CHEMISTRY STUDY MATERIALS FOR CLASS 12 (NCERT Based Notes of Chapter -10 to 13) GANESH KUMAR DATE: 21/10/2021

Organic Chemistry – Specific Name Reactions

21. Aldol reaction

Aldehydes and ketones having at least one α -hydrogen undergo a reaction in the presence of dilute alkali as catalyst to form β -hydroxy aldehydes (aldol) or β -hydroxy ketones (ketol), respectively. This is known as **Aldol reaction**. The name aldol is derived from the names of the two functional groups, aldehyde and alcohol, present in the products.

22. Aldol Condensation

The aldol and ketol readily lose water to give α , β -unsaturated carbonyl compounds which are aldol condensation products and the reaction is called **Aldol** condensation.



23. Kolbe electrolysis

An aqueous solution of sodium or potassium salt of a carboxylic acid on electrolysis gives alkane containing even number of carbon atoms. It is decarboxylation reaction. The reaction is known as Kolbe electrolysis.

$$2CH_{3}COO^{-}Na^{+} + 2H_{2}O$$

Sodium acetate
 \downarrow Electrolysis
 $CH_{3}-CH_{3}+2CO_{2}+H_{2}+2NaOH$

24. Cross aldol condensation:

When aldol condensation is carried out between two different aldehydes and / or ketones, it is called cross aldol condensation. If both of them contain α -hydrogen atoms, it gives a mixture of four products.



25. Cannizzaro reaction:

Aldehydes which do not have an α -hydrogen atom, undergo self oxidation and reduction (disproportionation) reaction on treatment with concentrated alkali. In this reaction, one molecule of the aldehyde is reduced to alcohol while another is oxidised to carboxylic acid salt.



26. Hell-Volhard-Zelinsky (HVZ) reaction.

Carboxylic acids having an α -hydrogen are halogenated at the α -position on treatment with chlorine or bromine in the presence of small amount of red phosphorus to give α -halocarboxylic acids. The reaction is known as Hell-Volhard-Zelinsky reaction.

$$\begin{array}{c} \text{R-CH}_2\text{-COOH} & \xrightarrow{\text{(i) } X_2/\text{Red phosphorus}} & \text{R-CH-COOH} \\ & & & & \\ & & & \\ & & & \\ & & & \\ & & & \\ & & X \\ & & X = \text{Cl, Br} \\ & & \alpha - \text{Halocarboxylic acid} \end{array}$$

27. Gabriel phthalimide synthesis

Gabriel synthesis is used for the preparation of pure primary amines.

Phthalimide on treatment with ethanolic potassium hydroxide forms potassium salt of phthalimide which on heating with alkyl halide followed by alkaline hydrolysis produces the corresponding primary amine



Note: Aromatic primary amines cannot be prepared by this method because aryl halides do not undergo nucleophilic substitution with the anion formed by phthalimide.

28. Hoffmann bromamide degradation reaction

An amide with bromine in an aqueous or ethanolic solution of sodium hydroxide gives primary amines.

In this degradation reaction, migration of an alkyl or aryl group takes place from carbonyl carbon of the amide to the nitrogen atom. The amine so formed contains one carbon less than that present in the amide.

 $\begin{array}{c} \mathbf{O} \\ || \\ \mathbf{R} - \mathbf{C} - \mathbf{NH}_2 \end{array} + \mathbf{Br}_2 + 4\mathrm{NaOH} \longrightarrow \mathbf{R} - \mathbf{NH}_2 + \mathrm{Na}_2\mathrm{CO}_3 + 2\mathrm{NaBr} + 2\mathrm{H}_2\mathrm{O} \end{array}$

29. Carbylamine reaction

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Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form isocyanides or carbylamines which are foul smelling substances. This reaction is known as carbylamines reaction or isocyanide test.

$$R-NH_2 + CHCl_1 + 3KOH \xrightarrow{Heat} R-NC + 3KCl + 3H_2O$$

Note: Secondary and tertiary amines do not show this reaction and is used as a test for primary amines.

30. Hinsberg's Test

Benzene sulphonyl chloride ($C_6H_5SO_2CI$), which is also known as Hinsberg's reagent, reacts with primary and secondary amines to form sulphonamides.

(a) The reaction of benzene sulphonyl chloride with primary amine yields N-ethyl benzene sulphonyl amide. The hydrogen attached to nitrogen in sulphonamide is strongly acidic due to the presence of strong electron withdrawing sulphonyl group. Hence, it is soluble in alkali

$$\begin{array}{c} & & & \\ &$$

(b) In the reaction with secondary amine, N,N-diethyl- benzene sulphonamide is formed. Since N, N- diethyl benzene sulphonamide does not contain any hydrogen atom attached to nitrogen atom; it is not acidic and hence insoluble in alkali.



(c) Tertiary amines do not react with benzene sulphonyl chloride.

Note: This test is used for the distinction of primary, secondary and tertiary amines and also for the separation of a mixture of amines. However, these days benzene sulphonyl chloride is replaced by p-toluenesulphonyl chloride

31. Coupling Reactions:

Benzene diazonium chloride reacts with phenol in which the phenol molecule at its para position is coupled with the diazonium salt to form p-hydroxyazobenzene. This type of reaction is known as coupling reaction.



p-Hydroxyazobenzene (orange dye)

Similarly the reaction of diazonium salt with aniline yields p-aminoazobenzene.


