could be used or the solution diluted with enough pure acetic anhydride to bring the concentration of the acetic acid to approximately 5%.

The last column of Table II shows that when from 1 to 4% of acetic acid is present the value [Velocity constant × concn. acetic acid] equals a constant. In other words the retardation of this reaction is directly proportional to the concentration of acetic acid. When more acetic acid is added this relationship does not hold.

Summary

1. A method for preparing acetic anhydride of a high degree of purity is described and certain physical properties of the anhydride have been determined.

2. The effect of different concentrations of acetic acid upon the rate of decomposition of formic acid in acetic anhydride solution, using strychnine as a catalyst, has been determined. This forms a basis for the quantitative analysis of acetic anhydride for acetic acid when 1 to 5% of this impurity is present.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

STUDIES CONCERNING THE DIRECT PREPARATION OF ORGANOBERYLLIUM HALIDES[1]

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Introduction

Much of the importance of organometallic compounds in synthetic work is confined to those compounds formed from metals of the second group of the periodic system. Zeltner,[2] from a study of many organometallic compounds, has called attention to two apparently general rules concerning the reactivity of such compounds which have each of the ordinary valences of the metal satisfied by an alkyl or aryl group. First, in a given group of metals having the same radicals attached to the metal, that organometallic compound with the metal of lowest atomic weight is most reactive. Second, with a given metal, that organometallic compound which has the lightest radicals is most reactive.

If these generalizations are true, it follows that one should expect an organoberyllium compound having alkyl groups of low molecular weight to be most reactive in a group which already contains several organometallic types of high reactivity. If organoberyllium halides could be prepared and if they should exhibit this reactivity, they might make pos-

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[1] An abstract of a paper presented at the Intersectional Meeting of the American Chemical Society held at Urbana, Illinois, May 5, 1923.

[2] Zeltner, *J. prakt. Chem.*, 77, 393 (1908).

sible a number of reactions which cannot be realized with the ordinary Grignard reagent of the general formula RMgX.

The organometallic halides or "mixed organometallic compounds," largely because of their ease of preparation, convenience in handling, and high reactivity, have displaced almost completely from synthetic work the longer known, simple organometallic compounds which have no halogen directly attached to the metal.

Simple organoberyllium compounds such as beryllium diethyl and dipropyl have long been known.[3] No mention, however, is to be found in the literature of an organoberyllium halide. Several investigators have attempted to prepare such compounds directly. Grignard[4] tried without success to bring metallic beryllium into reaction with a simple alkyl halide. Simonis[4] tried methyl iodide, bromobenzene, and benzyl bromide in absolute ether, using iodine as a catalyst, but could get no one of the compounds to react with his beryllium. Kamm[4] tried methyl iodide, ethyl iodide and ethyl bromide and, using freshly prepared Grignard reagent as a catalyst, likewise failed to bring about a reaction.

The following series of unsuccessful attempts was made to prepare organoberyllium halides.

Experimental Part

The metallic beryllium used was obtained from five different sources. Two samples came from foreign manufacturers, a third from Dr. Simonis of the Charlottenburg Technische Hochschule who sent a sample of the beryllium he had used, a fourth from Dr. Hopkins of the University of Illinois, and a fifth from Dr. Stock of the Kaiser Wilhelm-Institut. Although all samples have been shown by analysis to contain at least 98% of beryllium, that provided by Dr. Stock is claimed[5] to be the purest beryllium for which letters patent have been issued; it has been shown by analysis to contain more than 99% of beryllium.

All of the other chemicals used, particularly the ether and other solvents and the various alkyl and aryl halides, were prepared freshly in a very high state of purity. The apparatus was periodically tested in the sense that Grignard reagents were readily prepared in it, using both magnesium turnings and powder, various halides and various solvents.

The factors varied in the many studies were the halides, solvents, temperature, time of heating, and catalysts. The halides used were methyl iodide, ethyl iodide, benzyl bromide, bromobenzene, chlorobenzene and α-bromonaphthalene. In addition to the commonly used solvent, anhydrous ether, anisole, benzene and β-ethoxy-naphthalene were tried. Using the bromonaphthalene and ethoxy-naphthalene, the temperature of

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[3] Cahours, *Compt. rend.*, **76**, 1383 (1873).

[4] Private communication.

[5] U. S. pat., 1,427,919, Sept. 5, 1922.

one series of experiments was as high as 245–250°. The time allowed for some runs was as much as two weeks, and in the shorter runs, all of which extended over 12 hours, the material was stirred almost continuously. Conventional catalysts such as iodine, bromine, dimethyl aniline, freshly prepared Grignard reagent (sometimes directly prepared in the reaction mixture) were used repeatedly. Ethyl acetate, which is so useful in the preparation of organozinc iodides, was tried as a catalyst in one experiment.

In some experiments sublimed beryllium iodide, freshly prepared in a vacuum by subliming iodine onto heated beryllium, was used. Also, to overcome the objection that the metal might be coated with an oxide, it was shaken before use in one experiment with very dilute, pure nitric acid, and then while gas evolution continued was quickly filtered, washed, dried and used directly. In one experiment the reaction mixture was exposed to X-rays.[6]

As a final proof that conditions were as nearly satisfactory as possible for a reaction, some magnesium was added at the end of every experiment, either to a part or the whole of the reaction mixture, and in every case a reaction took place between the magnesium and halide.[7]

In no experiment was there any evidence of a reaction between the beryllium and halide.

Conclusion

The experiments outlined are sufficiently general to indicate that metallic beryllium does not enter directly into reaction with halides to form organoberyllium halides. There are, however, several methods for the indirect preparation of organoberyllium halides, and a study is being made of such reactions.

The author wishes to acknowledge gratefully the kindness of Doctors Grignard, Simonis, Stock, Kamm, and Hopkins for the help they have given in supplying some of the metal used, and for the unpublished accounts of their work.

Summary

A series of unsuccessful attempts has been made to bring metallic beryllium into reaction with a variety of halides in an effort to prepare organoberyllium halides.

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[6] Work done by Mr. B. Toubes.

[7] In connection with another study, the results of which will be published shortly, a detailed account will be given of a general test for some organometallic halides.