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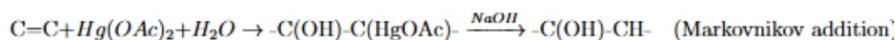
Title: Oxygen-Containing Organic Compound

## 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.

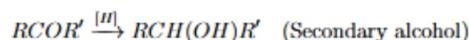


2. **Hydroboration-Oxidation:** Alkenes react with diborane to form trialkyl boranes. Treatment with alkaline  $H_2O_2$  gives alcohols via anti-Markovnikov addition of water.



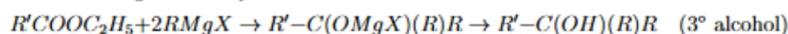
3. **From Carbonyl Compounds (Aldehydes and Ketones):**

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

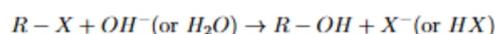


- **Using Grignard Reagents:**

- Formaldehyde gives primary alcohols.
- Other aldehydes give secondary alcohols.
- Ketones give tertiary alcohols.



4. **Hydrolysis of Alkyl Halides:**



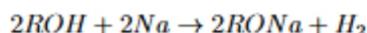
#### Physical Properties of Alcohols

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.

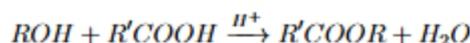
#### Chemical Properties of Alcohols

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

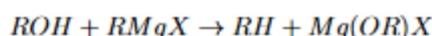
- **Reaction with active metals:**



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



- **Reaction with Grignard Reagents:**



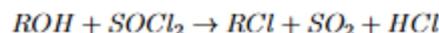
2. **Reactions involving C-O bond cleavage (Nucleophilic substitution):**

- **Reaction with HX:**



Reactivity order of alcohols:  $3^\circ > 2^\circ > 1^\circ$ . Reactivity order of HX:  $HI > HBr > HCl$ .

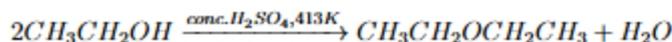
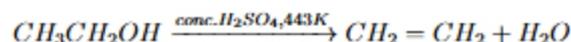
- Reaction with  $PCl_3$ ,  $PCl_5$ ,  $SOCl_2$ :



### 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.

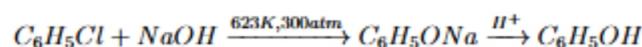
### 4. Dehydration: Forms alkenes or ethers depending on conditions.



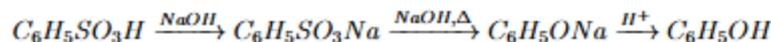
## Phenols

### Methods of Preparation of Phenols

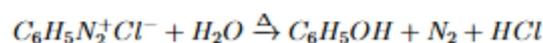
#### 1. From Haloarenes (Dow's Process):



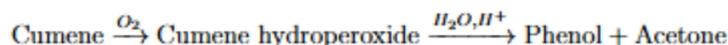
#### 2. From Benzene Sulphonic Acid:



#### 3. From Diazonium Salts:



#### 4. From Cumene:



### 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.

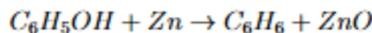
- Electron-withdrawing groups (e.g.,  $-NO_2$ ) increase acidity.
- Electron-donating groups (e.g.,  $-CH_3$ ) decrease acidity.

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.

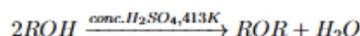


- **Oxidation:** Phenol oxidizes to benzoquinone.

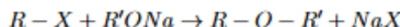
## Ethers

### Methods of Preparation of Ethers

1. **Dehydration of Alcohols:**



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



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).



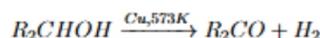
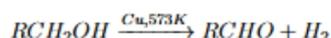
If excess HX is used, alcohol further reacts to form alkyl halide.

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.

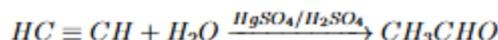


3. **From Hydrocarbons:**

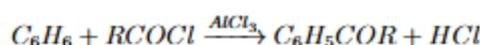
- **Ozonolysis of Alkenes:**



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



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



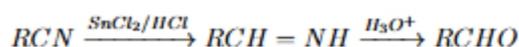
- **Etard Reaction (for aldehydes):** Toluene to benzaldehyde using chromyl chloride.
- **Gattermann-Koch Reaction (for aldehydes):** Benzene to benzaldehyde using CO and HCl.

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



5. **From Nitriles:**

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



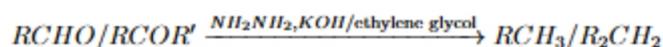
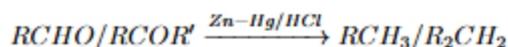
- Using DIBAL-H (Diisobutylaluminium hydride).

## 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.

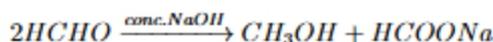
## Chemical Properties of Aldehydes and Ketones

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):**



3. **Oxidation:**

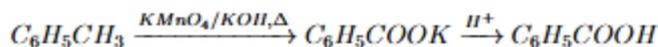
- Aldehydes easily oxidize to carboxylic acids (even with mild agents like Tollens' and Fehling's reagents).
  - Ketones resist oxidation under mild conditions; strong oxidation breaks C-C bonds.
4. **Aldol Condensation:** Carbonyl compounds with  $\alpha$ -hydrogens undergo self-condensation in presence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



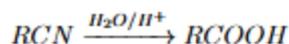
## Carboxylic Acids

### Methods of Preparation of Carboxylic Acids

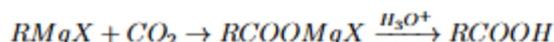
1. **From Primary Alcohols and Aldehydes:** Oxidation.
2. **From Alkylbenzenes:** Oxidation of alkyl side chain.



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



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



### 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)

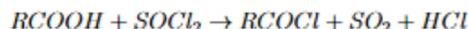
1. **Acidic Character:** Carboxylic acids are stronger acids than phenols and alcohols.

- 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:**

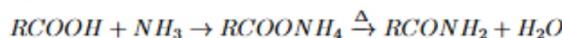
- **Acid Chlorides:** Reaction with  $PCl_3, PCl_5, SOCl_2$ .



- **Anhydrides:** Dehydration of two carboxylic acid molecules.
- **Esters (Esterification):** Reaction with alcohol in presence of acid catalyst.

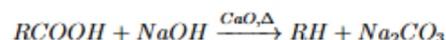


- **Amides:** Reaction with ammonia.



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

4. **Decarboxylation:** Removal of  $CO_2$  by heating with soda lime.



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

## Carboxylic Acid Anhydrides

### Reactions of Carboxylic Acid Anhydrides

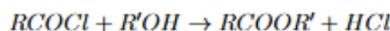
1. **Hydrolysis:** React with water to form carboxylic acids.
2. **Reaction with Alcohols:** Forms esters and carboxylic acids.
3. **Reaction with Amines:** Forms amides and carboxylic acids.

## Esters

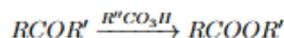
### Preparation of Esters

1. **Esterification:** (Already discussed under carboxylic acids).

2. **Esters from Acyl Chlorides:**

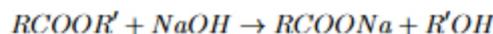


3. **From Ketones (Baeyer-Villiger Oxidation):** Ketones are oxidized by peroxy acids to esters.



### Reactions of Esters

1. **Base-promoted hydrolysis of esters (Saponification):**



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

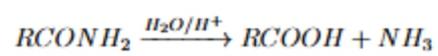
1. **Nucleophilic Substitution:** Amides can be synthesized by nucleophilic substitution of  $NH_3$  in acyl chloride, acid anhydride, or esters.

2. **By Heating Ammonium Carboxylate:**



### Reactions of Acid Amides

1. **Hydrolysis:**



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

3. **Dehydration:** Forms nitriles.

