

3 SEM TDC CHM M 3 (N/O)

2 0 1 7

(November)

CHEMISTRY

(Major)

Course : 303

(Organic Chemistry—I)

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

(New Course)

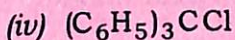
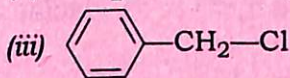
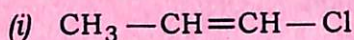
Full Marks : 48

Pass Marks : 14

Time : 2 hours

1. Select the correct answers from the following : 1×5=5

(a) Which one of the following compounds is most rapidly hydrolyzed by S_N1 mechanism?



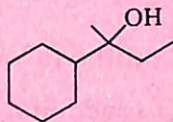
- (b) Aldol condensation between which of the following followed by dehydration gives mesityl oxide?
- 2 moles of acetaldehyde
 - 2 moles of acetone
 - CH_3CHO and HCHO
 - CH_3CHO and CH_3COCH_3
- (c) The product(s) obtained via oxymercuration-demercuration of butyne-1 would be
- $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CHO}$
 - $\text{CH}_3 - \text{CH}_2\text{CHO} + \text{HCHO}$
 - $\text{CH}_3 - \text{CH}_2 - \text{CO} - \text{CH}_3$
 - $\text{CH}_3 - \text{CH}_2\text{COOH} + \text{HCOOH}$
- (d) Among the following compounds, which is most acidic?
- p*-Nitrophenol
 - p*-Hydroxybenzoic acid
 - o*-Hydroxybenzoic acid
 - p*-Toluic acid
- (e) The best reagent to convert pent-3en-2ol into pent-3en-2one is
- acidified $\text{K}_2\text{Cr}_2\text{O}_7$
 - alkaline KMnO_4
 - chromic anhydride in glacial acetic acid
 - pyridinium chlorochromate

(3)

2. Answer any *four* of the following questions :

$1\frac{1}{2} \times 4 = 6$

- (a) Giving a suitable example, show that in an S_N2 reaction inversion takes place.
- (b) How would you synthesize the following alcohol from appropriate alkene(s)?



- (c) Neo-pentylbromide does not undergo S_N1 reaction without rearrangement. Explain.
- (d) Arrange the following acids in increasing order of acid strength with proper reasoning :

Benzoic acid, salicylic acid,
p-hydroxybenzoic acid and
m-hydroxybenzoic acid

- (e) Synthesize fumaric acid from glyoxalic acid and diethyl malonate, using Knoevenagel reaction.

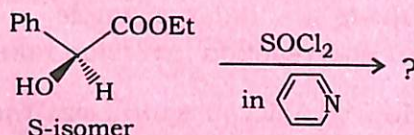
UNIT—I

Answer any *two* of the following questions : $4 \times 2 = 8$

3. (a) Benzyl chloride can undergo both S_N1 and S_N2 reactions with high rate. Explain.

2

- (b) Complete the following reaction and suggest the mechanism : 2



4. (a) Comment on the following statement : 2

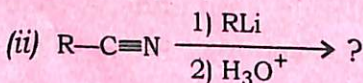
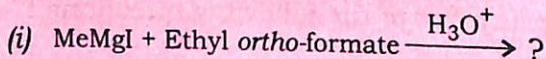
In all S_N2 reactions, the rate increases with increasing polarity of the solvent.

- (b) Synthesize the following : 1+1=2

- (i) 1-Bromobutane from pentanoic acid by Hunsdiecker's reaction
- (ii) Chloro- or bromo-benzene from aniline by using Sandmeyer reaction

5. (a) Discuss the benzyne mechanism for nucleophilic aromatic substitution reaction. Give evidences in support of the proposed mechanism. 2

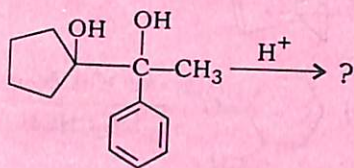
- (b) Complete the following organometallic reactions : 1+1=2



UNIT—II

Answer any two of the following questions : $5 \times 2 = 10$

6. (a) Complete the following reaction and suggest the mechanism : 3



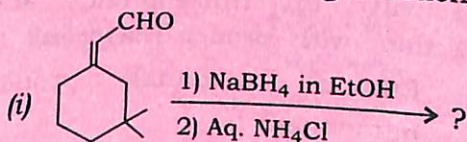
- (b) How is glycerol obtained from propene?
Convert glycerol into acrolein. $1+1=2$

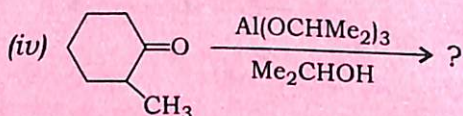
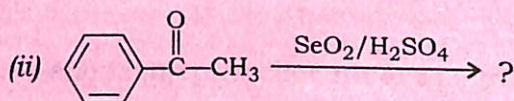
7. (a) What happens when *p*-cresol is treated with CHCl_3 in presence of NaOH ? Complete and give the mechanism of the reaction. 3

- (b) Synthesize the following : $1+1=2$
(i) *m*-Nitrophenol from benzene
(ii) *m*-Cresol from *p*-toluidine

8. (a) Esters of phenols on heating with anhydrous AlCl_3 undergo a rearrangement to give phenolic ketones. What is the reaction? Discuss the mechanism involved. 3

- (b) Complete the following reactions : $\frac{1}{2} \times 4 = 2$





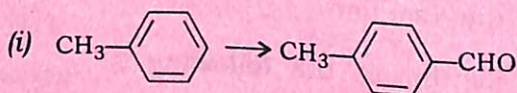
UNIT—III

Answer any *one* of the following questions :

8

9. (a) Carry out synthesis of the following (any one) :

2



(By Gattermann aldehyde synthesis)



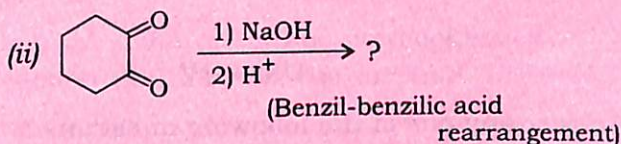
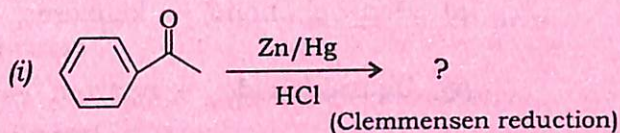
(By Stobbe condensation)

- (b) Arrange the following carbonyl compounds in increasing order of their reactivity in nucleophilic addition reaction, with proper reasoning :

2

Ethanal, propanal, propanone, butanone-2

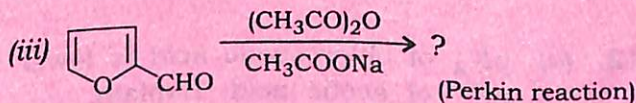
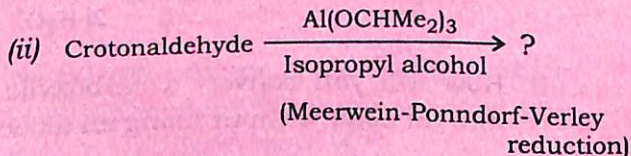
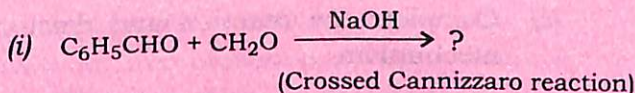
- (c) Discuss the mechanism of the following reactions : 2×2=4



10. (a) How will you obtain—

- (i) acetaldehyde from acetylene;
(ii) benzaldehyde from toluene? 1+1=2

- (b) Complete the following reactions and suggest the mechanism (any two) : 2×2=4



- (c) Complete any *one* of the following conversions : 2
- (i) Benzophenone \rightarrow ketoxime \rightarrow
benzanilide
- (ii) Benzaldehyde \rightarrow benzoin \rightarrow \rightarrow
benzilic acid

UNIT—IV

Answer any *one* of the following questions : 9

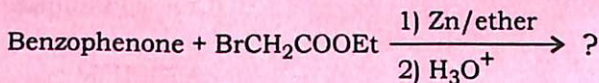
11. (a) Synthesize the following : 2×2=4

(i) Citric acid from oxalacetic ester by Reformatsky reaction

(ii) Pyruvic acid from acetaldehyde

(b) Convert benzoic acid to phenyl acetic acid by Arndt-Eistert synthesis. 2

(c) Complete the reaction and discuss the mechanism : 2



(d) How will you convert a carboxylic acid into an ester without using an alcohol? 1

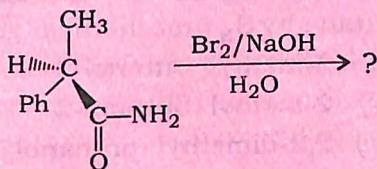
12. (a) pK_a of chloroacetic acid is lower than pK_a of acetic acid. Explain. 2

(b) Synthesize the following : 2×2=4

(i) Propanoic acid from butanoic acid
by Curtius reaction

(ii) Cinnamic acid from benzaldehyde
by Knoevenagel reaction

(c) Complete the following stereochemical
reaction and discuss the mechanism of
the reaction : 3



UNIT—V

Answer any *one* of the following questions : 2

13. What happens when a thiol reacts with an aldehyde in the presence of HCl? Give a method of preparation of thioether. 1+1=2

14. How would you prepare a sulphonic acid by the Strecker reaction? What happens when a thioether is oxidized with H_2O_2 ? 1+1=2

(10)

(Old Course)

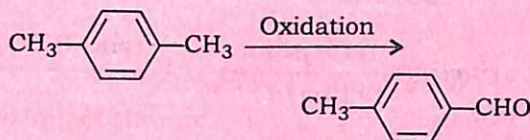
Full Marks : 48

Pass Marks : 19

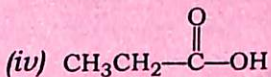
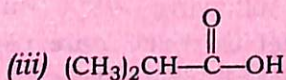
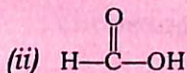
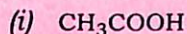
Time : 3 hours

1. Select the correct answers from the following : 1×5=5
- (a) The hydrolysis of 2-bromo-3-methyl butane by S_N1 mechanism gives mainly
- (i) 3-methyl butanol-2
 - (ii) 2-methyl butanol-2
 - (iii) 2,2-dimethyl propanol
 - (iv) 2-methyl butanol-1
- (b) Phenol is heated with phthalic anhydride in the presence of conc. H_2SO_4 . The product gives pink colour with alkali. The product is
- (i) salicylic acid
 - (ii) aspirin
 - (iii) phenolphthalein
 - (iv) fluorescein
- (c) An unknown compound gives a positive haloform test and positive Fehling's test. The compound is
- (i) formaldehyde
 - (ii) acetone
 - (iii) benzaldehyde
 - (iv) acetaldehyde

- (d) The appropriate reagent for the transformation is



- (i) PhCOOOH , CHCl_3
 (ii) alk. KMnO_4
 (iii) CrO_2Cl_2 , CCl_4
 (iv) PCC
- (e) Among the following, which has the lowest pK_a value?

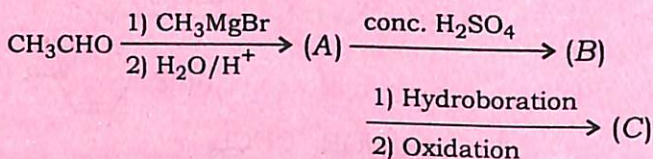


2. Answer any *four* of the following questions :

$1\frac{1}{2} \times 4 = 6$

- (a) Vinyl halides show low reactivity to nucleophilic substitution. Explain with reason.
- (b) Write the steps to carry out the conversion of phenol to salicylic acid.

- (c) Identify A, B and C in the following reactions :

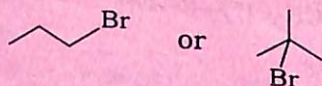


- (d) Explain that cyclohexanone forms cyanohydrin in good yield but 2,2,6-trimethyl cyclohexanone does not.
- (e) Synthesize MVK from acetone.

UNIT—I

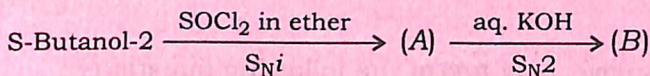
Answer any *two* of the following questions : 4×2=8

3. (a) Which of the following alkyl halides would you expect to react more rapidly by an $\text{S}_{\text{N}}1$ mechanism? Explain your answer :



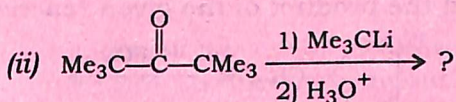
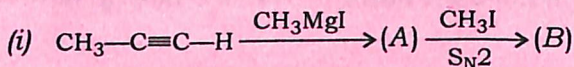
- (b) Using organometallic compound, how will you obtain the following (any one)?
- (i) A ketone from an amide
 - (ii) A *t*-alcohol from acetic anhydride
- (c) What products do you expect when *p*-bromoanisole reacts with KNH_2 in liq. NH_3 ?

4. (a) Complete the following reaction : 1



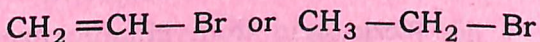
- (b) The rate of hydrolysis of $(\text{CH}_3)_3\text{C Br}$ in 50% aqueous methanol is thousand times faster than in pure methanol. Explain. 2

- (c) Complete the following reaction (any one) : 1



5. (a) A haloalkane reacts with KCN to form alkyl nitrile while AgCN forms alkyl isonitrile as major product. Explain. 1½

- (b) Which one will react more rapidly by $\text{S}_{\text{N}}\text{2}$ pathway and why? 1

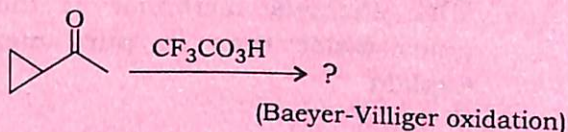


- (c) 2,4,6-Trinitrochlorobenzene is easily hydrolyzed with water but chlorobenzene is not. Why? 1½

UNIT—II

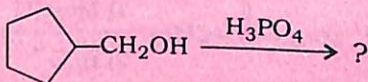
Answer any *two* of the following questions : $5 \times 2 = 10$

6. (a) Complete the following reaction and discuss the mechanism involved : 2



- (b) Synthesize *m*-cresol from *p*-toluidine. 2

- (c) Find the product of the given reaction : 1



7. (a) Outline all the steps involved in the synthesis of the following compounds (any one) : 2

(i) Benzyl alcohol from benzene through chloromethylation

(ii) Picric acid from chlorobenzene

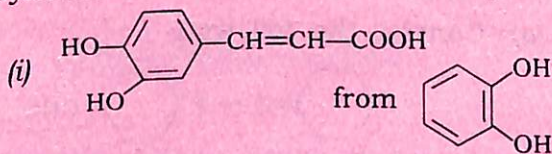
- (b) Discuss the mechanism of the oxidation reaction of 2° alcohol to ketone by chromic acid. 1½

- (c) Hydroxylation of stilbene by OsO_4 gives a *cis*-diol whereas hydroxylation via epoxidation of the same alkene gives a *trans*-diol. Explain. 1½
8. (a) Give evidences in favour of the intramolecularity of pinacol-pinacolone rearrangement. 1½
- (b) How does Lucas reagent help in the distinction of primary, secondary and tertiary alcohols? Discuss the reactions involved. 1½
- (c) *p*-Cresol reacts with CHCl_3 in alkaline medium to give compound (A), on treatment with HCN followed by acidic hydrolysis gives a chiral carboxylic acid. Assign the structure. 2

UNIT—III


Answer any one of the following questions : 8

9. (a) Synthesize the following (any two) : $2 \times 2 = 4$



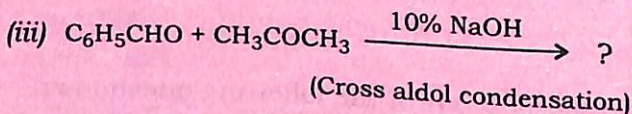
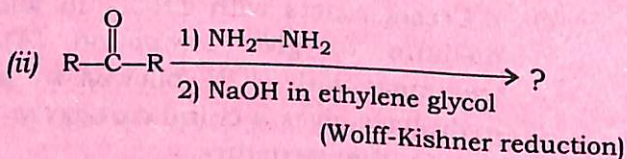
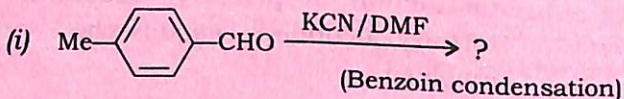
using Reimer-Tiemann and Perkin reactions

(ii) A β -hydroxy aldehyde from acetylene, using hydroboration-oxidation and aldol condensation

(iii) Caprolactam from , using oxime formation and Beckmann rearrangement

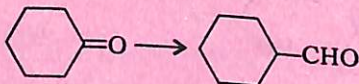
(b) Complete the following reactions and write down the mechanisms (any two) :

2×2=4



10. (a) Convert the following :

2



(By Darzens' glycidic ester synthesis and hydrolysis)

- (b) Arrange the following carbonyl compounds in increasing order of their reactivity in nucleophilic addition reaction with explanation : 2

Benzaldehyde, *p*-tolualdehyde, *p*-nitrobenzaldehyde and acetophenone

- (c) Synthesize the following : 1×2=2

(i) Cinnamaldehyde from benzaldehyde

(ii) Acrolein from glycerol

- (d) Give the mechanism of the following reaction (any one) : 2

(i) Acetone is treated with ethylchloroacetate in presence of NaNH_2

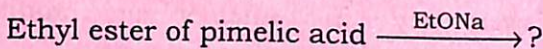
(ii) Benzaldehyde is treated with KCN

UNIT—IV

Answer any one of the following questions : 9

11. (a) Synthesize tartaric acid from acetylene. What happens when fumaric acid is treated with alkaline KMnO_4 ? 1+1=2

- (b) Complete the following reaction and discuss the mechanism involved : 3



(Dieckmann condensation)

- (c) How would you prepare the following? $2 \times 2 = 4$

(i) Phenyl acetic acid using an organometallic compound

(ii) Butanoic acid from propanoic acid using Arndt-Eistert synthesis

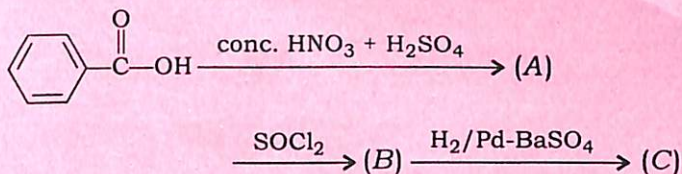
12. (a) Explain with a suitable example that optically active acyl azides undergo Curtius rearrangement with complete retention of configuration. 2

(b) Convert 2-phenylpropanamide to 2-phenylethylamine. 1

(c) Discuss the mechanism of acid-catalyzed hydrolysis of an ester. 2

(d) Explain why pK_a value of chloroacetic acid is lower than pK_a value of acetic acid. 2

(e) Complete the following reaction : 2



UNIT—V

Answer any one of the following questions : 2

13. Which is the stronger acid R—OH or R—SH?
 What happens when ethane thiol reacts with acetone in presence of HCl? 1+1=2
14. What are thioethers? How would you prepare a thioether from alkyl halide by S_N2 pathway? What happens when a thioether is oxidized with KMnO₄? ½+1+½=2

★★★