DMF.
14. Give product(s) of the erythro-3-bromo-2-butanol with hydrogen bromide. Show the stereochemical course of the reaction using sawhorse formula.
15. Explain why (+)-2-iodobutane reacts with iodide ion in acetone to give optically inactive ( $\pm$ )-2-iodobutane instead of only (-)-2-iodobutane.

➤ **Elimination reaction:**

16. With proper projection formulas draw the most plausible transition state leading to Hoffmann and Saytzeff elimination products when  $\text{Me}_2\text{CHBrMe}_2$  is treated with an alkoxide. Comment on the relative ratio of the products as a function of size of the attacking bases.

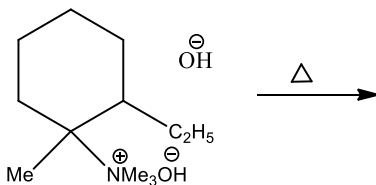
17. Discuss the stereochemistry of dehydroboration of meso-1,2-dibromo-1,2-diphenylethane with NaOEt in EtOH. Write down the product
18. Give the structure of the major product of the following reaction and explain its formation:



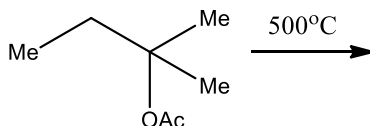
19. Write the product when β-phenylethyl bromide is treated with sodium ethoxide in the presence of C<sub>2</sub>H<sub>5</sub>OD. Give the mechanism of the reaction.
20. Predict the products and explain the stereochemical course of the following reaction:



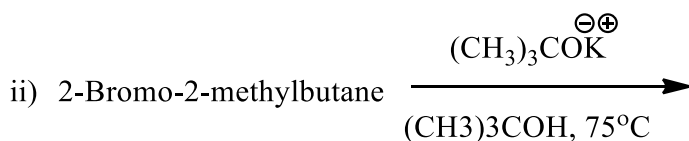
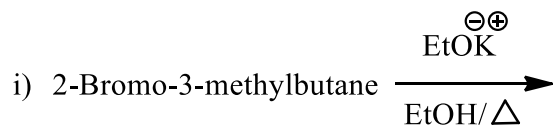
21. Explain showing the stereochemical course of the reaction, what happens when threo-1-bromo-1,2-diphenylpropane is treated with NaOEt in EtOH. Explain whether, under the same reaction conditions, the erythro isomer will undergo the same reaction at a faster rate or not.
22. E2-elimination of 2-bromobutane with NaOEt in EtOH yields 19% of 1-butene whereas same NaOEt in t-BuOH increases the yield of 1-butene to 38%-Explain.
23. Give the structure of all possible alkenes that could form in the following reaction. Indicate the major product and explain its formation.



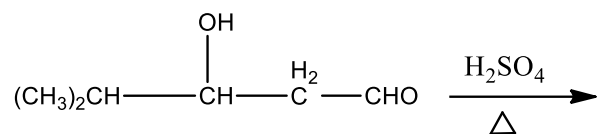
24. Predict the major product of the following reaction and suggest the plausible mechanism:



25. Predict the major products of the following reactions



26. Predict the major product obtained in the following reaction:



27. What will be the product/products obtained when erythro-1-bromo-1,2-diphenyl propane reacts with alcoholic KOH?

28. Convert : Ethylbenzene  $\longrightarrow$  Styrene

29. What is pyrolytic syn elimination? Give an example.

30. The dehydration of butan-2-ol with acid gives a mixture of 1- and 2-butenes. Write out the equations, and state which species will be predominant.