

## 10.6: REACTIONS OF ALKYL HALIDES - GRIGNARD REAGENTS

### OBJECTIVES

After completing this section, you should be able to

- write an equation to describe the formation of a Grignard reagent.
- give examples of Grignard reagents formed from aryl and vinyl halides as well as from alkyl halides.
- explain the reactivity of Grignard reagents in terms of the polarity of the carbon-magnesium bond.
- write an equation for the reaction of a Grignard reagent with a proton donor, such as water.
- predict the product formed from the reaction of a given organohalide with magnesium followed by a proton donor.
- identify the organohalide, the reagents, or both, needed to prepare a given alkane.
- describe how a deuterium atom may be introduced at a specific location in an organic molecule through use of a Grignard reagent.
- describe at least one limitation on the use of Grignard reagents in organic synthesis.
- write an equation for the direct conversion of an alkyl halide to an alkane using a hydride donor, such as lithium aluminum hydride.

### KEY TERMS

Make certain that you can define, and use in context, the key terms below.

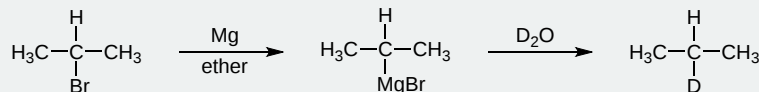
- carbanion
- Grignard reagent

### STUDY NOTES

The organomagnesium compounds formed by the reaction of an alkyl or aryl halide with magnesium are called *Grignard reagents*. As you will see throughout the remainder of this course, Grignard reagents can be used to synthesize a wide range of organic compounds and are extremely useful to the organic chemist.

In the introductory section, we tried to stress that the chemistry of alkyl halides is quite different from that of aryl (or vinyl) halides. However, both alkyl and aryl halides react with magnesium to form Grignard reagents.

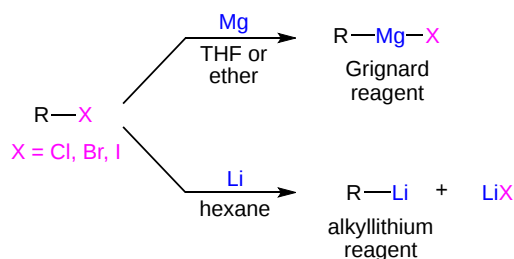
The reaction of a Grignard reagent with D<sub>2</sub>O ("heavy water") provides a convenient method for introducing a deuterium atom (remember D is equivalent to <sup>2</sup>H) into a molecule at a specific location. For example:



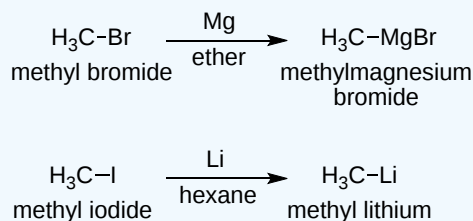
### FORMATION OF ORGANOMETALLIC REAGENTS

The **alkali metals** (Li, Na, K etc.) and the **alkaline earth metals** (Mg and Ca, together with Zn) are good reducing agents, of which the alkali metals are stronger. These same metals reduce the carbon-halogen bonds of alkyl halides. The halogen is converted to a halide anion, and the carbon bonds to the metal which has characteristics similar to a **carbanion** (R:-). Most alkyl halides can undergo this reaction including: 1°, 2°, 3°, vinyl, and aryl. Halide reactivity in these reactions increases in the order: Cl < Br < I and Fluorides are usually not used.

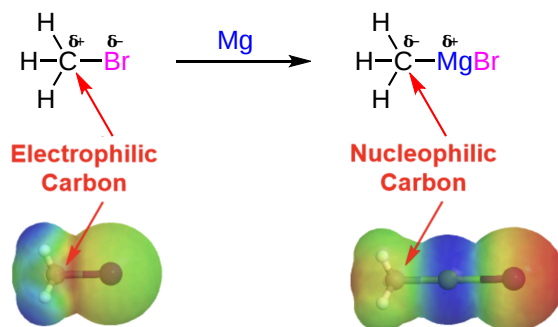
Many organometallic reagents are commercially available, however, it is often necessary to make them. The following equations illustrate these reactions for the commonly used metals lithium and magnesium (R may be hydrogen or alkyl groups in any combination). The alkyl magnesium halides described in the first reaction are called **Grignard Reagents** after the French chemist, Victor Grignard, who discovered them and received the Nobel prize in 1912 for this work. The products of the second reaction are called **Alkyl lithium Reagents**. The other metals mentioned above react in a similar manner, but Grignard and Alkyl lithium Reagents are most widely used. Although the formulae drawn here for the alkyl lithium and Grignard reagents reflect the stoichiometry of the reactions and are widely used in the chemical literature, they do not accurately depict the structural nature of these remarkable substances. Mixtures of polymeric and other associated and complexed species are in equilibrium under the conditions normally used for their preparation.



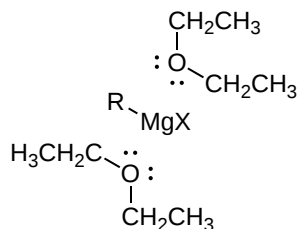
### ✓ EXAMPLE 10.6.1



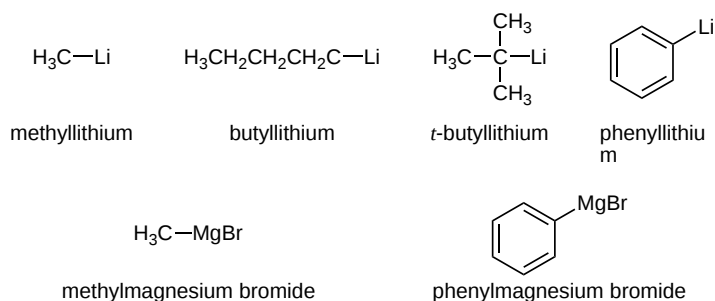
These reactions are obviously substitution reactions, but they cannot be classified as nucleophilic substitutions, as were the earlier reactions of alkyl halides. Because the functional carbon atom has been reduced, the polarity of the resulting functional group is inverted (an originally electrophilic carbon becomes nucleophilic). The Polarity change is evident when looking at the electrostatic maps of the alkyl halide and the Grignard reagent. In the alkyl halide, the electronegative halogen atom holds much of the electron density which gives the carbon a slight positive charge (shown in blue in the electrostatic potential map below) making it electrophilic. In the Grignard reagent, the carbon has a slight negative charge making it nucleophilic (shown in yellow & red).



A suitable solvent must be used for reactions that form organometallic molecules. For alkyl lithium formation pentane or hexane are usually used. Diethyl ether can also be used but the subsequent alkyl lithium reagent must be used immediately after preparation due to an interaction with the solvent. Diethyl ether or tetrahydrofuran (THF) are essential for Grignard reagent formation. Lone pair electrons from two ether molecules form a complex with the magnesium in the Grignard reagent (as pictured below). This complex helps stabilize the organometallic and increases its ability to react.

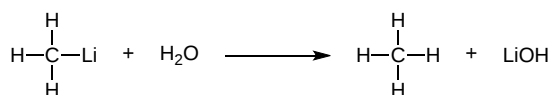


## COMMON ORGANOMETALLIC REAGENTS

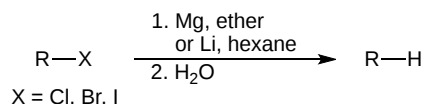


## ORGANOMETALLIC REAGENTS AS BASES

These reagents are very strong bases (pK<sub>a</sub>'s of saturated hydrocarbons range from 42 to 50). Although not usually done with Grignard reagents, organolithium reagents can be used as strong bases. Both Grignard reagents and organolithium reagents react with water to form the corresponding hydrocarbon. This is why so much care is needed to insure dry glassware and solvents when working with organometallic reagents.

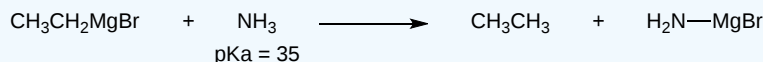
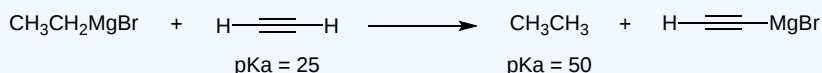


In fact, the reactivity of Grignard reagents and organolithium reagents can be exploited to create a new method for the conversion of halogens to the corresponding hydrocarbon (illustrated below). The halogen is converted to an organometallic reagent and then subsequently reacted with water to form an alkane.



### ? EXERCISE 10.6.1

How strong of a base would you expect ethyl Grignard to be? Would the following reactions be able to take place?



#### Answer

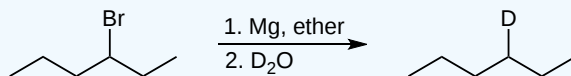
Because hydrocarbons like ethane are very weak acids (pK<sub>a</sub> = 50), then the corresponding carbanion (CH<sub>3</sub>CH<sub>2</sub><sup>-</sup>) is expected to be a strong base. Both reactions will occur.

### ? EXERCISE 10.6.2

How would you make a deuterated compound from an alkyl halide?

#### Answer

By first making a Grignard and then exposing it to heavy water.



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