[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

ORGANOBERYLLIUM HALIDES

BY HENRY GILMAN AND F. SCHULZE

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Introduction

Durand[1] has recently described the preparation of methylberyllium iodide by the action of finely-divided beryllium upon methyl iodide in ether, using a trace of mercuric chloride as a catalyst. Gilman[2] had previously found it impossible to prepare organoberyllium halides directly. More recently, Gilman and Schulze[3] have prepared these organometallic halides by indirect methods starting with beryllium dialkyls.

We have now attempted to prepare these substances following Durand's method, but without success. By the use of revised directions, in particular prolonged heating at elevated temperatures, we have succeeded in preparing organoberyllium halides directly. The methylberyllium iodide we obtained was, contrary to Durand's experiences, very soluble in ether. His method of purification, by ether washing, should, therefore, have completely removed the compound leaving no organoberyllium iodide for analysis. Finally we have shown that the gas Durand obtained by the hydrolysis of his reaction product was presumably hydrogen and not methane. Accordingly, our unavoidable conclusion is that Durand's product was not methylberyllium iodide.[4]

Experimental Part

When Durand's directions for the preparation of methylberyllium iodide were carried out in detail (using 0.091 g., 0.01 mole, of beryllium and corresponding amounts of methyl iodide, mercuric chloride and ether) a small amount of gray material remained suspended in the ether and most of the metal rested unchanged on the bottom of the flask. After removal of the ether by slow evaporation, the residue was washed twice with anhydrous ether leaving the grayish material and unused metal. The residue was analyzed after displacing all the air by carbon dioxide. Hydrolysis by dilute hydrochloric acid gave 216.5 cc. instead of the calculated 224 cc. of gas. Analysis by explosion with oxygen showed the gas to be pure hydrogen, and there was no trace of carbon dioxide. Qualitative analysis proved the absence of iodine in the "reaction product."

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[1] Durand, *Compt. rend.*, **182**, 1162 (1926).

[2] Gilman, THIS JOURNAL, **45**, 2693 (1923). References to all earlier work are contained in this article.

[3] Gilman and Schulze, *J. Chem. Soc.*, **1927**.

[4] His analogies with the related beryllium diethyl and magnesium diethyl are based in large part on Cahours' work with these compounds and we have shown much of Cahours' work to be incorrect (see ref. 3 and Gilman and Schulze, THIS JOURNAL, **49**, 2328 (1927) for an account of magnesium diethyl).

The local reaction reported by Durand is undoubtedly independent of the presence of methyl iodide or any other of the alkyl and aryl halides tried by us. This was shown by a wide variety of experiments in which beryllium powder was treated with varying quantities of mercuric chloride in the presence of ether and with or without the addition of various RX compounds. A local reaction invariably took place between the metal and mercuric chloride and a light gray solid formed. Larger quantities of mercuric chloride gave increasing amounts of the gray solid and free mercury appeared to deposit on the beryllium, probably forming an amalgam. Undoubtedly, the only reaction that occurred was a simple displacement of the mercury by the beryllium, inasmuch as free mercury was formed and in several cases the liquid etherate of beryllium chloride was noted.

The small amount of mercuric chloride (0.1 g.) taken by Durand would use up an extremely small quantity of the beryllium (9.1 g. of beryllium being equivalent to 271.5 g. of mercuric chloride) so that his gas analysis would hardly be affected. It is obvious that treatment with dilute hydrochloric acid would liberate the same volume of gas, regardless of whether the metal was essentially unchanged or had formed a quantitative yield of methylberyllium iodide.

Temperature.—No methylberyllium iodide is formed when 0.091 g. (0.01 mole) of finely-divided beryllium,[5] 1.4 g. (0.01 mole) of methyl iodide, 15 cc. of ether and a trace of mercuric chloride are shaken in a sealed test-tube at room temperature for one week.

Heating at 80–90° for fifteen hours was generally necessary to prepare appreciable quantities of the organoberyllium halide. The reaction product was a slightly turbid solution, resembling somewhat the solution of a Grignard reagent, although it was generally lighter in color than many RMgX solutions. The greater part of the metal invariably remained unattacked and rested on the bottom of the tube. In addition to the metal, there was usually present a small quantity of black material in the form of small scales or definite particles. This material was somewhat lighter than the metal, settling less rapidly when the tubes were agitated.

In many experiments the reagents were heated at 80–90° for periods in excess of fifteen hours and up to one week. Judging by the depth of the color test recommended by Gilman and Schulze[6] for RMgX and some other organometallic compounds, there was no appreciable increase in yield with these extended periods of heating. Incidentally, these experiments served to show that prolonged heating did not destroy the organoberyllium compounds. Only a few experiments were carried out at higher temperatures and positive tests were obtained after heating to 150°.

Catalysts.—Mercuric chloride, used by Durand, gave the best results with all the alkyl and aryl halides that were investigated. The other mercuric halides may be used but they are not as satisfactory. Beryllium chloride is next to mercuric chloride in order of effectiveness. Mercury and iodine together, iodine and bromine are about

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[5] The beryllium used in this study was obtained from the Beryllium Corporation of America. Their analysis showed it to contain more than 99.5% of beryllium, with about 0.2% iron, 0.1% silicon and no aluminum.

[6] Gilman and Schulze, THIS JOURNAL, **47**, 2002 (1925).

of equal value. It was disappointing to find that a finely-divided beryllium-copper alloy containing about 12% of copper and activated by heating with iodine in an evacuated, sealed tube gave but moderately successful results, inasmuch as Gilman, Schulze and Peterson[7] found that a magnesium-copper alloy containing 12.75% of copper is superior to Baeyer's activated magnesium in the preparation of some Grignard reagents that are formed with difficulty.

Solvents.—Ethyl ether was the only solvent used and it was dried by a sodium-potassium alloy. When beryllium was heated with methyl iodide and mercuric chloride at 80–90° for one week with no ether present a light gray solid and clear liquid resulted. This reaction product gave a positive color test directly without the usual necessity of heating until fumes were evolved.[3,8]

No reaction occurs when methyl and ethyl iodides are treated as above, but heated only for fifteen hours. Furthermore, beryllium with methyl or ethyl iodide, but no catalyst, showed no signs of having reacted after heating at 80–90° for several days. This is of interest in connection with Cahours' early work.[4,9]

Preparation of Methyl- and Ethylberyllium Iodide.—In general, only small quantities of materials were prepared at one time because of the difficulty and danger involved in the heating of large volumes of ether in sealed tubes. Convenient reaction vessels may be prepared from the commercially available small, heavy sealed bottles used for the shipment of low-boiling liquids.

About 0.5 g. of powdered beryllium, 0.2–0.5 g. of mercuric chloride, 5 cc. of the organic halide and 25 cc. of ether are placed in the bottle. The neck of the bottle is drawn down to a fine capillary, small enough so that particles of beryllium cannot pass through, and the end of the capillary is sealed. The bottle is placed inside a can, which acts as a shield in case of explosion, and this is set on a steam hot-plate. After maintaining a temperature of 80–90° for at least fifteen hours, the bottle is cooled and its capillary end is first inserted in a 50cc. Erlenmeyer flask and then broken by pressing it against the walls of the flask. The high pressure in the bottle forces the liquid out and the unused metal is retained by the capillary. It is advisable to wrap the bottle in a towel in order to guard against the danger of an explosion. If the bottle has a sufficiently long neck, it may be used again by adding a fresh portion of alkyl halide, ether and mercuric chloride to the residual metal, then sealing and heating as before.

Preparation of Other Organoberyllium Halides.—Ethylberyllium bromide and *n*-butylberyllium iodide were prepared in the presence of ether, with mercuric chloride or beryllium chloride or free bromine as a catalyst. Here it was necessary to heat at 80–90° for fifteen hours.

Phenylberyllium iodide gave a positive test when prepared in the presence of mercuric chloride after heating at 80–90° for fifteen hours. This experiment was not duplicated in another run. However, the phenyl-

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[7] A preliminary account of this work was presented at the Philadelphia, 1926, meeting of the American Chemical Society. The alloy has been referred to in several later studies. (See Gilman and Harris, THIS JOURNAL, **49**, 1827 (1927), ref. 10.)

[8] Methylberyllium iodide gives a positive color test when the solution is allowed to stand for ten to fifteen minutes with Michler's ketone before hydrolysis and the addition of the iodine-glacial acetic acid solution.[6] The beryllium dialkyls, formed by heating alkylberyllium halides, give a color test at once. The slower reaction of alkylberyllium halides is not unique, inasmuch as some tertiary alkylmagnesium halides also require up to five minutes' standing before a satisfactory color test is obtained. (See Gilman and Schulze, *Bull. soc. chim.*, **1927**.)

[9] Cahours, *Ann. chim. phys.*, [3] **58**, 5 (1860).

beryllium iodide was readily prepared by heating at a more elevated temperature (150 or 175°) with either mercuric chloride or beryllium chloride as a catalyst.

Tert.-butyl chloride and bromide appeared to have reacted when heated at 80–90° for fifteen hours with mercuric chloride as a catalyst. However, the products in both cases gave negative tests.[8] Under like conditions, benzyl bromide and *n*-butyl chloride showed no evidence of reaction.

Reactions of Alkylberyllium Halides.—All of these compounds are decomposed by water, with the formation of the corresponding hydrocarbon.

The ethereal solutions do not fume in the air. However, by driving off the ether a liquid residue results and this on further heating gives off dense white fumes, probably of beryllium oxide. This application of heat by a small luminous flame converts the alkylberyllium halide to a beryllium dialkyl. Beryllium dimethyl[3] was definitely identified in this manner when methylberyllium iodide was heated. The following equilibrium is quite probable under certain conditions

$$2RBeX \rightleftharpoons BeR_2 + BeX_2$$

inasmuch as alkylberyllium halides are formed when beryllium dialkyls are treated with a beryllium halide. Some experiments on the heating of RMgX compounds indicate that the same may be true with organomagnesium compounds.

When carbon dioxide was bubbled through an ethereal solution of methylberyllium iodide for three hours, the solution still gave a positive test and no acetic acid was found after hydrolysis.

The color test with Michler's ketone is developed only after ten to fifteen minutes' standing prior to hydrolysis.[8] Beryllium dialkyls give the test at once.

Acetanilide is formed from methylberyllium iodide and phenyl isocyanate. This is a standard reaction for organomagnesium, calcium and barium halides as well as for beryllium and magnesium dialkyls.

In general, the alkylberyllium halides are less reactive than the beryllium dialkyls and the RMgX compounds.

Summary

Organoberyllium halides could not be obtained directly by procedure given in the literature but were produced in the presence of various catalysts by prolonged heating in sealed tubes at temperatures up to 150°.

The properties of the methylberyllium iodide were markedly different from those given by Durand, so that our conclusion is that his product was not this substance.

Methyl- and ethylberyllium iodides, ethylberyllium bromide, *n*-butyl-

beryllium iodide and phenylberyllium iodide have been prepared and their reactions investigated.

AMES, IOWA

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF HARVARD UNIVERSITY AND THE UNIVERSITY OF ILLINOIS]

THE PREPARATION AND BASE STRENGTHS OF SOME AMINES

BY WALLACE H. CAROTHERS, C. F. BICKFORD AND G. J. HURWITZ

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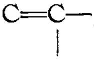
The measurements here recorded were made for the purpose of supplementing existing data on the base strengths of amines. The data obtained are summarized in the following table.

TABLE I

DATA ON BASE STRENGTHS OF AMINES

Formula	Neutral. equiv., calcd.	Neutral. equiv. found	$K_{\mathrm{hydr.}} \times 10^{10}$	$K_B \times 10^5$
			t = 25°	
($C_6H_5NH_2$)	...	...	(2.17×10^5)[1]	(4.6×10^{-5})[1]
$C_6H_5CH_2NH_2$	107.1	107.3	4.26	2.35
$C_6H_5(CH_2)_2NH_2$	121.1	...	1.48	6.78
$C_6H_5(CH_2)_3NH_2$	135.1	135.1	0.63	15.9
$C_6H_5(CH_2)_4NH_2$	149.2	149.4	.40	24.8
$C_6H_5(CH_2)_5NH_2$	163.2	163.1	.33	30.6
o-$CH_3C_6H_4CH_2NH_2$	121.1	121.5	5.89	1.70
m-$CH_3C_6H_4CH_2NH_2$	121.1	121.8	4.24	2.40
p-$CH_3C_6H_4CH_2NH_2$	121.1	121.1	3.98	2.55
o-$CH_3OC_6H_4CH_2NH_2$	137.1	137.9	1.81	5.56
m-$CH_3OC_6H_4CH_2NH_2$	137.1	137.5	6.46	1.56
p-$CH_3OC_6H_4CH_2NH_2$	137.1	137.2	3.10	3.22
$C_6H_5CH_2NHCH_3$	121.1	121.3	2.63	3.80
$C_6H_5CH_2NHCH_2CH_3$	135.1	134.8	2.10	4.75
$C_6H_5CH_2NHCH_2CH_2CH_3$	149.1	149.1	2.40	4.18
$C_6H_5CH_2CH_2NHCH_3$	135.1	135.6	0.75	13.9

The first five amines constitute a series of the type $R(CH_2)_xNH_2$ where R is the negative phenyl group. The data are of some interest in connection with the transmission of polar effects through a chain of atoms. Data are available on several similar series of acids and it is well known that the effect of the substituent R on the dissociation of the acid diminishes continuously with the increasing values of x. Where R is $-CH{=}CH$, however, the dissociation constants appear to alternate with increasing values of x. Data on the acids $C_6H_5(CH_2)_xCOOH$ are not available, but since phenyl contains the group  $\mathrm{C{=}\underset{|}{C}{-}}$, there was some possibility that alternation might be observed in the series of amines here under discussion.

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[1] Lunden, *Z. physik. Chem.*, **54**, 532 (1906).