Grignard Reactions

A Grignard reagent is an organic magnesium halide. It can be either an alkyl or an aryl compound (RMgX or ArMgX). Grignard (pronounced green yard) reagents were first prepared in France around 1900 by Victor Grignard (1871-1935). Grignard reagents are usually made by reacting an organic halide and magnesium metal in an ether solvent:

\[
\begin{align*}
RX + Mg & \rightarrow \text{ether} \rightarrow RMgX & X = \text{Cl, Br, or I} \\
ArX + Mg & \rightarrow \text{ether} \rightarrow ArMgX & X = \text{Br}
\end{align*}
\]

In the Grignard reagent, the bonding electrons between carbon and magnesium are shifted away from the electropositive Mg to form a strongly polar covalent bond. As a result the charge distribution in the Grignard reagent is such that the organic group (R) is partially negative and the –MgX group is partially positive. This charge distribution directs the manner in which Grignard reacts with other compounds.

\[
\begin{align*}
\delta^- & \quad \delta^+ \\
RMgX
\end{align*}
\]

The Grignard reagent is one of the most versatile and widely used reagents in organic chemistry. We will consider only its reactions with aldehydes and ketones at this time. Grignards react with aldehydes and ketones to give intermediate products that form alcohols when hydrolyzed. With formaldehyde, primary alcohols are formed; with other aldehydes, secondary alcohols are formed; with ketones, tertiary alcohols are formed.

| Grignard reagent + formaldehyde → 1º ROH | Grignard reagent + other aldehydes → 2º ROH | Grignard reagent + ketones → 3º ROH |
---|---|---|
\[
\begin{align*}
\text{H}_2\text{C} == \text{O} + \text{CH}_3\text{MgBr} & \rightarrow \text{ether} \rightarrow \text{H}_2\text{C} == \text{OMgBr} & \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CH}_2\text{OH} + \text{Mg(OH)Br}
\end{align*}
\]

Specific examples of each type of reaction follow:

formaldehyde
The Grignard reaction with acetone may be explained in this way. In the first step of the addition of ethyl magnesium bromide, the partially positive –MgBr of the Grignard bonds to the oxygen atom, and the partially negative CH₃CH₂~ bonds to the carbon atom of the carbonyl group of acetone.

In the hydrolysis step, a proton [H⁺] from water bonds to the oxygen atom, leaving the hydroxyl group [-OH] to combine with the +MgBr. So, the alcohol is formed.