

Experiment 16: Triphenylmethanol by a Grignard reaction

Objectives

The purpose of this experiment is to provide the student with practical experience in the preparation of a Grignard reagent. It also illustrates how such reagents can be used to prepare a tertiary alcohol from an ester. The student will also obtain further experience in the use of thin-layer chromatography--a technique that was introduced in Experiment 12. The ease of formation of certain resonance-stabilized carbocations is also illustrated.

Introduction

Francois Auguste Victor Grignard (1871-1935). Professor of Chemistry at the University of Lyons and Nancy. Received Nobel Prize in 1912 for his work on organometallic compounds.

Although Grignard reagents can be used to synthesize a wide range of organic compounds, it is perhaps their reactions with carbonyl compounds (aldehydes, ketones and esters) to yield alcohols that are most utilized by organic chemists. In this experiment (see Fig. 16.1), you will react phenylmagnesium bromide with ethyl benzoate to obtain triphenylmethanol.

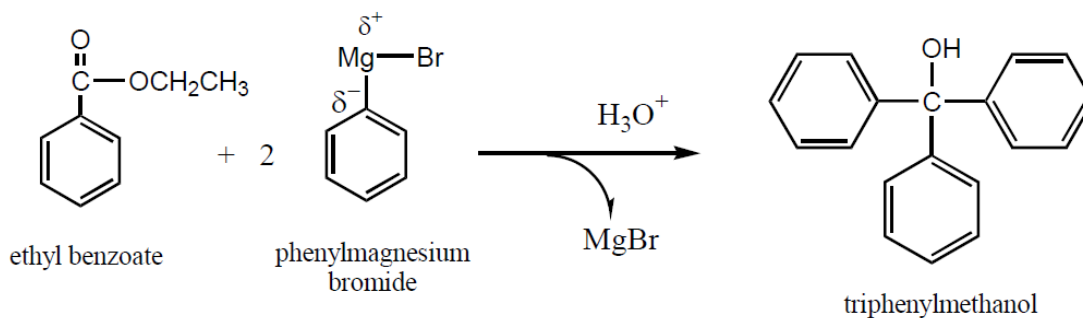


Figure 16.1 Overall reaction for formation of triphenylmethanol

The Grignard reagent (phenylmagnesium bromide) is prepared by the reaction of bromobenzene with magnesium as shown in Fig. 16.2:

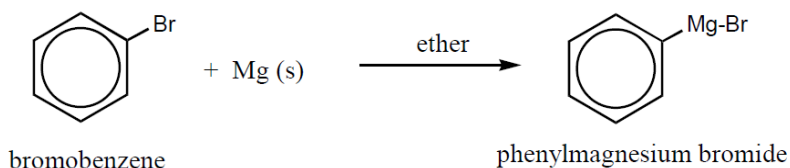


Figure 16.2 Formation of phenylmagnesium bromide from bromobenzene

This overall reaction to produce an alcohol is carried out in anhydrous diethyl ether and is sometimes difficult to initiate. Once the Grignard reagent has been formed, it behaves as a typical nucleophile and can attack a carbonyl group to form an intermediate magnesium salt (see Fig. 16.3). The latter may then be hydrolyzed to the desired alcohol.

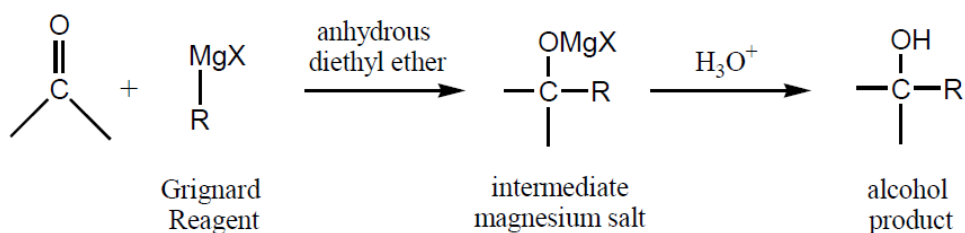


Figure 16.3 Formation of alcohols by hydrolysis of magnesium salt.

(R = 1°, 2°, or 3° alkyl, aryl or alkenyl; X = Cl, Br, or I)

Reaction of Grignard Reagents with Certain Functional Groups

Figure 16.4 below shows the type of products formed from the reaction of Grignard reagents with certain functional groups. Please note that **the reaction between an ester (see Fig. 16.1) and a Grignard reagent** is slightly more complicated than indicated in the above mechanism because of the ability of the ester to react with two mole equivalents of Grignard reagent rather than one.

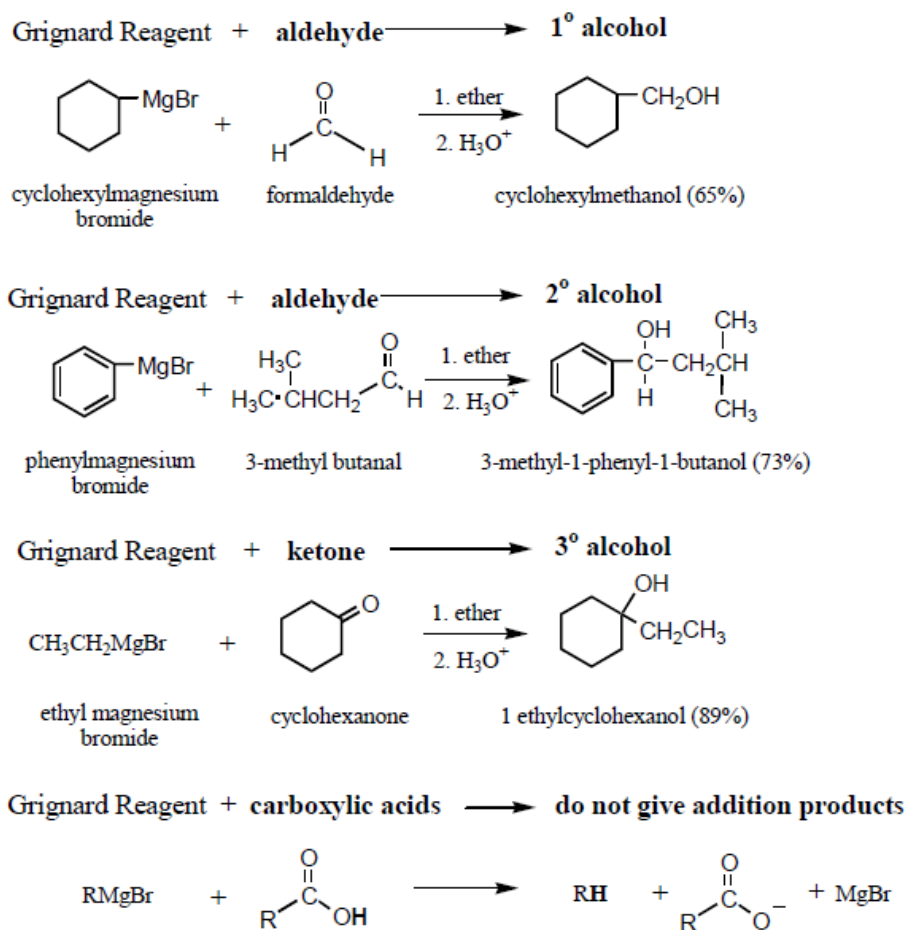


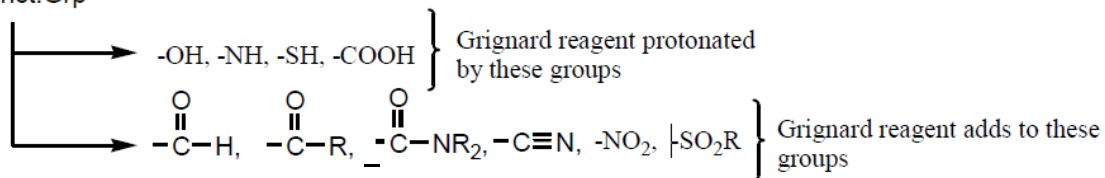
Figure 16.4 The reaction of Grignard reagents with certain functional groups

Severe Limitations of Grignard Reagents

1. The Grignard reagent cannot be prepared from an organohalide if there are other 'reactive' functional groups present in the molecule.

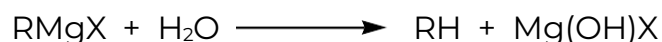
Alkyl halide with other functional groups

Br—alkyl—Funct.Grp



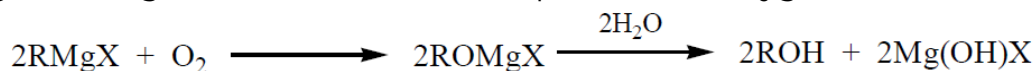
Note that bromobenzene is a suitable organohalide for preparation of a Grignard reagent.

- Grignard reagents are very sensitive to moisture and can only be prepared under anhydrous conditions.



This is overcome in this experiment by thoroughly drying the glassware prior to use and the use of anhydrous reagents (they are more expensive!).

- Grignard reagents are sensitive to the presence of oxygen



This is mostly overcome in this experiment by keeping the solvent warm during preparation of the Grignard reagent. The diethyl ether forms a thick 'vapour barrier' above the reaction mixture thereby reducing the diffusion of oxygen gas into the solution.

- Grignard reagents can, through a complex radical reaction, couple with themselves to form high molecular weight byproducts. It is the reason for biphenyl forming as the major byproduct in this experiment.

