Named Reactions Of Haloalkanes and haloarenes

1) Finkelstein Reaction
This reaction used for the preparation of iodoalkenes from the corresponding chloroalkanes or bromo alkanes.

\[ \text{CH}_3\text{Br} + \text{NaI} \rightarrow \text{CH}_3\text{-I} + \text{NaBr} \]

Methyl bromide \hspace{1cm} \text{Methyl Iodide}

2) Fittig Reaction
In the reaction haloarene is reacted with metallic sodium in the presence of anhydrous ether to form Diphenyl which is an aromatic hydrocarbon

\[ \text{Cl} + \text{Cl} \rightarrow 2\text{Na} \rightarrow \text{Cl} + \text{NaCl} \]

Chlorobenzene \hspace{1cm} \text{Biphenyl}

3) Friedel craft’s reaction
In this reaction, benzene is treated with alkyl halide or acyl chloride in the presence of anhydrous aluminium chloride acting as a catalyst. As a result, a hydrogen atom in the ring gets replaced either by alkyl group or acyl group.

Friedel Craft Alkylation

\[ \text{Benzene} + \text{H}_3\text{C-Cl} \rightarrow \text{Anhydrous AlCl}_3 \rightarrow \text{Methyl Benzene} \]
Friedel Craft Acylation

4) **Swarts reaction**— The synthesis of alkyl fluoride is best accomplished by heating n alkyl chloride in the presence of metallic fluoride such as AgF, Hg₂F₂, CoF₂

\[
\text{CH}_3\text{Br} + \text{AgF} \rightarrow \text{CH}_3\text{F} + \text{AgBr}
\]

Methyl bromide Methyl Fluoride

5) **Wurtz reaction**— Alkyl halides react with sodium in dry ether to give hydrocarbon containing double the no of carbon atoms present in halide.

\[
2\text{RX} + 2\text{Na} \rightarrow \text{R—R} + 2\text{NaX}
\]

6) **Wurtz-fitting reaction**— A mixture of an alkyl halide gives an alkyl arene when treated with sodium in presence of dry ether.

**Named Reactions of Alcohols, Phenols and Ethers**

1) **Dow’s Process**: This process is used for the formation of phenols from chlorobenzene.
2) Reimer Tiemann Reaction: In this reaction, salicyaldehyde (2-Hydroxy benzaldehyde) is prepared on reaction of phenols with chloroform while salicylic acid (2-Hydroxy benzoic acid) is formed when phenols are treated with carbon tetrachloride.

![Reimer Tiemann Reaction diagram]

3) Kolbe’s Reaction: In this reaction, salicylic acid is prepared by the reaction of sodium phenoxide with carbon dioxide followed by acidification.

![Kolbe’s Reaction diagram]

4) Williamson synthesis: This reaction is used for the synthesis of symmetrical and unsymmetrical ethers.

\[ R-X + R'-\text{Na} \rightarrow R-\text{O}-R' + \text{NaX} \]

**Named Reactions of Aldehydes, Ketones and Carboxylic Acids**

1) Rosenmund Reaction: This reaction is used for the preparation of aldehydes by the hydrogenation of acyl chlorides in presence of palladium supported over barium sulphate poisoned by sulphur.

\[ \text{RCOCl} \xrightarrow{\text{H}_2, \text{Pd} - \text{BaSO}_4} \text{RCHO} \]

**Acyl chloride**

**Aldehyde**

2) Stephen Reaction: This reaction is used for the preparation of aldehydes from nitriles by their reduction in presence of stannous chloride followed by hydrolysis.
3) Etard Reaction: In this reaction, chromyl chloride oxidises methyl group to a chromium complex, which on hydrolysis gives corresponding benzaldehyde.

4) Gattermann – Koch reaction: this reaction is used for the preparation of benzaldehyde from benzene or its derivatives.

5) Clemmenson’s Reduction: The carbonyl group of aldehydes and ketones is reduced to CH₂ group on treatment with zinc- amalgam and concentrated hydrochloric acid.

6) Wolf Kishner Reduction: The carbonyl group of aldehydes and ketones is reduced to CH₂ group on treatment with hydrazine followed by heating with sodium or potassium hydroxide in high boiling solvent such as ethylene glycol.
7) **Aldol condensation**: 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 which readily undergoes condensation.

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\[
2 \text{H}_3\text{C}-\text{CHO} \xrightarrow{\text{dil NaOH}} \text{H}_3\text{C}-\text{CH}-\text{CH}_2-\text{CHO} \xrightarrow{\Delta} \text{H}_3\text{C}-\text{CH}=\text{CH}-\text{CHO}
\]
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3-hydroxy butanal

But-2-enal

Ethan al

8) **Cross aldol condensation**: When aldol condensation is carried out between two different aldehydes and / or ketones, it is called cross aldol condensation.

```
\[
\begin{align*}
\text{CH}_3\text{CHO} + \text{CH}_3\text{CH}_2\text{CHO} & \xrightarrow{1. \text{NaOH}} \text{CH}_3\text{CH}=&\text{CH}-\text{CHO} + \text{CH}_3\text{CH}_2\text{CH}=&\text{C}-\text{CHO} \\
& \xrightarrow{2. \Delta} \text{But-2-enal} \\
& \text{simple or self aldol products} \\
& \text{from two molecules of ethanal} \\
& \text{2-Methylpent-2-enal} \\
& \text{from two molecules of propanal} \\
& \text{2-Methylbut-2-enal} + \text{Pent-2-enal} \\
& \text{from one molecule of ethanal and one molecule of propanal} \\
& \text{cross aldol products}
\end{align*}
\]
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9) **Cannizzaro reaction**: Aldehydes which do not have an α-hydrogen atom, undergo self oxidation and reduction (disproportionation) reaction on treatment with concentrated alkali.

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\[
\text{H}_2\text{C}=&\text{O} + \text{H}_2\text{C}=&\text{O} + \text{Conc. KOH} \rightarrow \text{H}_2\text{C}-\text{OH} + \text{H}_2\text{C}=&\text{OK}
\]
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Formaldehyde

Methanol

Potassium formate

10) **Hell-Volhard-Zelinsky 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.
Named Reactions Of Amines

1) Hoffmann Ammonolysis reaction:
This reaction yields a mixture of primary, secondary and tertiary amines and quaternary ammonium salt on reaction of alkyl halide with ammonia.

\[
\text{NH}_3 + R-X \rightarrow R-\text{NH}_3^+X
\]

Substituted ammonium salt

\[
R-\text{NH}_3^+X + \text{NaOH} \rightarrow R-\text{NH}_2 + H_2O + \text{NaX}
\]

2) Hoffmann bromamide degradation reaction:
This is a method for preparation of primary amines by treating an amide with bromine in an aqueous or ethanolic solution of sodium hydroxide.

\[
R - C - \text{NH}_2 + \text{Br}_3 + 4\text{NaOH} \rightarrow R - \text{NH}_2 + \text{Na}_2\text{CO}_3 + 2\text{NaBr} + 2\text{H}_2\text{O}
\]

3) Gabriel phthalimide synthesis:
This method is used for the preparation of primary amines from phthalimide.

\[
\begin{align*}
\text{Phthalimide} & \quad \overset{\text{KOH}}{\longrightarrow} \quad \overset{\text{RX}}{\longrightarrow} \quad \overset{\text{RX}}{\longrightarrow} \\
\text{N-Alkylphthalimide} & \quad \overset{\text{NaOH}(aq)}{\longrightarrow} \quad \overset{\text{R-\text{NH}_2}}{\longrightarrow}
\end{align*}
\]

\[
\text{Phthalimide} \quad \overset{\text{NaOH}(aq)}{\longrightarrow} \quad \overset{\text{R-\text{NH}_2}}{\longrightarrow}
\]

(1° amine)
4) Carbylamine reaction:
Aliphatic and aromatic primary amines on heating with chloroform and ethanolic potassium hydroxide form isocyanides or carbylamine

\[ R-\text{NH}_2 + \text{CHCl}_3 + 3\text{KOH} \xrightarrow{\text{Heat}} R-\text{NC} + 3\text{KCl} + 3\text{H}_2\text{O} \]

5) Sandmeyer reaction:
In this reaction, chlorine or bromine or cyanide can also be introduced in the benzene ring by treating the diazonium salt solution with corresponding halogen acid in the presence of copper(I) ion.

\[ \begin{align*}
\text{ArN}_2^+X & \xrightarrow{\text{Cu}_2\text{Cl}_2/\text{HCl}} \text{ArCl} + \text{N}_2 \\
\text{ArN}_2^+X & \xrightarrow{\text{Cu}_2\text{Br}_2/\text{HBr}} \text{ArBr} + \text{N}_2 \\
\text{ArN}_2^+X & \xrightarrow{\text{CuCN}/\text{KCN}} \text{ArCN} + \text{N}_2 
\end{align*} \]

6) Gatterman reaction:
In this reaction, chlorine or bromine or cyanide can also be introduced in the benzene ring by treating the diazonium salt solution with corresponding halogen acid in the presence of copper powder.

\[ \begin{align*}
\text{ArN}_2^+X & \xrightarrow{\text{Cu/HCl}} \text{ArCl} + \text{N}_2 + \text{CuX} \\
\text{ArN}_2^+X & \xrightarrow{\text{Cu/HBr}} \text{ArBr} + \text{N}_2 + \text{CuX} 
\end{align*} \]

7) Diazotisation:
Aromatic primary amines react with nitrous acid (prepared in situ from NaNO₂ and mineral acid like HCl) at low temperature (273-278 K) to form diazonium salts. This conversion of primary aromatic amines into diazonium salts is known as diazotisation.

\[ \text{C}_6\text{H}_5\text{NH}_2 + \text{NaNO}_2 + 2\text{HCl} \xrightarrow{273-278\text{K}} \text{C}_6\text{H}_5\text{N}_2^+\text{Cl}^- + \text{NaCl} + 2\text{H}_2\text{O} \]

8) Coupling Reaction:
The reaction of joining two aromatic rings through \(-\text{N=N-}\) is known as coupling reaction. Arenediazonium salts react with phenols or aromatic amines to form coloured azo compounds.
Benzenediazonium chloride + Phenol → $\text{Ar}^+\text{N}=\text{N}^+\text{Cl}^- + \text{Ar}^-\text{O}^-\text{H}^- → \text{Ar}^+\text{N}=\text{N}^-\text{Ar}^-\text{OH}^- + \text{Cl}^- + \text{H}_2\text{O}$

$p$-Hydroxyazobenzene (Orange dye)

Benzenediazonium chloride + Aniline → $\text{Ar}^+\text{N}=\text{N}^+\text{Cl}^- + \text{Ar}^-\text{NH}_2^-\text{H}^- → \text{Ar}^+\text{N}=\text{N}^-\text{Ar}^-\text{NH}_2^- + \text{Cl}^- + \text{H}_2\text{O}$

$p$-Aminoazobenzene (yellow dye)