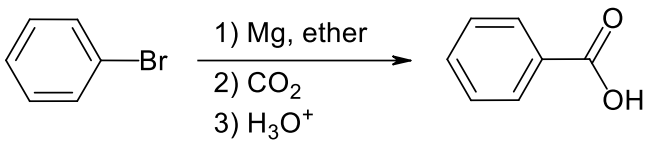
ORGANIC SYNTHESIS: BENZOIC ACID VIA A GRIGNARD REACTION

TECHNIQUES REQUIRED : Reflux with addition apparatus, rotary evaporation

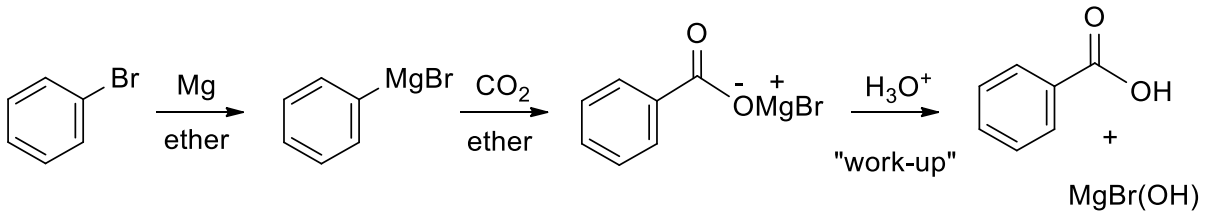
OTHER DOCUMENTS Experimental procedure, product spectra

INTRODUCTION

In this experiment you will synthesise benzoic acid using bromobenzene to prepare a Grignard reagent, which is then reacted with solid carbon dioxide, worked-up and purified to give the carboxylic acid. This sequence serves to illustrate some important concepts of practical synthetic organic chemistry : preparing and working with air and moisture sensitive reagents, the "work-up", extractions, apparatus set-up, *etc*. The synthesis utilises one of the most important type of reagents discussed in introductory organic chemistry, organometallic reagents, of which Grignard reagents are probably the most important at the introductory level.



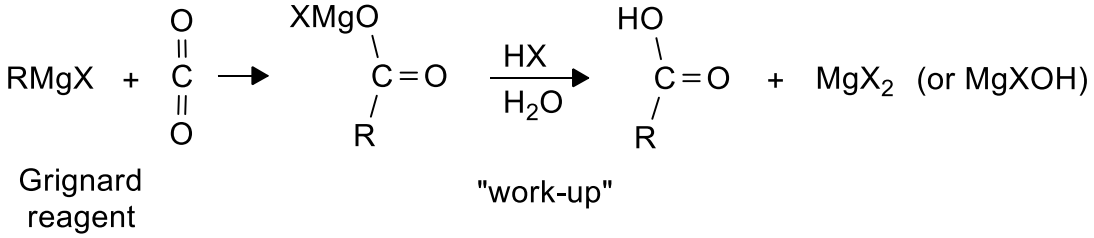
In this experiment, the **Grignard reagent** (an organomagnesium compound), phenylmagnesium bromide is prepared by reaction of bromobenzene with magnesium metal in diethyl ether (the solvent). The Grignard reagent will then be converted to benzoic acid using the reaction of the Grignard reagent with excess dry ice (solid CO_2) followed by a dilute aqueous acid "work-up" to neutralise the carboxylate to obtain the carboxylic acid:



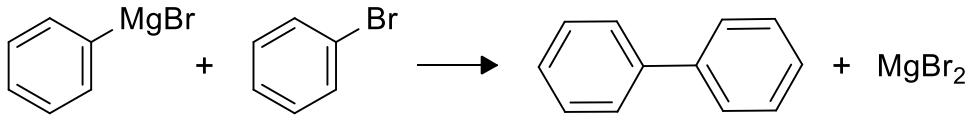
The aryl (or alkyl or vinyl) group of Grignard reagents behaves as if it has the characteristics of a carbanion so it is a source of **nucleophilic carbon** which can be utilised to make new C-C bonds. It is reasonable to represent the structure of the Grignard reagent as a partly ionic compound, $R^{\delta-}\ ....^{\delta+}MgX$. This partially-bonded carbanion is a very strong base and will react with acids (HA) to give an alkane:

Therefore any compound with suitably acidic hydrogens will readily donate a proton to destroy the reagent. Water, alcohols, terminal acetylenes, phenols and carboxylic acids are just some of the functional groups that are sufficiently acidic to bring about this reaction which is usually an unwanted side reaction that destroys the Grignard reagent.

The Grignard reagents typically function as a strong nucleophiles. A common application has the Grignard reagent adding to the electrophilic carbon of a "carbonyl group" - hence the reactions of Grignard reactions with aldehydes, ketones and certain carboxylic acid derivatives (especially esters) are very important reactions. Here, we can view carbon dioxide as two "back-to-back" carbonyl groups. The Grignard reagent reacts with the CO_2 to form an intermediate carboxylate salt which is not usually isolated. Instead, the intermediate carboxylate salt is neutralised and converted into the product during the "work-up" steps by addition of dilute aqueous acid to create the desired organic compound, the carboxylic acid.



In general, the "work-up" steps are simple acid or base neutralisations that are required in order to convert the initial polar (ionic) intermediate obtained from the reaction into the neutral organic product in a reasonably pure state. The “work-up” steps often neutralise any excess reagents and add acid or base as appropriate (*e.g.* a reaction that is carried out under basic conditions is usually neutralised with acid) to create the neutral product. Extraction steps may also be used to remove impurities (such as unreacted starting materials) or other by-products. The chief impurities in this Grignard reaction mixture include the hydrocarbon, biphenyl, formed by an unwanted coupling reaction:



This hydrocarbon by-product is easily removed from the main product, benzoic acid, due to the polarity differences and hence solubility differences as the hydrocarbon remains in the organic solvent ether during the extraction steps of the procedure.

REFERENCES

1. https://www.chem.ucalgary.ca/courses/351/Carey5th/Ch14/ch14-2-2.html
https://www.chem.ucalgary.ca/courses/351/Carey5th/Ch19/ch19-2-1.html