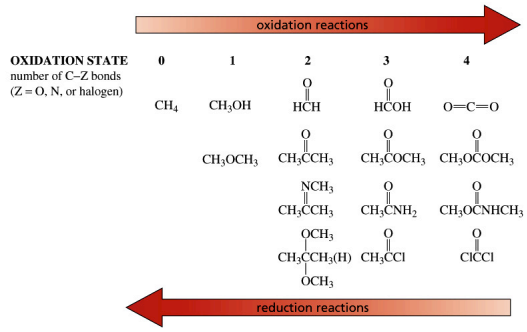
Chapter 20

More About Oxidation–Reduction Reactions



Reducing Agents

$RCH{=}CHR \xrightarrow[Pt]{H_2} RCH_2CH_2R$
an alkene

$RCH(=O) \xrightarrow[2.\ H^+,\ H_2O]{1.\ NaBH_4} RCH_2OH$
an aldehyde

$RCR(=O) \xrightarrow[HO^-,\ \Delta]{H_2NNH_2} RCH_2R$
a ketone

Oxidizing Agents

$RCH{=}CHR \xrightarrow{Br_2} RCHBrCHBrR$
an alkene

$RCH(=O) \xrightarrow{H_2CrO_4} RCOH(=O)$
an aldehyde

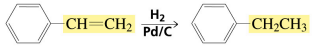
$RCHR(OH) \xrightarrow{H_2CrO_4} RCR(=O)$
an alcohol

Catalytic Hydrogenation

$CH_3CH_2CH{=}CH_2 + H_2 \xrightarrow{Pt,\ Pd,\ or\ Ni} CH_3CH_2CH_2CH_3$
1-butene → butane

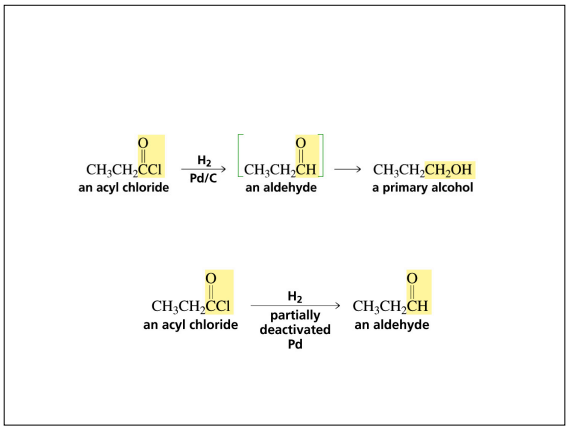
$CH_3CH_2CH_2C{\equiv}CH + 2\,H_2 \xrightarrow{Pt,\ Pd,\ or\ Ni} CH_3CH_2CH_2CH_2CH_3$
1-pentyne → pentane

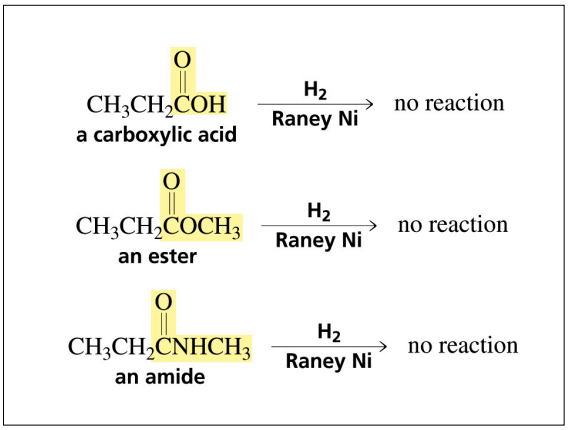
$CH_3C{\equiv}CCH_3 + H_2 \xrightarrow[catalyst]{Lindlar's} cis\text{-}CH_3CH{=}CHCH_3$
2-butyne → *cis*-2-butene



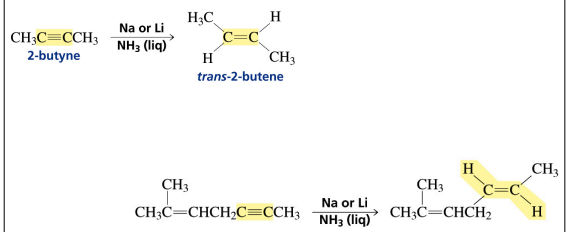
$CH_3CH_2CH{=}NCH_3 + H_2 \xrightarrow{Pd/C} CH_3CH_2CH_2NHCH_3$
methylpropylamine

$CH_3CH_2CH_2C{\equiv}N + 2\,H_2 \xrightarrow{Pd/C} CH_3CH_2CH_2CH_2NH_2$
butylamine

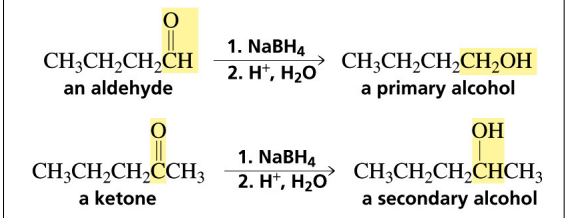




Dissolving-Metal NH_3 Reduction

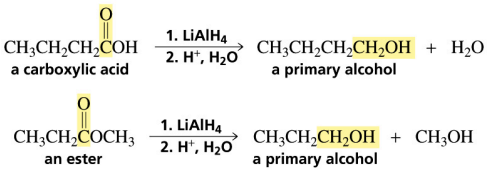


Hydride Reductions

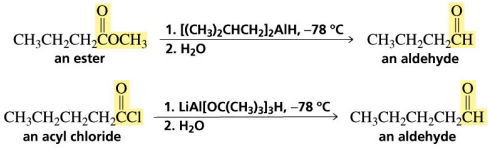


$LiAlH_4$ is a stronger reducing agent than $NaBH_4$

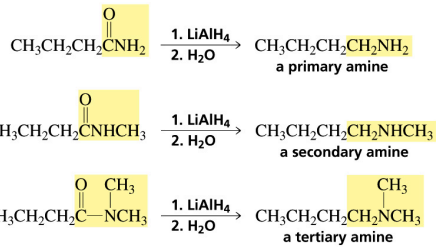
$LiAlH_4$ is used to reduce compounds that are nonreactive toward $NaBH_4$



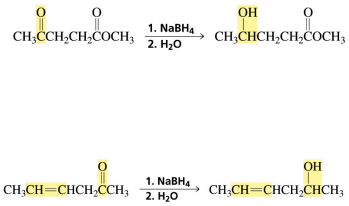
DIBAL allows the addition of one equivalent of hydride to an ester



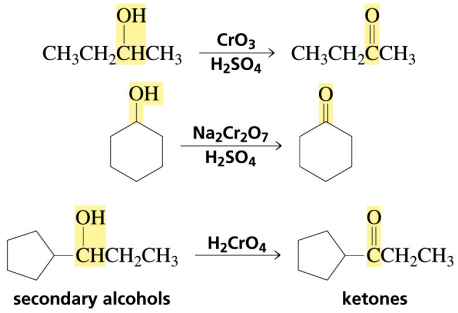
Formation of Amines by Reduction



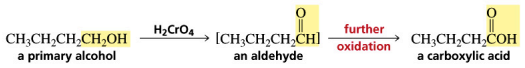
$NaBH_4$ can be used to selectively reduce an aldehyde or a keto group in a compound



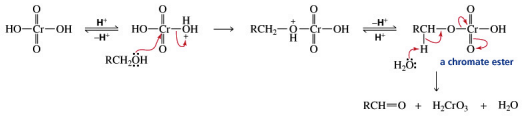
Oxidation of Alcohols



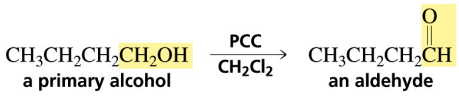
Oxidation of a Primary Alcohol



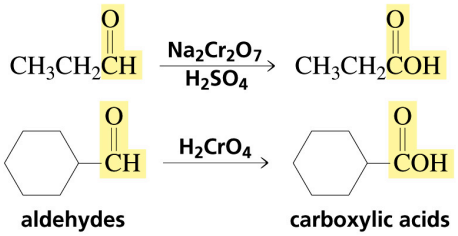
Mechanism of Alcohol Oxidation by Chromic Acid



The oxidation of a primary alcohol can be stopped at the aldehyde if pyridinium chlorochromate (PCC) is used as the oxidizing agent



Oxidation of Aldehydes and Ketones



aldehydes **carboxylic acids**

Tollens Reagent Oxidizes Only Aldehydes