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Aldehydes and Ketones

Carbonyl Group and Classification

The carbonyl group (>C=O) is the functional group present in aldehydes and ketones. Aldehydes have the carbonyl group attached to at least one hydrogen atom, while ketones have the carbonyl group attached to two carbon atoms.

Nomenclature

Aldehydes are named by replacing the terminal 'e' of the corresponding alkane with 'al'. Ketones are named by replacing the terminal 'e' with 'one'. The position of the carbonyl group in ketones is indicated by a number.

Preparation of Aldehydes

Aldehydes can be prepared by oxidation of primary alcohols, dehydrogenation of alcohols, ozonolysis of alkenes, hydration of alkynes, Rosenmund reduction of acyl chlorides, and reduction of nitriles and esters.

Preparation of Ketones

Ketones are prepared by oxidation of secondary alcohols, dehydrogenation of secondary alcohols, ozonolysis of alkenes, hydration of alkynes (Kucherov’s reaction), reaction of acyl chlorides with organocadmium compounds, and reaction of nitriles with Grignard reagents.

Physical Properties

Aldehydes and ketones are generally colorless liquids with pleasant smells. They have higher boiling points than hydrocarbons due to the polar carbonyl group but lower than alcohols. Lower members are soluble in water due to hydrogen bonding.

Chemical Properties

Aldehydes and ketones undergo nucleophilic addition reactions such as addition of hydrogen cyanide, sodium hydrogen sulphite, Grignard reagents, alcohols, and ammonia derivatives. They also undergo reduction to alcohols and hydrocarbons, oxidation (aldehydes to acids), aldol condensation, Cannizzaro reaction, and electrophilic substitution (aromatic aldehydes and ketones).

Tests

Fehling’s test and Tollen’s test distinguish aldehydes from ketones. Iodoform test identifies methyl ketones and aldehydes with one alpha hydrogen.

Uses

Aldehydes and ketones are used as solvents, preservatives (formaldehyde), in perfumery (benzaldehyde), and for their characteristic odors and flavors (vanillin, camphor).

Solved Examples

Example 1: Write the reaction for the preparation of benzaldehyde by the Etard reaction.

Solution:

Toluene reacts with chromium oxychloride (CrO_2Cl_2) in carbon disulfide (CS_2) to form a chromium complex, which on hydrolysis with acid gives benzaldehyde.

$C_6H_5CH_3 + CrO_2Cl_2 \rightarrow [Cr\ complex] \rightarrow C_6H_5CHO$

Example 2: Explain the Cannizzaro reaction with an example.

Solution:

Aldehydes without alpha hydrogen undergo self-oxidation and reduction in the presence of concentrated alkali to give an alcohol and a carboxylate salt.

$2\ C_6H_5CHO + NaOH \rightarrow C_6H_5CH_2OH + C_6H_5COONa$

Practice Set

- **Level 1:** What is the functional group present in aldehydes and ketones?
- **Level 1:** Name the test used to distinguish aldehydes from ketones.
- **Level 2:** Write the reaction for the oxidation of a primary alcohol to an aldehyde.
- **Level 3:** Explain the mechanism of aldol condensation.
- **Level 3:** Calculate the amount of acetaldehyde formed by oxidation of 10 g of ethanol. (Molar mass of ethanol = 46 g/mol, acetaldehyde = 44 g/mol)

Answer Key

Level 1: The functional group is the carbonyl group (>C=O).

Level 1: Tollen’s test is used to distinguish aldehydes from ketones.

Level 2: Oxidation of primary alcohol:

$RCH_2OH + [O] \rightarrow RCHO + H_2O$

Level 3: Aldol condensation involves the formation of an enolate ion from an aldehyde or ketone in the presence of dilute alkali, which then attacks another molecule of aldehyde or ketone to form β-hydroxy aldehyde or ketone, followed by dehydration to form α,β-unsaturated aldehyde or ketone.

Level 3 (Numerical):

Moles of ethanol = 10/46 = 0.217 mol

From the reaction, 1 mole of ethanol gives 1 mole of acetaldehyde.

Mass of acetaldehyde = 0.217 × 44 = 9.55 g

Carboxylic Acids

Structure and Nomenclature

Carboxylic acids contain the carboxyl group (-COOH), consisting of a carbonyl group (>C=O) and a hydroxyl group (-OH) attached to the same carbon atom. They are named by replacing the terminal 'e' of the alkane with 'oic acid'.

Preparation Methods

Carboxylic acids are prepared by oxidation of primary alcohols and aldehydes, hydrolysis of nitriles and amides, reaction of Grignard reagents with carbon dioxide, hydrolysis of acyl halides and acid anhydrides, hydrolysis of esters, and oxidation of alkylbenzenes.

Physical Properties

Lower carboxylic acids are colorless liquids with pungent smell and are soluble in water due to hydrogen bonding. Higher acids are waxy solids and less soluble. They have higher boiling points due to intermolecular hydrogen bonding.

Chemical Properties

Carboxylic acids react by cleavage of C–OH bond (formation of anhydrides, esters, acyl chlorides), cleavage of O–H bond (reaction with metals and bases), reduction to alcohols, decarboxylation, electrophilic substitution on aromatic acids, halogenation (Hell-Volhard-Zelinsky reaction), and ring substitution.

Uses

Methanoic acid is used in rubber and textiles, ethanoic acid as vinegar and solvent, hexanedioic acid in nylon manufacture, esters in perfumery, sodium benzoate as food preservative, and higher fatty acids in soaps and detergents.

Solved Examples

Example 1: Write the reaction for the preparation of benzoic acid from toluene.

Solution:

Toluene is oxidized by potassium permanganate under basic conditions and then acidified to give benzoic acid.

$C_6H_5CH_3 + KMnO_4 + OH^- \rightarrow C_6H_5COOK + MnO_2 + H_2O$

$C_6H_5COOK + H_3O^+ \rightarrow C_6H_5COOH + K^+ + H_2O$

Example 2: Explain the Hell-Volhard-Zelinsky reaction.

Solution:

Carboxylic acids with alpha hydrogens react with halogens (Cl_2 or Br_2) in the presence of red phosphorus to form alpha-halo acids.

$RCH_2COOH + X_2 + P \rightarrow RCHXCOOH + HX$

Practice Set

- **Level 1:** What is the functional group in carboxylic acids?
- **Level 1:** Name the reaction in which carboxylic acids react with alcohols to form esters.
- **Level 2:** Write the reaction for the preparation of carboxylic acid from nitriles.
- **Level 3:** Explain the mechanism of esterification.
- **Level 3:** Why do aromatic carboxylic acids not undergo Friedel-Crafts reactions?

Answer Key

Level 1: The functional group is the carboxyl group (-COOH).

Level 1: The reaction is called esterification.

Level 2: Hydrolysis of nitriles:

$R\text{-}C\equiv N + 2H_2O + H_3O^+ \rightarrow R\text{-}COOH + NH_4^+$

Level 3: Esterification mechanism involves protonation of the carbonyl oxygen of the acid, nucleophilic attack by the alcohol oxygen, proton transfers, and loss of water to form the ester.

Level 3: Aromatic carboxylic acids do not undergo Friedel-Crafts reactions because the carboxyl group is deactivating and binds to the Lewis acid catalyst, preventing the reaction.

Quick Reference Table

Common Mistakes and Misconceptions

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