13.8: ORGANOMETALLIC REAGENTS

INTRODUCTION

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. A typical Grignard reagent might be $\mathrm{CH_3CH_2MgBr}$. Organolithium reagents have the chemical formula RLi. A typical reagent might be $\mathrm{CH_3CH_2Li}$.

FORMATION OF ORGANOMETALLIC REAGENTS

Many organometallic reagents are commercially available, however, it is often necessary to make then. The following equations illustrate these reactions for the commonly used metals lithium and magnesium (R may be hydrogen or alkyl groups in any combination).

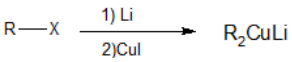
- **An Alkyl Lithium Reagent**

$$\mathrm{R_3C{-}X + 2\,Li \rightarrow R_3C{-}Li + LiX} \tag{13.8.1}$$

- **A Grignard Reagent**

$$\mathrm{R_3C{-}X + Mg \rightarrow R_3C{-}MgX} \tag{13.8.2}$$

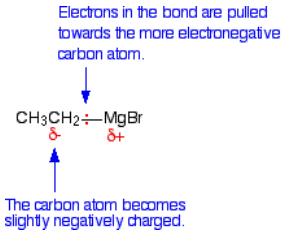
- **An Organocuprate Reagent**



Halide reactivity in these reactions increases in the order: Cl < Br < I and Fluorides are usually not used. The alkyl magnesium halides described in the second 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 other metals mentioned above react in a similar manner, but Grignard and Alky Lithium Reagents most widely used. Although the formulas 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. Organocuprate reagents have limited reactivity and will be used for ketone synthesis.

ORGANOMETALLIC REAGENTS ARE STRONG NUCLEOPHILES

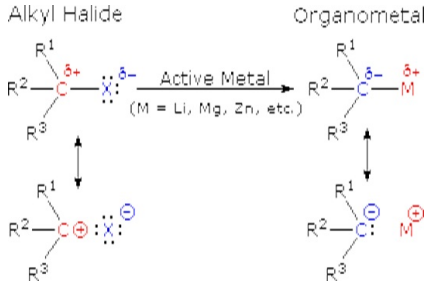
The bond between the carbon atom and the metal atom is polar. Therefore, organometallic reagents are strong nucleophiles. Using the Grignard reagent as an example, the carbon is more electronegative than magnesium, so the bonding pair of electrons is pulled towards the carbon creating a partial negative charge. Grignard reagents are strong nucleophiles. Nucleophilic carbon atoms are very useful in building carbon chains in multiple step systhesis.



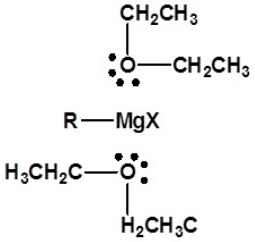
Grignard reactions create the possibility for substitution reactions at vinylic carbons. This reaction pathway is very useful since vinyl halides cannot react by the SN1 and SN2 mechanisms.

ORGANOMETALLIC REAGENTS AND PROTIC SOLVENTS (LIKE WATER)

Everything **must** be perfectly dry because organometallic reagents react with water (see below) or any protic solvent. Reactions using the Grignard reagent must use an ether as the solvent. Organolithium reactions also require aprotic solvents, but ethers are not required and alkanes can be used as solvents. The resulting reaction mixture is used directly for the next reaction. There are no separation and isolation procedures between reaction steps. Organometallic reagents react with water or any protic solvent to produce alkanes. For this reason, everything has to be **very dry** during the preparation above. The term **dry** means that no water or other protonated solvents are present. There is still a **liquid** ether solvent.

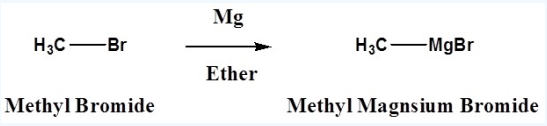


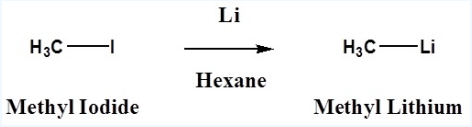
A suitable solvent must be used. For alkyl lithium formation pentane or hexane are usually used. Diethyl ether can also be used but the subsequent alkyl lithium reagent must be used immediately after preparation due to an interaction with the solvent. Ethyl ether or THF are essential for Grignard reagent 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.



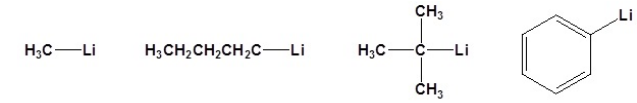
These reactions are obviously substitution reactions, but they cannot be classified as nucleophilic substitutions, as were the earlier reactions of alkyl halides. Because the functional carbon atom has been reduced, the polarity of the resulting functional group is inverted (an originally electrophilic carbon becomes nucleophilic). This change, shown below, makes alkyl lithium and Grignard reagents excellent nucleophiles and useful reactants in synthesis.

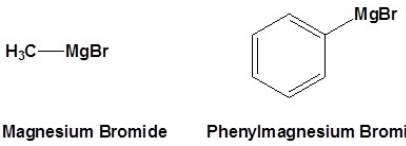
Example:





COMMON ORGANOMETALLIC REAGENTS

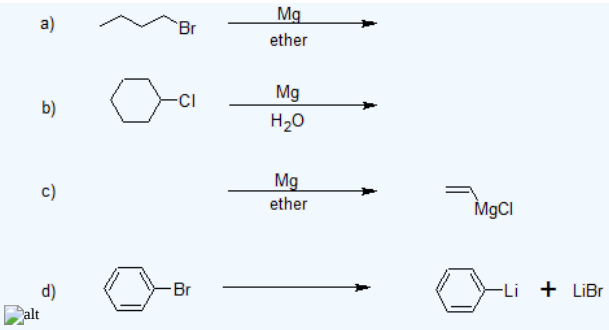




Exercises

13.

Predict the product or specify the missing regent(s) in the reactions below.



Answer

13.