A Grignard reagent has a formula RMgX where X is a halogen, and R is an alkyl or aryl (based on a benzene ring) group. For the purposes of this page, we shall take R to be an alkyl group (e.g., CH₃CH₂MgBr). Grignard reagents are made by adding the halogenoalkane to small bits of magnesium in a flask containing ethoxyethane (commonly called diethyl ether or just “ether”). The flask is fitted with a reflux condenser, and the mixture is warmed over a water bath for 20 - 30 minutes.

\[
\text{CH}_3\text{C}≡\text{H}_2\text{Br} + \text{Mg} \xrightarrow{\text{ethoxyethane}} \text{CH}_3\text{C}≡\text{H}_2\text{MgBr}
\]

Everything must be perfectly dry because Grignard reagents react with water. Any reactions using the Grignard reagent are carried out with the mixture produced from this reaction; you cannot separate it out in any way. Any excess Grignard reagent must be quenched before disposal.

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**Reactions of Grignard reagents with aldehydes and ketones**

These are reactions of the carbon-oxygen double bond, and so aldehydes and ketones react in exactly the same way - all that changes are the groups that happen to be attached to the carbon-oxygen double bond. It is much easier to understand what is going on by looking closely at the general case (using "R" groups rather than specific groups) - and then slotting in the various real groups as and when you need to. The "R" groups can be either hydrogen or alkyl in any combination.

In the first stage, the Grignard reagent adds across the carbon-oxygen double bond:

\[
\text{CH}_3\text{CH}_2\text{MgBr} + R\text{C}=\text{O} \rightarrow \text{CH}_3\text{CH}_2\text{O}−\text{MgBr} + \text{R}−
\]

Dilute acid is then added to this to hydrolyse it.

\[
\text{CH}_3\text{CH}−\text{O}−\text{MgBr} + \text{H}_2\text{O} \rightarrow \text{CH}_3\text{CH}−\text{OH} + \text{Mg(OH)Br}
\]

An alcohol is formed. One of the key uses of Grignard reagents is the ability to make complicated alcohols easily. What sort of alcohol you get depends on the carbonyl compound you started with - in other words, what R and R' are.

**Example 1**: Reaction with Methanal

Methanal is the simplest possible aldehyde with hydrogen as both R groups.
Assuming that you are starting with \( \text{CH}_3\text{CH}_2\text{MgBr} \) and using the general equation above, the alcohol you get always has the form:

\[
\text{CH}_3\text{CH}_2-\text{C} - \text{OH} \\
\text{R} - \text{R}'
\]

Since both R groups are hydrogen atoms, the final product will be:

\[
\text{H} \\
\text{CH}_3\text{CH}_2-\text{C} - \text{OH} \quad \text{or} \quad \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \\
\text{H}
\]

A primary alcohol is formed. A primary alcohol has only one alkyl group attached to the carbon atom with the \(-\text{OH}\) group on it. You could obviously get a different primary alcohol if you started from a different Grignard reagent.

Example \(\PageIndex{2}\): Reaction with Aldehyde

The next biggest aldehyde is ethanal with one of the R groups is hydrogen and the other \( \text{CH}_3 \).

\[
\text{CH}_3 - \text{C} \quad \text{O} \\
\text{H} \\
\text{ethanal}
\]

Again, think about how that relates to the general case. The alcohol formed is:

\[
\text{H} \\
\text{R} \\
\text{CH}_3\text{CH}_2-\text{C} - \text{OH} \quad \text{or} \quad \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \\
\text{R}'
\]

So this time the final product has one \( \text{CH}_3 \) group and one hydrogen attached:

\[
\text{CH}_3 \\
\text{CH}_3\text{CH}_2-\text{C} - \text{OH} \quad \text{or} \quad \text{CH}_3\text{CH}_2\text{CH}_2\text{OH} \\
\text{H} \\
\text{a secondary alcohol}
\]

A secondary alcohol has two alkyl groups (the same or different) attached to the carbon with the \(-\text{OH}\) group on it. You could change the nature of the final secondary alcohol by either:

• changing the nature of the Grignard reagent - which would change the \( \text{CH}_3\text{CH}_2 \) group into some other alkyl group;
• changing the nature of the aldehyde - which would change the \( \text{CH}_3 \) group into some other alkyl group.

Example \(\PageIndex{3}\): Reactions with Propanone
Ketones have two alkyl groups attached to the carbon-oxygen double bond. The simplest one is propanone.

\[
\begin{align*}
\text{CH}_3 & \quad \text{C} \\
& \quad \text{O} \\
\text{CH}_3 & \\
\text{propanone}
\end{align*}
\]

This time when you replace the R groups in the general formula for the alcohol produced you get a tertiary alcohol.

\[
\begin{align*}
\text{CH}_3 & \\
\text{CH}_3\text{CH}_2 & \quad \text{C} \\
& \quad \text{OH} \\
\text{CH}_3 &
\end{align*}
\]

A tertiary alcohol has three alkyl groups attached to the carbon with the -OH attached. The alkyl groups can be any combination of same or different. You could ring the changes on the product by:

- changing the nature of the Grignard reagent - which would change the CH\textsubscript{3}CH\textsubscript{2} group into some other alkyl group;
- changing the nature of the ketone - which would change the CH\textsubscript{3} groups into whatever other alkyl groups you choose to have in the original ketone.

**Contributors**

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