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Title: Oxygen-Containing Organic Compound

Organic Compounds Containing Oxygen

Alcohols

Methods of Preparation of Alcohols

1. **Oxymercuration-Demercuration:** Alkenes react with mercuric acetate and water, followed by reduction with NaOH, to yield alcohols via Markovnikov addition.

   $\text{C=C} + Hg(OAc)_2 + H_2O \rightarrow \text{-C(OH)-C(HgOAc)-} \xrightarrow{NaOH} \text{-C(OH)-CH-}$ (Markovnikov addition)

2. **Hydroboration-Oxidation:** Alkenes react with diborane to form trialkyl boranes. Treatment with alkaline H_2O_2 gives alcohols via anti-Markovnikov addition of water.

   $\text{C=C} + (BH_3)_2 \rightarrow \text{-C(H)-C(BH}_2\text{)} - \text{-C(H)-C(BH}_2\text{)} - \text{-C(H)-C(BH}_2\text{)} - \text{-C(H)-C(OH)-} + \xrightarrow{H_2O_2, OH^-}$

3. **From Carbonyl Compounds (Aldehydes and Ketones):**

   - **Reduction:** Aldehydes yield primary alcohols, and ketones yield secondary alcohols upon reduction with $LiAlH_4$, $NaBH_4$, or catalytic hydrogenation.

     $$RCHO \xrightarrow{[H]} RCH_2OH \quad \text{(Primary alcohol)}$$

     $$RCOR' \xrightarrow{[H]} RCH(OH)R' \quad \text{(Secondary alcohol)}$$

   - **Using Grignard Reagents:**
     - Formaldehyde gives primary alcohols.
     - Other aldehydes give secondary alcohols.
     - Ketones give tertiary alcohols.

     $R'COOC_2H_5 + 2RMgX \rightarrow R'-C(OMgX)(R)R \rightarrow R'-C(OH)(R)R$ (3° alcohol)

4. **Hydrolysis of Alkyl Halides:**

   $$R - X + OH^- (\text{or } H_2O) \rightarrow R - OH + X^- (\text{or } HX)$$

Physical Properties of Alcohols

1. **Boiling Points:** Higher than corresponding hydrocarbons, ethers, or haloalkanes due to intermolecular hydrogen bonding. Boiling points increase with molecular mass. For isomeric alcohols, branching decreases boiling point.

2. **Solubility:** Lower alcohols are soluble in water due to hydrogen bonding. Solubility decreases with increasing alkyl chain length.

Chemical Properties of Alcohols

1. **Reactions involving O-H bond cleavage (Acidic nature):**

   - **Reaction with active metals:**

     $$2ROH + 2Na \rightarrow 2RONa + H_2$$

   - **Esterification:** Reaction with carboxylic acids, acid chlorides, or acid anhydrides.

     $$ROH + R'COOH \xrightarrow{H^+} R'COOR + H_2O$$

   - **Reaction with Grignard Reagents:**

     $$ROH + RMgX \rightarrow RH + Mg(OR)X$$

2. **Reactions involving C-O bond cleavage (Nucleophilic substitution):**

   - **Reaction with HX:**

     $$ROH + HX \rightarrow RX + H_2O$$

     Reactivity order of alcohols: 3° > 2° > 1°. Reactivity order of HX: $HI > HBr > HCl$.

- **Reaction with $PCl_3, PCl_5, SOCl_2$:**

$$ROH + PCl_5 \rightarrow RCl + POCl_3 + HCl$$

$$ROH + SOCl_2 \rightarrow RCl + SO_2 + HCl$$

3. **Oxidation:**
   - Primary alcohols give aldehydes, then carboxylic acids.
   - Secondary alcohols give ketones.
   - Tertiary alcohols resist oxidation under mild conditions; strong oxidation breaks C-C bonds.
4. **Dehydration:** Forms alkenes or ethers depending on conditions.

$$CH_3CH_2OH \xrightarrow{conc.H_2SO_4, 443K} CH_2 = CH_2 + H_2O$$

$$2CH_3CH_2OH \xrightarrow{conc.H_2SO_4, 413K} CH_3CH_2OCH_2CH_3 + H_2O$$

Phenols

Methods of Preparation of Phenols

1. **From Haloarenes (Dow's Process):**

$$C_6H_5Cl + NaOH \xrightarrow{623K, 300atm} C_6H_5ONa \xrightarrow{H^+} C_6H_5OH$$

2. **From Benzene Sulphonic Acid:**

$$C_6H_5SO_3H \xrightarrow{NaOH} C_6H_5SO_3Na \xrightarrow{NaOH, \Delta} C_6H_5ONa \xrightarrow{H^+} C_6H_5OH$$

3. **From Diazonium Salts:**

$$C_6H_5N_2^+Cl^- + H_2O \xrightarrow{\Delta} C_6H_5OH + N_2 + HCl$$

4. **From Cumene:**

$$\text{Cumene} \xrightarrow{O_2} \text{Cumene hydroperoxide} \xrightarrow{H_2O, H^+} \text{Phenol} + \text{Acetone}$$

Physical Properties of Phenols

1. **Boiling Points:** Higher than corresponding hydrocarbons and haloarenes due to intermolecular hydrogen bonding.
2. **Solubility:** Sparingly soluble in water due to hydrogen bonding.

Chemical Properties of Phenols (Acidic Nature and Electrophilic Substitution)

1. **Acidic Character:** Phenols are more acidic than alcohols but less acidic than carboxylic acids.
   - Electron-withdrawing groups (e.g., $-NO_2$) increase acidity.
   - Electron-donating groups (e.g., $-CH_3$) decrease acidity.

   Order of acidity: Picric acid > p-nitrophenol > m-nitrophenol > o-nitrophenol > phenol.
2. **Electrophilic Substitution Reactions:** The -OH group is ortho-para directing and activating.
   - **Halogenation (Bromination):** Phenol reacts with bromine water to give 2,4,6-tribromophenol.
   - **Nitration:** Phenol reacts with dilute HNO_3 to give ortho- and para-nitrophenols. With concentrated HNO_3, it gives picric acid (2,4,6-trinitrophenol).
   - **Sulphonation:** Phenol reacts with concentrated H_2SO_4 to give ortho- and para-phenolsulfonic acids.
   - **Kolbe's Reaction:** Phenol reacts with CO_2 under pressure to form salicylic acid.
   - **Reimer-Tiemann Reaction:** Phenol reacts with chloroform and NaOH to form salicylaldehyde.
   - **Reaction with Zinc Dust:** Phenol is reduced to benzene.

- **Reaction with Zinc Dust:** Phenol is reduced to benzene.

$$C_6H_5OH + Zn \rightarrow C_6H_6 + ZnO$$

- **Oxidation:** Phenol oxidizes to benzoquinone.

Ethers

Methods of Preparation of Ethers

1. **Dehydration of Alcohols:**

$$2ROH \xrightarrow{conc.H_2SO_4, 413K} ROR + H_2O$$

2. **Williamson's Synthesis:** Alkyl halide reacts with sodium alkoxide.

$$R - X + R'ONa \rightarrow R - O - R' + NaX$$

This is a good method for preparing unsymmetrical ethers. Primary alkyl halides are preferred.

Physical Properties of Ethers

1. **Boiling Points:** Lower than alcohols of comparable molecular mass (no hydrogen bonding).
2. **Solubility:** Slightly soluble in water due to hydrogen bonding with water.

Chemical Properties of Ethers

1. **Cleavage of C-O bond by HX:** Ethers react with concentrated HX (HI ¿ HBr ¿ HCl).

$$ROR' + HX \rightarrow RX + R'OH$$

If excess HX is used, alcohol further reacts to form alkyl halide.

2. **Electrophilic Substitution (for aromatic ethers):** The –OR group is ortho-para directing and activating.

Aldehydes and Ketones (Carbonyl Compounds)

Methods of Preparation of Aldehydes and Ketones

1. **Oxidation of Alcohols:** Primary alcohols give aldehydes, secondary alcohols give ketones.
2. **Dehydrogenation of Alcohols:** Vapors of alcohols passed over heated Cu.

$$RCH_2OH \xrightarrow{Cu, 573K} RCHO + H_2$$

$$R_2CHOH \xrightarrow{Cu, 573K} R_2CO + H_2$$

3. **From Hydrocarbons:**
   - **Ozonolysis of Alkenes:**

$$\text{Alkene} \xrightarrow{O_3} \text{Ozonide} \xrightarrow{Zn/H_2O} \text{Aldehyde/Ketone}$$

   - **Hydration of Alkynes:** Ethyne gives acetaldehyde; other alkynes give ketones.

$$HC \equiv CH + H_2O \xrightarrow{HgSO_4/H_2SO_4} CH_3CHO$$

   - **Friedel-Crafts Acylation (for ketones):**

$$C_6H_6 + RCOCl \xrightarrow{AlCl_3} C_6H_5COR + HCl$$

   - **Etard Reaction (for aldehydes):** Toluene to benzaldehyde using chromyl chloride.
   - **Gattermann-Koch Reaction (for aldehydes):** Benzene to benzaldehyde using CO and HCl.

4. **From Acyl Chlorides (Acid Chlorides): Rosenmund Reduction:**

$$RCOCl + H_2 \xrightarrow{Pd/BaSO_4} RCHO + HCl$$

5. **From Nitriles:**
   - **Stephen Reaction:** Nitriles reduced to imines, then hydrolyzed to aldehydes.

$$RCN \xrightarrow{SnCl_2/HCl} RCH = NH \xrightarrow{H_3O^+} RCHO$$

   - Using DIBAL-H (Diisobutylaluminium hydride).

Physical Properties of Aldehydes and Ketones

1. **Boiling Points:** Higher than hydrocarbons and ethers, lower than alcohols of comparable molar mass (no intermolecular H-bonding).
2. **Solubility:** Lower members soluble in water due to H-bonding. Solubility decreases with increasing chain length.

Chemical Properties of Aldehydes and Ketones

1. **Nucleophilic Addition Reactions:** Due to polarity of C=O bond.
   - **Addition of HCN:** Forms cyanohydrins.
   - **Addition of $NaHSO_3$:** Forms bisulphite addition products.
   - **Addition of Grignard Reagents:** Forms alcohols.
   - **Addition of Alcohols:** Forms hemiacetals/acetals (from aldehydes) or hemiketals/ketals (from ketones).
   - **Addition of Ammonia derivatives:** Forms imines, oximes, hydrazones, semicarbazones.
2. **Reduction:**
   - **To Alcohols:** Aldehydes to primary, ketones to secondary alcohols.
   - **To Hydrocarbons (Clemmensen, Wolff-Kishner):**

$$RCHO/RCOR' \xrightarrow{Zn-Hg/HCl} RCH_3/R_2CH_2$$

$$RCHO/RCOR' \xrightarrow{NH_2NH_2,KOH/\text{ethylene glycol}} RCH_3/R_2CH_2$$

3. **Oxidation:**
   - Aldehydes easily oxidize to carboxylic acids (even with mild agents like Tollens' and Fehling's reagents).
   - Ketones resist oxidation under mild conditions; strong oxidation breaks C-C bonds.
4. **Aldol Condensation:** Carbonyl compounds with α-hydrogens undergo self-condensation in presence of dilute alkali.
5. **Cannizzaro Reaction:** Aldehydes without α-hydrogens undergo disproportionation in concentrated alkali.

$$2HCHO \xrightarrow{conc.NaOH} CH_3OH + HCOONa$$

Carboxylic Acids

Methods of Preparation of Carboxylic Acids

1. **From Primary Alcohols and Aldehydes:** Oxidation.
2. **From Alkylbenzenes:** Oxidation of alkyl side chain.

$$C_6H_5CH_3 \xrightarrow{KMnO_4/KOH,\Delta} C_6H_5COOK \xrightarrow{H^+} C_6H_5COOH$$

3. **From Nitriles and Amides:** Hydrolysis.

$$RCN \xrightarrow{H_2O/H^+} RCOOH$$

$$RCONH_2 \xrightarrow{H_2O/H^+} RCOOH$$

4. **From Grignard Reagents:** Reaction with CO_2, followed by hydrolysis.

$$RMgX + CO_2 \rightarrow RCOOMgX \xrightarrow{H_3O^+} RCOOH$$

Physical Properties of Carboxylic Acids

1. **Boiling Points:** Higher than alcohols, aldehydes, ketones, and ethers of comparable molar mass due to strong intermolecular hydrogen bonding (forming dimers).
2. **Solubility:** Lower members soluble in water. Solubility decreases with increasing chain length.

Chemical Properties of Carboxylic Acids (Acidic Nature and Reactions of -COOH group)

1. **Acidic Character:** Carboxylic acids are stronger acids than phenols and alcohols.
   - Electron-withdrawing groups increase acidity.
   - Electron-donating groups decrease acidity.

   Order of acidity of haloacetic acids: $FCH_2COOH > ClCH_2COOH > BrCH_2COOH > CH_3COOH$.

2. **Formation of Acid Derivatives:**
   - **Acid Chlorides:** Reaction with $PCl_3, PCl_5, SOCl_2$.
   $$RCOOH + SOCl_2 \rightarrow RCOCl + SO_2 + HCl$$
   - **Anhydrides:** Dehydration of two carboxylic acid molecules.
   - **Esters (Esterification):** Reaction with alcohol in presence of acid catalyst.
   $$RCOOH + R'OH \rightleftharpoons RCOOR' + H_2O$$
   - **Amides:** Reaction with ammonia.
   $$RCOOH + NH_3 \rightarrow RCOONH_4 \xrightarrow{\Delta} RCONH_2 + H_2O$$

3. **Reduction:** Carboxylic acids are reduced to primary alcohols by $LiAlH_4$.

4. **Decarboxylation:** Removal of CO_2 by heating with soda lime.
   $$RCOOH + NaOH \xrightarrow{CaO,\Delta} RH + Na_2CO_3$$

5. **Hell-Volhard-Zelinsky (HVZ) Reaction:** Carboxylic acids with α-hydrogens react with halogen in presence of red phosphorus to give α-halo carboxylic acids.

Carboxylic Acid Anhydrides

Reactions of Carboxylic Acid Anhydrides

1. **Hydrolysis:** React with water to form carboxylic acids.
2. **Reaction with Alcohols:** Forms esters and carboxylic acids.
3. **Reaction with Amines:** Forms amides and carboxylic acids.

Esters

Preparation of Esters

1. **Esterification:** (Already discussed under carboxylic acids).
2. **Esters from Acyl Chlorides:**
   $$RCOCl + R'OH \rightarrow RCOOR' + HCl$$
3. **From Ketones (Baeyer-Villiger Oxidation):** Ketones are oxidized by peroxy acids to esters.
   $$RCOR' \xrightarrow{R''CO_3H} RCOOR'$$

Reactions of Esters

1. **Base-promoted hydrolysis of esters (Saponification):**
   $$RCOOR' + NaOH \rightarrow RCOONa + R'OH$$
   The carboxylate ion is unreactive towards nucleophilic substitution, making the reaction essentially irreversible.
2. **Reaction with Grignard Reagent:** Forms tertiary alcohols (except for formates, which give secondary alcohols).

Acid Amides

Preparation of Acid Amides

1. **Nucleophilic Substitution:** Amides can be synthesized by nucleophilic substitution of NH_3 in acyl chloride, acid anhydride, or esters.
2. **By Heating Ammonium Carboxylate:**
   $$RCOONH_4 \xrightarrow{\Delta} RCONH_2 + H_2O$$

Reactions of Acid Amides

1. **Hydrolysis:**

$$RCONH_2 \xrightarrow{H_2O/H^+} RCOOH + NH_3$$

2. **Hofmann's Bromamide Reaction:** (Already discussed under Amines preparation).

3. **Dehydration:** Forms nitriles.

$$RCONH_2 \xrightarrow{P_2O_5,\Delta} RCN + H_2O$$