

17: Oxidation and Reduction

17.1 Oxidation and Reduction Occur Together

Redox Reactions Involve Electron Transfer (17.1A)

Inorganic Redox Reactions

Organic Redox Reactions

Oxidation Levels of Organic Compounds (17.1B)

Carbon Oxidation Numbers

Definitions of Organic Oxidation and Reduction

Presentation of Redox Reactions in this Chapter

17.2 Oxidation of Alcohols and Aldehydes

Oxidation Using Cr(VI) Reagents (17.2A)

Chromate and Dichromate Reagents

Unwanted Oxidation of Aldehydes

Jones Oxidation

Modified Cr(VI) Reagents

Cr(VI) Oxidation Mechanisms

Other Inorganic Oxidizing Agents (17.2B)

MnO₂

Sodium Hypochlorite (NaOCl)

Organic Oxidizing Agents (17.2C)

Ketones to Esters

Aldehydes to Carboxylic Acids and Alcohols

Alcohols to Ketones or Aldehydes

17.3 Oxidation of Carbon-Carbon Multiple Bonds

Addition of Oxygen to C=C Bonds (17.3A)

Epoxide Formation Using Peroxyacids

Formation of syn-1,2-Diols Using OsO₄ or MnO₄⁻

Formation of anti-1,2-Diols

Oxidative Cleavage of Carbon-Carbon Multiple Bonds (17.3B)

Cleavage Using Ozone (O₃)

Cleavage Using CrO₃ or KMnO₄

Cleavage of 1,2-Diols Using HIO₄ or Pb(OAc)₄

17.4 Oxidation of Alkyl Groups

Metal Oxide Oxidations (17.4A)

KMnO₄ and CrO₃

Cl₂CrO₂

SeO₂ Oxidations

O₂ Oxidations (Autoxidation) (17.4B)

Autoxidation Mechanism

Synthetic Utility

17.5 Phenols, Hydroquinones, and Quinones

Formation of Phenols (17.5A)

From Cumene

From Aryl Halides

From Arylsulfonic Acids

From Diazonium Ions

Formation of Quinones and Hydroquinones (17.5B)

17.6 Reduction Reactions

General Features (17.6A)

Types of Reduction Reactions (17.6B)

Reduction Using H_2

Metal Hydride Reagents

Presentation of Reduction Reactions

17.7 Reduction of Ketones and Aldehydes

Alcohols from Metal Hydride Reductions (17.7A)

$LiAlH_4$ Mechanism

$NaBH_4$ Mechanism

Alcohols from Diborane Reduction

Alcohols from Organic Reducing Agents (17.7B)

Cannizzaro Reaction

Meerwein-Ponndorf-Verley Reduction

Alkyl Groups from $C=O$ Reduction (17.7C)

Clemmensen Reduction

Wolff-Kishner Reaction

17.8 Reduction of $R-C(=O)-Z$ and Related Compounds

General $LiAlH_4$ Mechanism

Carboxylic Acid Reduction

Diborane Reduction of Carboxylic Acids

Amine Formation (17.8B)

Reduction of Amides

Reduction of $R-C\equiv N$ and $R-NO_2$

Aldehyde Formation (17.8C)

Acid Halides and $LiAlH(O-C(CH_3)_3)_3$

Esters and Diisobutylaluminum Hydride (DIBAL)

Nitriles and DIBAL

Rosenmund Reduction

17.9 Reduction of $C=C$ and $C\equiv C$ Bonds

Reduction of Alkenes and Alkynes (17.9A)

Reduction of Arenes (17.9B)