

Organometallic Chemistry

Organometallic compounds contain a metal covalently bonded within an organic compound, example:

- hemoglobin in blood contains iron bonded to a N–C ring structure,
- Chlorophyll in green plants contains magnesium similarly bonded,
- tetramethyl lead, $\text{Pb}(\text{CH}_3)_4$ —was used as a petroleum additive,
- triethylaluminium, $\text{Al}(\text{C}_2\text{H}_5)_3$, is an important catalyst in many polymerization reactions.

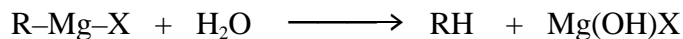
A group of organometallic compounds known as Grignard reagents are very important in synthesis reactions.

The Grignard compounds are characterized by the presence of magnesium and a halogen giving the general formula: $\text{R} - \text{Mg} - \text{X}$, example $\text{C}_2\text{H}_5 - \text{Mg} - \text{Br}$.

The halogen can be Cl, Br, or I, but not F as the C–F bond is very strong, (why?), so fluorides do not react.

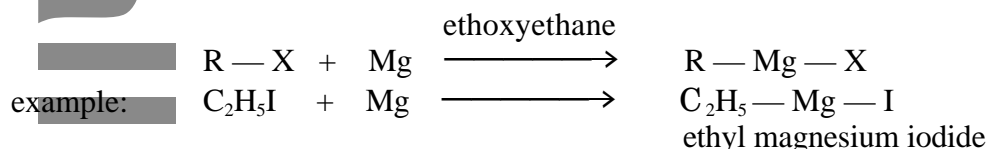
The Grignard reagents are useful in extending the length of the Carbon—chain in reaction pathways.

The Grignard reagents are not very stable, require anhydrous conditions for their preparation as they react with moisture:

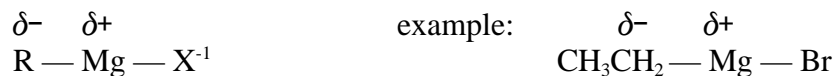


They are prepared by reacting magnesium turnings with a solution of the halogenoalkane in dry ethoxyethane that has been dried by having sodium wire in it.

(The ether solvent used is ‘dry’ because the products would react with water.)

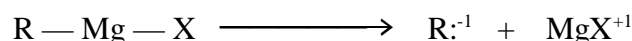


Since Mg lies to the left of carbon in the Periodic Table, carbon is the most electronegative atom. Thus, the Mg–C bond is largely covalent and highly polar, thus we get a dipole where the carbon (of the alkyl, R) has a slightly negative charge, whilst magnesium being the more electropositive element has a slightly positive charge, and the Mg–X bond being predominantly ionic:



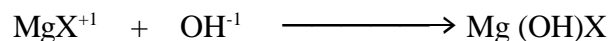
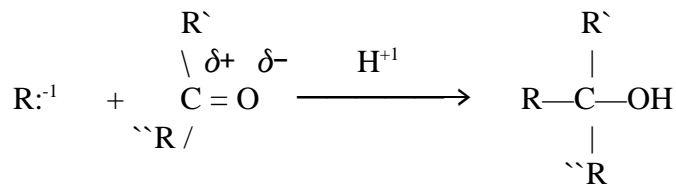
Since the carbon attached to the magnesium has a δ^- charge, it behaves as a carbanion, i.e. it can act as a nucleophile.

If the C–Mg bond breaks, the electron pair moves towards the carbon, the carbon of the R–Mg–X acts as the nucleophile.



Once this has happened, the nucleophilic $R:^-$, can react with any electrophile.

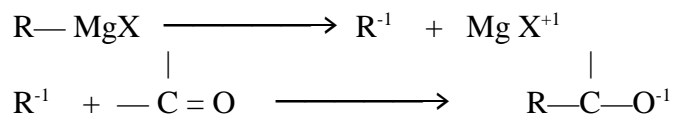
Example:



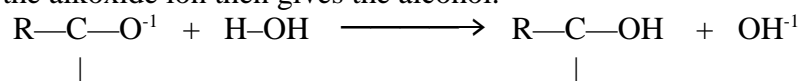
Typical reactions of Grignard reagent which increase the length of the carbon chain occur in two steps:

1. Addition of the Grignard reagent,
2. Hydrolysis in acid solution.

In general, the electrophilic carbon of a carbonyl (i.e an aldehyde or ketone) reacts with the nucleophilic carbon of the Grignard reagent to form an alkoxide .



Hydrolysis of the alkoxide ion then gives the alcohol.



Methanal, is the only aldehyde that reacts with Grignard reagent to give a **primary alcohol**.

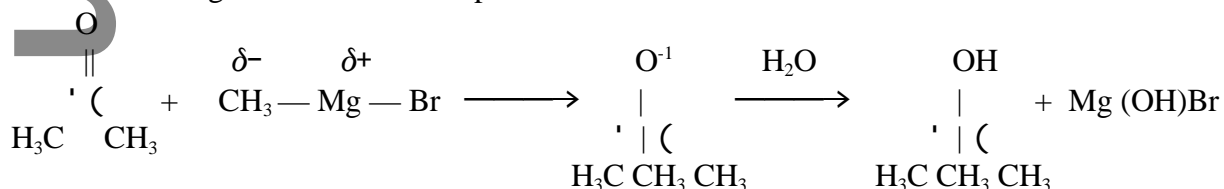
Aldehydes react with Grignard reagent to give **secondary alcohols**, whilst **ketones** react with Grignard reagent to give **tertiary alcohols**.

Example: The reaction of methylmagnesium bromide and propanone

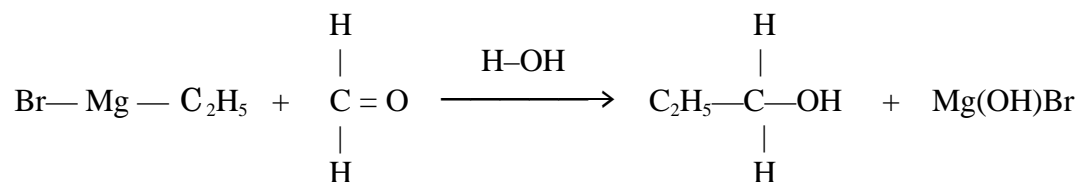
The first step is where the nucleophilic carbon of the Grignard reagent behaves as a nucleophile and attacks the electrophilic carbon of the propanone.

The π -bond of the carbonyl, ($C=O$), is broken and those two electrons are transferred to the more electronegative oxygen, making the anion.

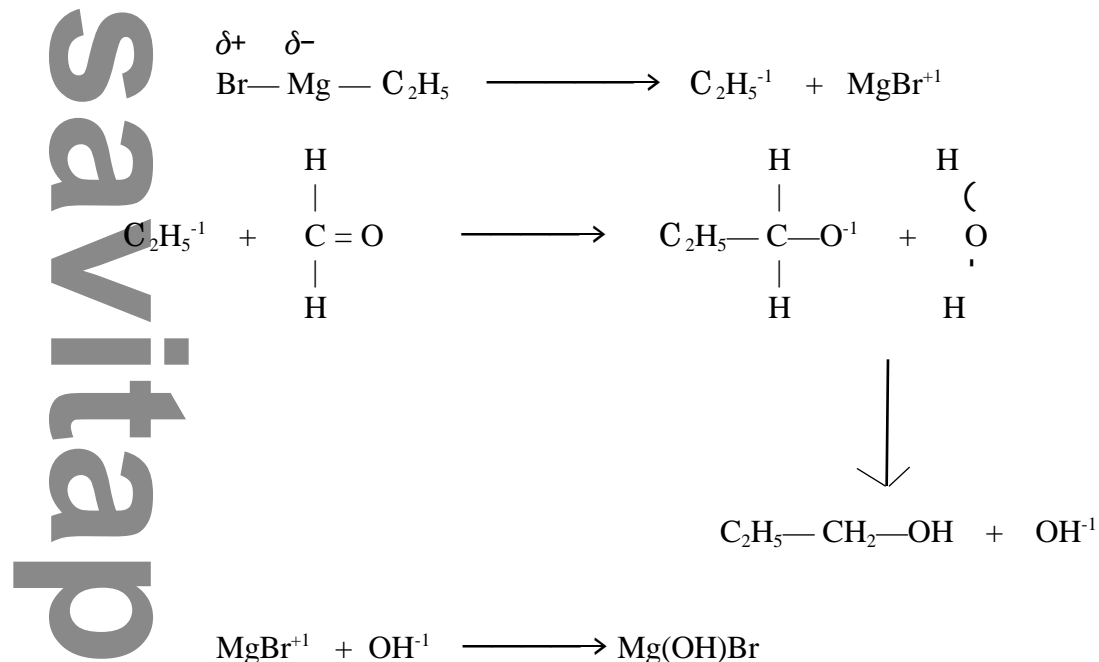
In the second step, hydrolysis is required in which aqueous acid is added to protonate the alkoxide ion and generate the alcohol product.



Examples of other reactions of Grignard reagent:

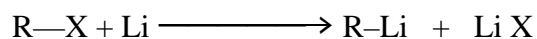


Mechanism:



Reaction with Lithium

Just as magnesium reacts with alkyl halides to form Grignard reagents, lithium reacts with alkyl halides to form organolithium reagents. This is another example of organometallic compounds.



Organolithium reagents are characterized by a C-Li bond, which is polarized similarly to the C-Mg bond of a Grignard reagent, C-Li has the polarization $\delta^- \text{C}-\text{Li}^{\delta+}$.

The C-Li bond is more highly polarized than the C-Mg bond. Therefore the δ^- charge on the carbon of the organolithium reagent is greater (more carbanionic).

Organolithium reagents will, therefore function as nucleophiles in the presence of an electrophilic species such as ketones and aldehydes.