ORGANIC CHEMISTRY 2 LECTURE GUIDE 2019

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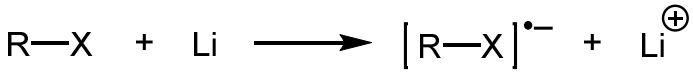
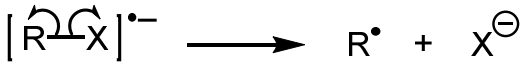
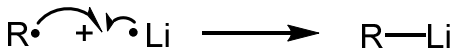
Lesson V.2. Preparation of RLi, Grignard and Gilman Reagents

Organolithium reagent preparation

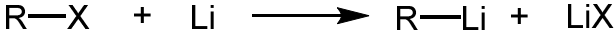
Organolithium species (RLi) are a highly reactive source of anionic C:







NET REACTION:



This is an example of an:

One safety note: organolithium species are often **pyrophoric** (spontaneously ignite in air) and can be extremely dangerous to handle without specialized training.

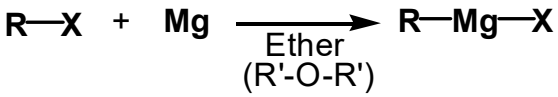
Notes

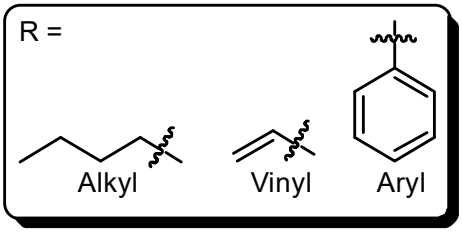
Lesson V.2. Preparation of RLi, Grignard and Gilman Reagents

Grignard Reagent preparation

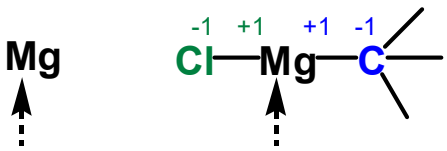
One type of easily prepared organometallic species are the **Grignard reagents** (RMgX, where X = Cl, Br or I).

Preparation:





Oxidation states:



A

Grignard reagents are not quite as reactive as organolithium species, so they are (although still dangerous and requiring specialized training to handle) more desirable for lab use.

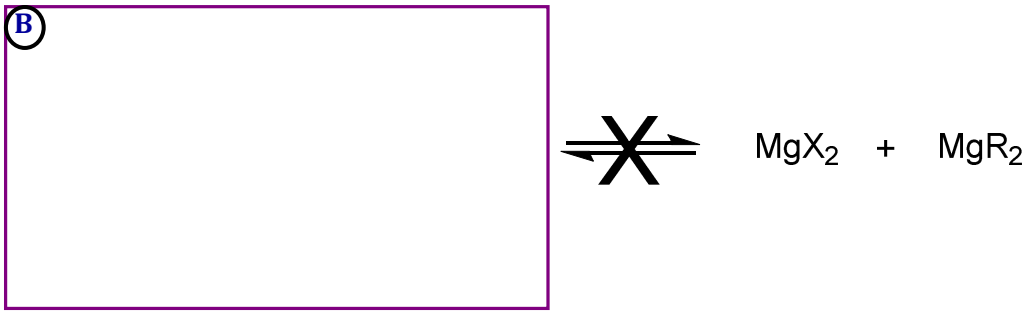
Notes

Lesson V.2. Preparation of RLi, Grignard and Gilman Reagents

Schlenk equilibrium

You may have noticed that we specify an ether solvent for preparation of Grignard reagents. In the absence of an ether, Grignard reagents actually exist as an equilibrium mixture of multiple species due to ligand exchange:

This process for Grignard reagents specifically is called the **Schlenk equilibrium,** and it complicates the reactivity of Grignard reagents. In ether solvents, the O of the ether coordinates to the Mg center and stops this process:



Notes

Lesson V.2. Preparation of RLi, Grignard and Gilman Reagents

Basicity and nucleophilicity of Grignard reagents

Although Grignard reagents are good sources of nucleophilic C, they are also strongly basic. This causes problems in cases where acid-base and nucleophilic reactions compete (like E2 versus S_N2):

1. As a base:

Grignard Reagents will also deprotonate more acidic groups, i.e.:

A

2. As a nucleophile:

B

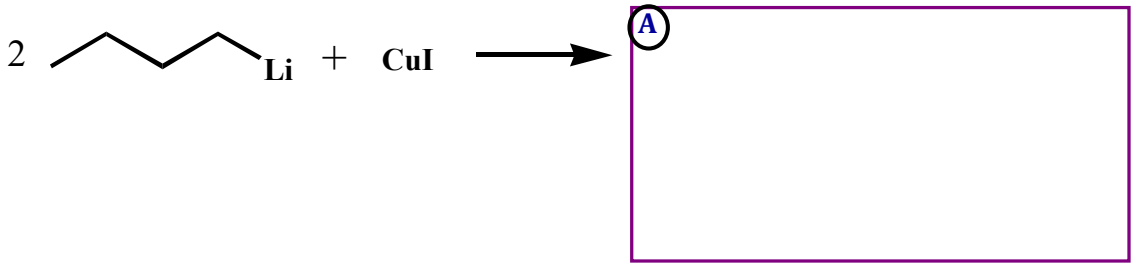
In cases where lower basicity is needed (to favor substitution, for example), scientists have developed less reactive organometallics of the form $LiCuR_2$, called **Gilman Reagents**.

Notes

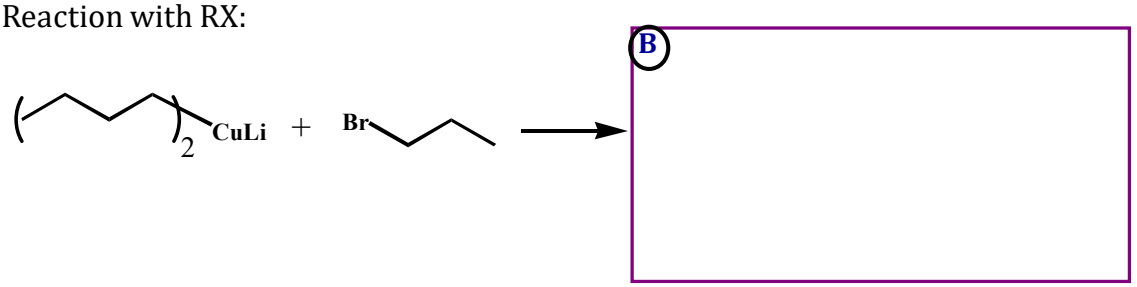
Lesson V.2. Preparation of RLi, Grignard and Gilman Reagents

Preparation of Gilman reagents

Preparation from RLi:



Reaction with RX:



Not a simple S_N2

Notes