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1 No. of Printed Pages—19

3 SEM TDC CHM M 3 (N/O)

2017

(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

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?

(i) $CH_3-CH=CH-Cl$

(ii) $CH_2=CH-CH_2-Cl$

(iii) 

(iv) $(C_6H_5)_3CCl$

(Turn Over)

(b) Aldol condensation between which of the following followed by dehydration gives mesityl oxide?

(i) 2 moles of acetaldehyde

(ii) 2 moles of acetone

(iii) CH_3CHO and HCHO

(iv) CH_3CHO and CH_3COCH_3

(c) The product(s) obtained via oxymercuration-demercuration of butyne-1 would be

(i) $CH_3—CH_2—CH_2—CHO$

(ii) $CH_3—CH_2CHO + HCHO$

(iii) $CH_3—CH_2—CO—CH_3$

(iv) $CH_3—CH_2COOH + HCOOH$

(d) Among the following compounds, which is most acidic?

(i) *p*-Nitrophenol

(ii) *p*-Hydroxybenzoic acid

(iii) o-Hydroxybenzoic acid

(iv) *p*-Toluic acid

(e) The best reagent to convert pent-3en-2ol into pent-3en-2one is

(i) acidified $K_2Cr_2O_7$

(ii) alkaline $KMnO_4$

(iii) chromic anhydride in glacial acetic acid

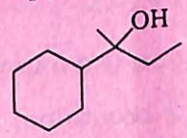
(iv) pyridinium chlorochromate

(Continued)

2. Answer any *four* of the following questions : 1½×4=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.

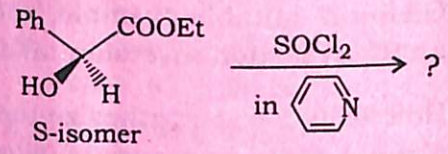
UNIT—I

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

3. (a) Benzyl chloride can undergo both S_N1 and S_N2 reactions with high rate. Explain. 2

(Turn Over)

(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

(i) MeMgI + Ethyl *ortho*-formate $\xrightarrow{H_3O^+}$?

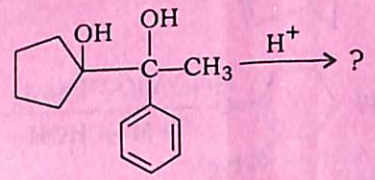
(ii) $R-C\equiv N \xrightarrow[2)\ H_3O^+]{1)\ RLi}$?

(Continued)

UNIT—II

Answer any *two* of the following questions : 5×2=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

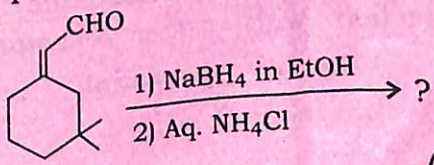
(b) Synthesize the following : 1+1=2

(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 : ½×4=2

(i) 

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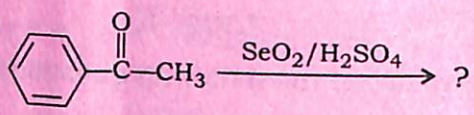
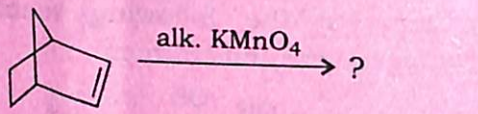
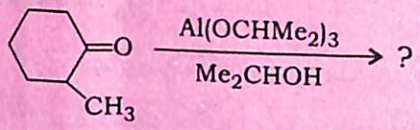
(ii) 

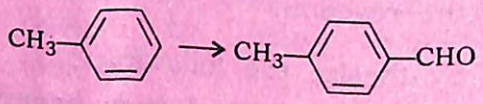
(iii) 

(iv) 

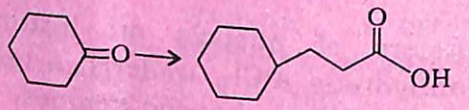
UNIT—III

Answer any *one* of the following questions : 8

9. *(a)* Carry out synthesis of the following (any *one*) : 2

(i) 

(By Gattermann aldehyde synthesis)

(ii) 

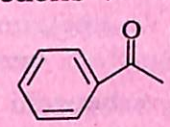
(By Stobbe condensation)

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

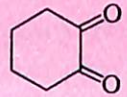
Ethanal, propanal, propanone, butanone-2

(Continued)

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

(i) 

(Clemmensen reduction)

(ii) 

(Benzil-benzilic acid rearrangement)

10. *(a)* How will you obtain—

(i) acetaldehyde from acetylene;

(ii) benzaldehyde from toluene? 1+1=2

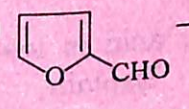
(b) Complete the following reactions and suggest the mechanism (any *two*) : 2×2=4

(i) $C_6H_5CHO + CH_2O \xrightarrow{NaOH} ?$

(Crossed Cannizzaro reaction)

(ii) Crotonaldehyde $\xrightarrow[\text{Isopropyl alcohol}]{Al(OCHMe_2)_3} ?$

(Meerwein-Ponndorf-Verley reduction)

(iii) 

(Perkin reaction)

(Turn Over)

(c) Complete any *one* of the following conversions : 2

(i) Benzophenone → ketoxime → benzanilide

(ii) Benzaldehyde → benzoin → → 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

$$\text{Benzophenone} + BrCH_2COOEt \xrightarrow[2)\ H_3O^+]{1)\ Zn/ether} ?$$

(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

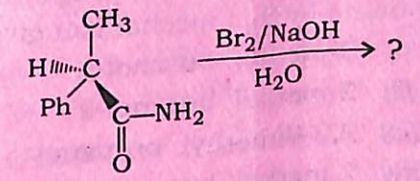
(Continued)

(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

(Turn Over)