not give concordant results, especially when the volumes of the solution and the amounts of sodium cyanide were large.

Pure benzaldehyde must be used as a starting material and the weight must be corrected for the small amount of benzoic acid present or the value of K will appear larger than it actually is.

The solvent used in the most satisfactory method for preparing benzoin is 50% alcohol. The larger yield obtained when this solvent is used is due to the benzoin precipitating out of solution, thus allowing the reaction to go nearer to completion.

The senior author is investigating the equilibrium reached in the reversal of other similar reactions, the temperature coefficients, and the velocities of some of these reactions.

The authors desire to thank Dr. H. G. Deming for helpful suggestions made during the course of the investigation.

Summary

1. The benzoin condensation is a reversible process.

2. The equilibrium constant between benzaldehyde and benzoin at 79° is very nearly 0.245.

LINCOLN, NEBRASKA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

A NEW TYPE OF SYNTHESIS. I. THE REACTION BETWEEN HALOGEN-ALKYL SULFONATES AND ORGANOMAGNESIUM HALIDES

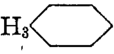
Preliminary Note

BY HENRY GILMAN AND N. J. BEABER

Received December 26, 1922

Introduction

There are but few reactive substances which exceed in importance the alkyl and aryl halides. This is particularly true from the viewpoint of synthetic chemistry because of the many classes of compounds prepared either directly or indirectly from such halogen-containing substances. The methods available to organic chemists for the introduction of halogens into compounds removed from the simpler types are very few in number and generally unsatisfactory in the sense that the yields are poor, the technique is involved, and the reactions are sometimes "unreliable" in the determination of molecular structures.

The present work is a preliminary account of a method which obviates to some extent these difficulties. It has been found that when organomagnesium halides are treated in ethereal solution with halogen-alkyl esters of aromatic sulfonic acids a smooth reaction takes place at the boiling point of ether, giving reasonably good yields of compounds which contain the halogen-alkyl group in place of the original MgX group, where X represents a halogen. The following is a typical reaction: CH_3$SO_2OCH_2CH_2Cl + RMgX = RCH_2CH_2Cl + CH_3$SO_2OMgX.

Primarily the problem had its origin in the need of reagents for studies concerned with some relationships between physiological action and chemical constitution, and some theoretical considerations of new classes of organic compounds. It is the immediate result of several unpromising experiments which were carried out in order to prepare in reasonable quantity and at low cost various alkyl and aryl sulfates, substituted as well as unsubstituted.

The reaction between sulfonic esters and related compounds and organomagnesium halides is not new. In a recent paper by Gilman and Hoyle[1] on the reaction between organomagnesium halides and diethyl sulfate, attention was called to the studies of Werner and Zilkens[2] and of Houben[3] on the preparation of a few hydrocarbons by the action of the Grignard reagent on dimethyl sulfate. Before that time Moureu[4] mentioned the apparently discouraging results with some reactions between the Grignard reagent and diethyl sulfate, and also methyl benzene sulfonate. He described his reactions as taking place with great vigor, and mentioned the formation of very volatile sulfur products of disagreeable odor. A natural inference to be made from his abbreviated account is that the reactions were essentially without value. Work already completed[1] and now in prosecution discloses none of the phenomena he has described; however, it is quite possible that neither the experimental conditions nor the Grignard reagents used have been duplicated in the two laboratories.

Ferns and Lapworth[5] in a study of the preparation and properties of sulfonic esters have made some generalizations on the reaction between the Grignard reagent and ethyl ethanesulfonate, menthyl benzenesulfonate, bornyl toluene-*p*-sulfonate and ethyl toluene-*p*-sulfonate. With esters of aliphatic sulfonic acids the chief product of reaction is a sulfone; however, contrary to the work of Strecker,[6] they obtained a small quantity of ethyl benzene when ethyl ethanesulfonate was treated with phenylmagnesium bromide. The menthyl and bornyl sulfonates appear to give as chief products the corresponding unsaturated hydrocarbons, menthene and camphene. Ethyl toluene-*p*-sulfonate and phenylmagnesium bromide gave mainly ethyl benzene.

Because of the apparent promise of work now being done in this Laboratory, rather extensive studies are being made of the reaction between organomagnesium halides and a wide variety of substituted as well as unsubstituted aliphatic and aromatic esters of sulfonic acids. A paper which is to appear shortly will contain a comprehensive account of the introduction of halogen-alkyl groups into organic compounds.

---

[1] Gilman and Hoyle, THIS JOURNAL, **44**, 2621 (1922).

[2] Werner and Zilkens, *Ber.*, **36**, 2116 (1903); **37**, 488 (1904).

[3] Houben, *ibid.*, **36**, 3083 (1903). Also Werner, *ibid.*, **36**, 3618 (1903).

[4] Moureu, *Compt. rend.*, **132**, 837 (1901).

[5] Ferns and Lapworth, *Proc. Chem. Soc. London*, **28**, 18 (1912); *J. Chem. Soc.*, **101**, 273 (1912).

[6] Strecker, *Ber.*, **43**, 1131 (1910).

Procedure

Inasmuch as several steps are necessary in order to procure the needed halogen-alkyl compounds, an optimum procedure desirable in such cases is to effect the successive reactions in the same flask, as in the work on diethyl sulfate.[1] Several experiments indicated that this was possible without any apparent detrimental effect on the yield or the purity of the product. First, the reaction between phenylmagnesium bromide and β-chloro-ethyl-*p*-toluene sulfonate gave approximately the same yield of β-chloro-ethyl-benzene, irrespective of the order of addition. Second, β-chloro-ethyl-*p*-toluene sulfonate underwent apparently no reaction with magnesium under conditions simulating those ordinarily used in Grignard reactions. Third, γ-chloropropyl benzene was not reduced in ethereal solution when dil. sulfuric acid was added to a mixture containing several equivalents of magnesium.

Slow addition of the ethereal solution of halogen-alkyl sulfonate to the organomagnesium halide produced no evident heat evolution in most cases. The reaction mixture generally thickened appreciably and a white voluminous solid formed. To complete the reaction, the mixture was refluxed on a water-bath for about 1 hour, stirring being continued. In some cases, it may be desirable to commence refluxing with the first addition of ester.

When reaction was completed, dil. sulfuric acid was slowly added to the cold mixture. Inasmuch as a considerable volume of water is sometimes required to effect complete solution of the reaction products, it is recommended that the last additions of water or dil. acid be made after the mixture has been transferred to a large flask. The upper ethereal layer containing the desired compound is then washed with dil. alkali and water, dried, and distilled in a vacuum after boiling off the ether.

Experimental Results

The β-chloro-ethyl-*p*-toluene sulfonate was prepared after the method described by Clemo and Perkin.[7] Although the yield described by them was not quite equalled, it was found that significant improvements were effected by using freshly distilled toluene-*p*-sulfonyl chloride and by the direct application of heat. A single run of sulfonyl chloride and trimethylene chlorohydrin gave a 57% yield of γ-chloropropyl-*p*-toluene sulfonate.

These two reagents were treated with several organomagnesium halides, and the yields, on the whole, compare quite favorably with those given by diethyl sulfate with corresponding compounds. Of the compounds so far investigated, butylmagnesium bromide was the only one to give a significantly low yield. However, minor alterations of procedure have

---

[7] Clemo and Perkin, *J. Chem. Soc.*, **121**, 642 (1922).

made it possible to improve the yield in this case, and a study of the optimum conditions of this reaction is in progress. The following table includes some of the results thus far obtained. Equivalent molecular quantities were used in each case, and all entries excepting the last refer to experiments with β-chloro-ethyl-*p*-toluene sulfonate.

Reagent	Product	Yield %
Bromobenzene	β-chloro-ethyl benzene[8]	36
Benzyl chloride	γ-chloropropyl benzene	59
Phenyl-acetylene	β-chloro-ethyl-phenyl-acetylene[9]	75
$C_6H_5COOMgBr$	β-chloro-ethyl benzoate[10]	5
Bromobenzene and γ-chloropropyl-*p*-toluene sulfonate[11]	γ-chloropropyl benzene	31

Summary

1. A preliminary study has been made of the reaction between various organomagnesium halides and halogen-alkyl esters of *p*-toluene-sulfonic acid.

2. In all cases the MgX group has been replaced by the halogen-alkyl group.

AMES, IOWA

---

[8] The derivative used to identify this compound completely was hydrocinnamic acid. This was prepared by passing carbon dioxide into the Grignard reagent obtained from the β-chloro-ethyl benzene.

[9] Phenyl-acetylene was first treated with 1.1 equivalents of ethylmagnesium bromide, and this reaction as usual was slow and incomplete, a large quantity of unchanged phenyl-acetylene being recovered subsequently. The yield of β-chloro-ethyl-phenyl-acetylene is based on the quantity of phenyl-acetylene which had entered into reaction. Like many halogen-alkyl compounds of high boiling point, it underwent a slight decomposition when distilled under atmospheric pressure at 245–246°, liberating hydrogen chloride.

[10] Halogen-alkyl esters are more conveniently prepared by other methods. The only object of this experiment was to determine whether the MgX group attached to oxygen could suffer *any* replacement by the chloro-ethyl group. A grouping of this type is sluggish in its reactivity towards dimethyl and diethyl sulfates.

[11] *Properties:* b. p., 216–219° (17 mm.); n^{20}, 1.5230; d_4^{20}, 1.2674. *Analysis.* Calc. for $C_{10}H_{13}O_3ClS$: Cl, 14.27. Found: 14.16.