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Organometallic compounds of group II

Ferdinand Schulze

Iowa State College

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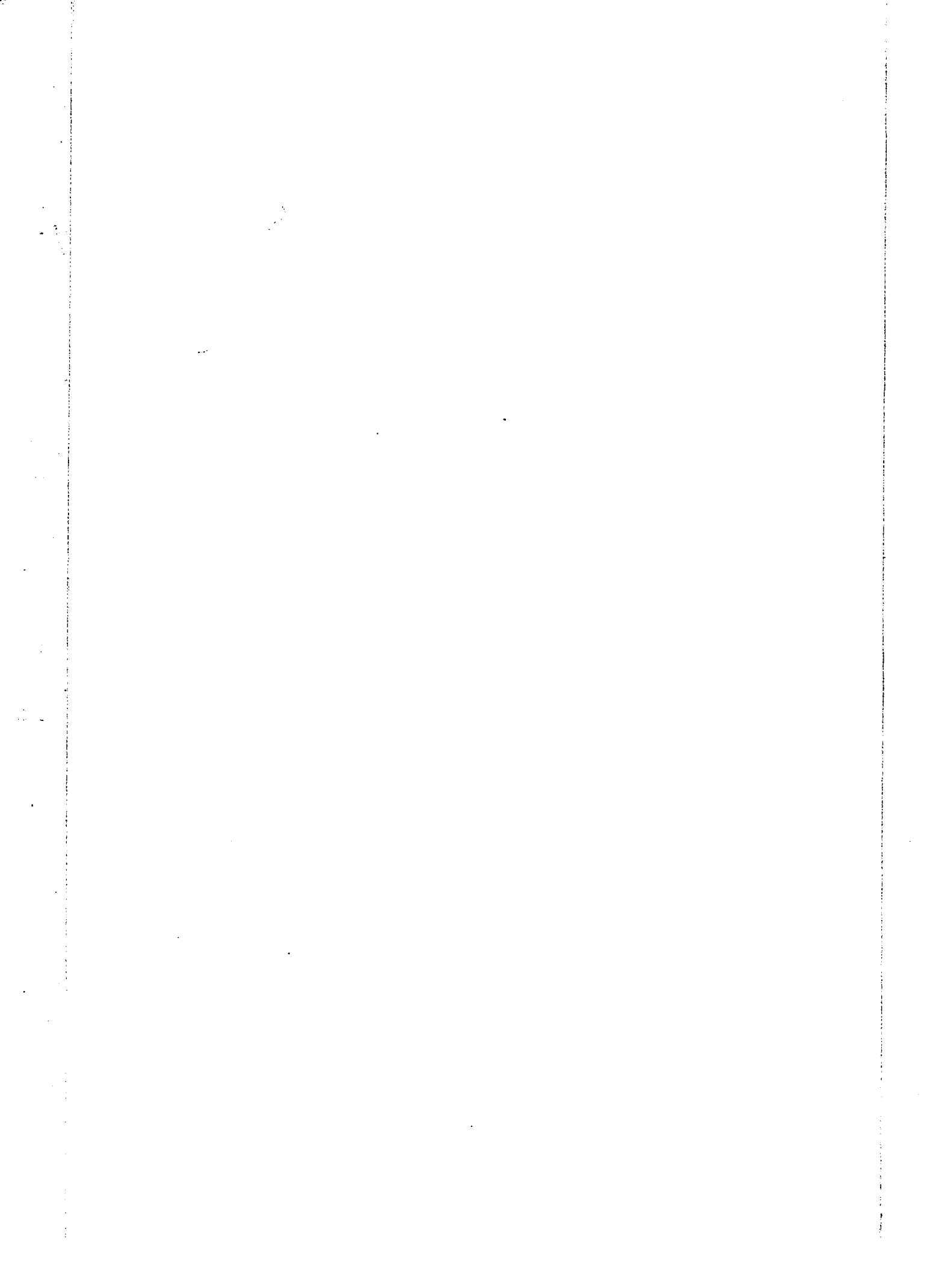
ORGANOMETALLIC COMPOUNDS OF GROUP II

A Thesis Submitted

to the Graduate Faculty in Candidacy

for the Degree of

DOCTOR OF PHILOSOPHY

by

Ferdinand Schulze

Major Subject: Organic Chemistry

Approved:

In Charge of Major Work

Head of Major Department

Graduate Dean

Iowa State College

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PART I

ORGANOCALCIUM IODIDES

INTRODUCTION

In connection with studies on the mechanism of some re-
actions involving organomagnesium halides it is necessary to
replace the -MgX group of the intermediate compound by another
in order to get a compound that lends itself to ready identi-
fication. Unfortunately this is not always possible. Accord-
ingly a study has been made of the related organocalcium io-
dides in order to determine whether the -CaI group is more suit-
able for such replacements than is the -MgX group.

Beckmann[1] has made the only extensive study of organocalcium
halides. Dufford, Nightingale and Calvert[2] investigated the
luminescence of phenylcalcium and ethylcalcium iodides, and
Gilman and Pickens[3] used phenylcalcium iodide in a study of the
mechanism of the reduction of azobenzene by organometallic hal-
ides.

A number of experiments have shown that the organocalcium
halides are generally devoid of any promise in reactions that
have made the organomagnesium halides so useful. First, the
formation of organocalcium halides appears to be restricted to

1. Beckmann, Ber., 38, 904 (1905).
2. Dufford, Nightingale and Calvert, J. Am. Chem. Soc. 47, 95 (1o25)
3. Gilman and Pickens, J. Am. Chem. Soc., 47, 2406 (1925)

iodides. Second, only primary alkyl iodides undergo reaction
with calcium. Even in this limited category there is an exception, for benzyl iodide gave no positive test to indicate the
formation of benzylcalcium iodide. Third, the reaction between
the RI compound and calcium is quite sluggish and irregular and
not always certain. Fourth, the yields of organocalcium iodides
are far from satisfactory. This is due in part to a pronounced
coupling side reaction leading to the formation of R-R compounds.
Fifth, the organocalcium iodides are less reactive generally than
the corresponding organomagnesium halides.

Contrary to the results of Beckmann[1] the organo-calcium
iodides are not sparingly soluble in ether. The solid compound
invariably deposited during the preparation of organocalcium
iodide is not the organometallic halide. Instead it is very
probably the di-etherate of calcium iodide.

EXPERIMENTAL

PREPARATION OF ORGANOCALCIUM IODIDES

The start and progress of reaction between calcium and
iodide varies with the kind of calcium and the degree of fineness. A variety of rasped calcium obtained from Kahlbaum was
somewhat less active than shavings freshly turned from sticks
of calcium. Even a given type of calcium gave irregular results, depending in large part on exposure to the atmosphere.
The material was always covered, prior to use, with kerosene.

However, even such covered calcium tarnished when the containers were loosely stoppered. The tarnished material entered very sluggishly into reaction with the iodides and was, therefore, not used.

It is necessary to use a higher concentration of iodine in ether to catalyse reactions with calcium than is needed with magnesium. The beginning of reaction between calcium and the organic iodide is shown by the disappearance of the free iodine used to catalyse the reaction, followed by the formation of a light grey or white precipitate. At times the reaction is brisk enough to cause the ether to reflux gently. These changes cannot be taken as absolute criteria for the formation of organocalcium iodides, inasmuch as the RCaI compounds appear to have a pronounced tendency to couple with the excess RI compound that is generally present. The color test with Michler's ketone, previously described by Gilman and Schulze[4], is reliable.

The reaction between calcium and the RI compound in ether can be carried out in the conventional three-necked flask provided with a mechanical stirrer, or the reactants can be sealed in a glass container that is shaken mechanically at room temperatures. The latter arrangement offers certain advantages in some preparations. Reaction between ethyl iodide in ether and calcium started in various experiments over a time range of 15 minutes to 6 hours. n-Butyl iodide started to react after

4. Gilman and Schulze. J. Am. Chem. Soc., 47, 2002, (1925)

10 hours, and in one experiment after 48 hours. However, the same halide when shaken in a sealed tube gave a positive test[4] after 2 hours. n-Octyl iodide gave a positive test after shaking for 24 hours in a sealed glass container. Iodobenzene, when stirred with ether, a little iodine and calcium in a three-necked flask gave a positive test in some cases after 2 hours and in others up to 7 1/2 hours. In one experiment when stirring was not used, a positive test was only obtained after 72 hours.

Ethyl bromide, iso-propyl iodide, tert.-butyl iodide, benzyl bromide and benzyl iodide gave no positive tests after shaking with calcium. The tert.-butyl iodide underwent a reaction but there was no positive test for the corresponding organocalcium iodide. Benzyl iodide when shaken in a sealed bottle for 2-3 weeks also underwent a reaction but gave no positive test.

It was hoped that the secondary reaction between RCaI and RI compounds could be overcome by removing the organocalcium halide as fast as it formed. For this purpose, advantage was taken of the very suggestive experiments made by Gilliland and Blanchard[5]. They prepared phenylmagnesium bromide by allowing an etheral solution of bromobenzene to descend through a column of magnesium turnings, the solution being highly diluted, before reaching the column, by the ether condensed from the vapors of the solution boiling in the receiving flask. In this manner there is a minimal contact between the organometallic halide and the organic halide from which it prepared. However the same principle

5. Gilliland and Blanchard, J. Am. Chem. Soc., 48, 410 (1926)

when extended to the preparation of ethylcalcium iodide was found to be unsuccessful. When ethyl iodide was percolated through a column of calcium shavings contained in a tube 20 cm. long and 1.5 cm. in diameter the reaction could only be started by using a concentrated solution of iodide in ether, and once started it proved difficult of control. When the solution was less concentrated with respect to ethyl iodide, the reaction stopped altogether. And, when the solution was sufficiently concentrated to insure a continuous reaction, very little ethylcalcium iodide formed,--probably as a result of the above mentioned coupling reaction. A further difficulty in the use of the column of calcium is the marked clogging due to the deposition of the di-etherate of calcium iodide. Quite probably there is an effective concentration of ethyl iodide to warrant the use of the column, but such optimal conditions were not further investigated.

ETHYLCALCIUM IODIDE

The white precipitate that forms when calcium reacts with ethyl iodide in ether was analysed by Beckmann[1], and he concluded that it was a mono-etherate of ethylcalcium iodide, $C_2H_5CaI \cdot (C_2H_5)_2O$. This formula is very probably incorrect, for apparently the same compound is formed when calcium undergoes reaction with any alkyl iodide. In no case did it give a positive color test[4] for an organocalcium iodide after being filtered and washed with anhydrous

ether. When organocalcium iodides were shown to be present by the preparation of characteristic derivatives, the perfectly clear supernatant liquid always gave a positive color test whereas the precipitate never gave a test. Evidently, the few organocalcium iodides that were studied are soluble in ether. However, since they were never obtained in high yields no reasonable predictions can be made concerning their solubility in more concentrated solutions.

It is difficult to obtain a perfectly pure sample of the white precipitate. The compound is usually contaminated with bits of unaltered calcium, calcium oxide, basic calcium iodide and possible calcium hydroxide. Because of these impurities not much reliance can be placed on the calcium analysis made by Beckmann[1], and the only quantitative analysis he made was for calcium. A fairly homogeneous sample was obtained by treating calcium with a liberal excess of ethyl iodide in a dry atmosphere. The material was rapidly filtered, washed with anhydrous ether, transferred to a glass stoppered weighing bottle, dried in a vacuum desiccator, and weighed by difference directly in the weighing bottle.

A sample prepared in this manner for analysis contained 58.18 and 57.97% of iodine. The compound that best agrees with such results is the di-etherate of calcium iodide, $CaI_2 \cdot 2(C_2H_5)_2O$ which requires 57.4% of iodine. Beckman's ethylcalcium iodide mono-etherate, $C_2H_5CaI \cdot (C_2H_5)_2O$, requires 46.9% of iodine. A gas is evolved when this solid is treated with water. Beckmann stated that the gas was ethane contaminated with some ether. The gas was

not unsaturated, and its characteristic ethereal odor coupled with its complete solubility in conc. sulfuric acid indicated that it was ether and not ethane. Two samples were analysed: 0.3382 g. gave 37.3 cc. of gas (corrected): and 0.2944 g. gave 32.7 cc. of gas (corrected). The di-etherate of calcium iodide requires 34.2 cc. and 29.8 cc. of ether, respectively.

The small amount of ethylcalcium iodide present account, in part, for the lack of success in obtaining characteristic anilides with phenyl and naphthyl isocyanates. However, another alkylcalcium iodide (n-butyl) gave the characteristic derivative with α-naphthyl isocyanate.

N-BUTYLCALCIUM IODIDE.

When 12 g. (0.3 mole) of calcium was treated with 55.2 g. (0.3 mole) of n-butyl iodide in 100 cc. of ether, considerable insoluble material was deposited. During the preparation, about two liters of gas were evolved. The gas was saturated, inflammable and insoluble in conc. sulfuric acid. Undoubtedly it was largely n-butane, formed by the reaction of a trace of moisture in the reagents with n-butylcalcium iodide.

After the reaction had been allowed to complete itself, over two days, the mixture was hydrolyzed with dil. hydrochloric acid. Considerable heat is evolved during the hydrolysis of any organocalcium halide, and a part of this is very probably due to the hydration of calcium iodide. The ethereal layer was separated, dried and 10 g. of liquid was obtained boiling between 120-130°. If the mixture was entirely n-octane this would correspond to a

59% yield. However, n-butyl alcohol and n-butyl iodide might have been contained in this fraction. Accordingly, the mixture was first refluxed for 4 hours with 10% sodium hydroxide; then extracted with ether; then carefully shaken with conc. sulfuric acid to remove ether and n-butyl alcohol, and finally fractionally distilled. In this way, despite mechanical losses, there was obtained a 29.2% yield of n-octane.

In another run the n-butylcalcium iodide was characterized by the preparation of n-valeryl α-naphthalide obtained from the reaction with α-naphthyl isocyanate.

n-OCTYLCALCIUM IODIDE

0.05 mole of calcium and an equivalent amount of n-octyl iodide in an excess of ether were shaken for 24 hours in a sealed flask. A heavy white precipitate formed, and the supernatant liquid gave a positive color test for n-octyl calcium iodide. After hydrolysis, the ether layer yielded 2 g. or a 17.8% yield of hexadecane, $C_{16}H_{24}$.

PHENYLCALCIUM IODIDE

Phenylcalcium iodide was treated with phenyl isocyanate, and to the reaction mixture was then added a slight excess of diethyl sulfate. After refluxing for an hour the mixture was hydrolysed and then worked up in a customary manner. Some benzanilide, the normal reaction product of phenylcalcium iodide and phenyl iso-cyanate, was obtained. Practically all of the diethyl sulfate was recovered, and there was no indication of the formation of the

desired imino ether. $C_2H_5N=C(OC_2H_5)(C_2H_5)$. This ether would have resulted by the replacement of the -CaI attached to oxygen by an ethyl group of diethyl sulfate[6].

A vigorous reaction occurs during the addition of an equivalent of benzoyl chloride to phenylcalcium iodide. At the end of the addition there was a strong test for phenylcalcium iodide and benzoyl chloride was present as evidenced by its characteristic odor. In order to complete the reaction, the mixture was refluxed for 24 hours. Even after this protracted digestion of a 0.1 mole run, there was present in the mixture not only benzoyl chloride, as might have been expected, but also some phenylcalcium iodide. This emphasized in a striking manner the relatively lesser activity of organocalcium iodides when compared with the corresponding organomagnesium halides[7]. On working up the hydrolyzed reaction products there was obtained a 35% yield of iodobenzene and 5% triphenylmethane. The triphenylmethane probably owes its formation to the reduction of triphenyl carbinol when the unaltered calcium reacts with water during hydrolysis.

In another experiment the reaction between phenylcalcium iodide and benzoyl chloride was forced by refluxing for several hours in an ether-benzene solution. Under these conditions the phenylcalcium iodide was used up, and about 1% of triphenyl carb-

6. Under like conditions, phenylmagnesium bromide also gives benzanilide and there is no replacement of the -MgX group by ethyl. Cf. Gilman and Kinney, J. Am. Chem. Soc., 46, 493 (1924).
7. In this connection mention should be made of the unreactivity of phenylcalcium iodide towards azobenzene (Gilman and Pickens, J. Am. Chem. Soc., 47, 2406 (1925).

inol was obtained in addition to some unaltered iodobenzene and benzoyl chloride, benzoic acid and a small amount of an apparently intractable tar.

Despite the significant amounts of iodobenzene recovered it appears that phenylcalcium iodide is obtained in higher yields than the other organocalcium iodides that were studied. With this arylcalcium iodide less of the di-etherate of calcium iodide separates than is the case with the alkylcalcium iodides.

SUMMARY

Organo calcium iodides can be prepared in poor yields from a limited class of iodides. They are soluble in ether and less reactive than the corresponding organomagnesium halides.

PART II

ORGANOSTRONTIUM HALIDES

INTRODUCTION

In continuation of studies concerned with the mechanism of reaction of organomagnesium halides, attempts were made to prepare organometallic compounds of strontium. The literature contains no reference to the preparation of organostrontium halides. Apparently, these compounds cannot be directly prepared by the methods used in preparing organocalcium iodides.

EXPERIMENTAL

The general procedure used in the study of the preparation of organometallic compounds of calcium and barium was followed in the present study. The metal, organic halide, ether and iodine were agitated for various lengths of time in small sealed test tubes. The materials were given an opportunity to react for periods of time extending from several days to over a year. From time to time the tubes were unsealed and the contents were tested for the presence of organometallic compounds by the Michler's ketone color test[4]. The tubes were agitated at room temperature in all but two experiments in which the tubes were heated to 170° and 225°. The organic halides used in this study were ethyl iodide and iodobenzene since these had been found most satisfactory in the work on calcium. Iodine was used as catalyst in every experiment except one in which mercuric chloride was used in addition to iodine.

Three varieties of strontium metal were used. One variety of supposed strontium which contained a high percentage of mercury

and was undoubtedly an amalgam, showed no tendency to react with the organic halide in ether. Two samples of electrolytic strontium appeared to be quite pure and reacted superficially with the organic halide and iodine, as indicated by the removal of free iodine from the solution and clouding of the mixture. A variety of metal, kindly supplied by Dr. Phillip S. Danner[8], which had been prepared by sublimation under high vacuum was probably of higher purity than the other two samples. This material was as inactive toward iodobenzene and ethyl iodide as the electrolytic metal. Since this metal was softer than the other samples it became very finely divided after prolonged agitation. It gave a slight positive color test after it had been shaken with a mixture of ethyl iodide and iodobenzene in ether. However, not much reliance can be placed in this positive test since the finely divided metal would give the same color reaction and, furthermore, the test could not be duplicated.

The mixtures of electrolytic metal, iodobenzene, ether, and iodine which were heated to $170°$ for 10 hours and $225°$ for 36 hours contained some unused metal and a light gray powder. Both gave negative color tests.

Mercuric chloride and iodine were added to one mixture of strontium, iodobenzene, and ether. Although the mixture appeared to have undergone some change, as shown by the formation of a bright yellow solid, it gave a negative color test after a month of agitation. There is a possibility that mercuric chloride may

8. The preparation of very pure strontium and barium by Dr. Phillip S. Danner is described in J. Am. Chem. Soc., 46, 2382 (1924).

have reacted with any phenylstrontium iodide that was formed and thus have interfered with the color test. The presence of phenyl-mercuric iodide or chloride was not determined.

Table I contains a summary of the experimental work on strontium.

TABLE I

Metal	RX	Catalyst	Time & Temp.	Reaction	Test
Sr. (a) Sublimed	C_6H_5I	Iodine	10 days to 6 months, room temp.	Slight Grey Precipitate	Negative
" " (a)	$C_6H_5I + C_2H_5I$	Iodine	7 days to 6 months, room temp.	" " "	Very faint positive after 7 days (e)
Sr. (b) Electroly-tic	C_6H_5I	Iodine	Several months, room temp.	" " "	Negative
" " (b)	"	Iodine	10 hours 170 C	Much grey Precipitate	Negative
" " (b)	C_2H_5I	Iodine	5 weeks, room temp.	Slight clouding	Negative
" " (b)	C_6H_5I	Iodine	36 hours 225° C	Light brown residue	Negative
" " (c)	C_6H_5I	Iodine	Several months, room temp.	Cloudiness	Negative

TABLE I (CONTINUED)

Metal	RX	Catalyst	Time & Temp.	Reaction	Test
Sr. (c) Electrolytic	C_2H_5I	Iodine	Several months, room temp.	Cloudiness	Negative (f)
" " (c)	C_2H_5I	$I_2 + HgCl_2$	" " "	Bright yellow ppt. formed	Negative
Sr. (d) Amalgam	C_2H_5I	Iodine	" " "	No evidence of reaction	Negative (f)
" " (d)	C_2H_5I	Iodine	" " "	" "	"

NOTES ON TABLE I

(a). This metal was obtained through the kindness of Dr Phillip S. Danner[8].

(b). This was a sample of commercially available electrolytic strontium.

(c). This was a fresh sample of electrolytic strontium.

(d). This was a sample of strontium amalgam containing only a small proportion of strontium.

(e). This positive test may have been caused by finely divided strontium. The positive test could not be duplicated.

(f). These experiments were duplicated in runs lasting over one year. The results of these experiments are the same as those given in the table.

SUMMARY

In view of these negative results it is apparent that organo-strontium halides cannot be directly prepared by the same means as those employed for the preparation of organocalcium halides.

PART III

ORGANOBARIUM HALIDES

INTRODUCTION

In continuation of studies on mechanism of reaction of organomagnesium halides, the preparation of organobarium halides was undertaken. Organometallic compounds of barium are not mentioned in the literature.

It first appeared that phenylbarium iodide could be readily prepared by methods similiar to those used in the study on organocalcium iodides. However, subsequent work showed that the solutions containing the supposed phenylbarium iodide contained mainly calcium and only a trace of barium. Furthermore, samples of very pure barium gave no indication of the formation of organobarium derivatives.

EXPERIMENTAL

In general, the same method of proceedure was used in the study of the preparation of organobarium halides as was used in the corresponding study on calcium and strontium organometallic halides. The reactants, metallic barium, organic halide, ether and catalyst, were agitated in small sealed test tubes. The materials were allowed to remain in the tubes until the appearance of the contents indicated that a change had taken place. The tubes were then unsealed and a small amount of the solution was tested for the presence of an organometallic compound by means of the Michler's ketone color test[4]. When no change in

appearance was noticable the contents were usually tested after the elapse of several weeks. A number of the experiments were continued for over one year.

The barium used was from four sources. Commercial barium-amalgam failed to react with either ethyl iodide or iodobenzene. An analysis of the material showed approximately 26% barium and 64% mercury. A sample of sublimed barium, kindly supplied by Dr Phillip S. Danner[8], also failed to react with ethyl iodide or iodobenzene. Another sample, kindly supplied by Dr. A. J. King, said to be of high purity, also failed to react. The only type of metal which gave positive results was a sample of barium prepared by electrolysis, obtained from a foreign source.

When small portions of the electrolytic barium were shaken with iodobenzene, ether and a trace of iodine, the color of the iodine disappeared in from one-half to four hours and the solution became turbid. After shaking over night the reaction mixture consisted of a clear light brown solution and a light brown precipitate.

Only the clear ethereal solution gave a positive color test. The light brown residue failed to give a positive color test after two washings with anhydrous ether. The reaction mixture yielded benzoic acid when it was treated with carbon dioxide, with α-naphthyl isocyanate it yielded benzoyl α-naphthalide, and with ethyl benzoate it yielded triphenyl carbinol. These three derivatives were identified by mixed melting point determinations.

The clear supernatant ethereal solution was decanted from the

reaction product of iodobenzene with electrolytic barium, and was found to give a positive color test. It was hydrolysed and analysed for metallic constituents. Only a trace of barium was detected but a large amount of calcium was found. No other metals were present. It thus appears that the reaction obtained with this electrolytic metal was due to calcium and not to barium.

Ethyl iodide gave a very slight positive test in one experiment in which a sample of electrolytic metal was used.

All experiments in which barium from other sources was used gave negative results, even after the reactants were kept together for over one year.

Mercuric chloride and iodine failed to bring about a reaction between pure barium, (from Dr. A. J. King) iodobenzene and ether after the reactants had been agitated together for one month. There is a possibility of the mercuric chloride having reacted with any phenylbarium iodide that was formed, thus preventing a positive color test. The mixture was not investigated for possible reaction products, namely, phenylmercuric chloride or iodide.

A summary of all experimental work on barium is given in Table II.

TABLE II

Metal	RX	Catalyst	Time & Temp.	Reaction	Test
Ba, (a). Electrolytic	C_2H_5I	Iodine	40 hours. Room temp	Solution turned grey solid ppt separated	Positive (f)
" "	C_2H_5I	Iodine	20 hours. Room temp.	Heavy white ppt formed.	Very slight positive test.
Ba, (b). Distilled Very pure	C_2H_5I	Iodine	Nearly two years. Room temp.	Small amt of white ppt.	Negative test from beginning to end of experiment
Ba, (a). Electrolytic De Haen	C_2H_5I	Iodine	2 days. Room temp.	Reaction began in 15 minutes	Positive test. (g)
" " " (a)	CH_3I	Iodine	Several weeks. Room temp.	Cloudiness in tube	Negative
" " " (a)	C_2H_5I	Iodine	Several weeks. Room temp	" " "	" " "
" " " (a)	$\underline{n}C_4H_9I$	Iodine	Several weeks. Room temp	" " "	" " "
Ba, (c)	C_2H_5Br	Iodine	Several months. Room temp	White ppt. formed after several wks	Negative (d)
" " "	C_2H_5I	Iodine	" " "	" " "	" " (d)

TABLE II (CONTINUED)

Metal	RX	Catalyst	Time & Temp.	Reaction	Test
Ba. (c)	C_6H_5Br	Iodine	Several months. Room temp	White ppt. formed after several wks	Negative (d)
" " "	C_6H_5I	Iodine	" " "	" " "	" " "(d)
" " "	C_6H_5I	I_2 + $HgCl_2$	" . " "	Some white ppt.	" " "
Ba. (a) Electroly- tic	C_6H_5I	Iodine	" " "	Good re- action	Strong pos- itive test

NOTES ON TABLE II

(a). This was a sample of commercially available, electrolytic barium.

(b). This was a sample of sublimed barium obtained through the kindness of Dr. Phillip S. Danner[8].

(c). This was a sample of very pure barium obtained through the kindness of Dr. A. J. King of Syracuse University.

(d). This experiment was duplicated several times.

(e). The clear, upper layer, which gave a strong positive test, was decanted off. Qualitative analysis showed only a trace of barium, but much calcium.

(f). This reaction product yielded benzoic acid after treatment with carbon dioxide.

(g). Benzoyl α-naphthalide and triphenyl carbinol were obtained from this reaction product.

SUMMARY

Pure metallic barium does not react with alkyl or aryl iodides, in the presence of ether, under conditions which lead to the formation of organocalcium iodides from calcium and organic iodides.

Since it has been shown that in those instances in which reaction did take place, the reaction mixture contained but a trace of barium and much calcium, it is apparent that the formation of organobarium halides took place to a very slight extent, if at all.

PART IV

CALCIUM, STRONTIUM, AND BARIUM DIALKYLS AND DIARYLS

INTRODUCTION

The failure to obtain organostrontium halides and organo-barium halides let to an attempt to synthesize the dialkyl and diaryl derivatives of the alkaline earth metals. It would be possible, once the dialkyls and diaryls were formed, to prepare the organometallic halides by treatment of the dialkyls or di-aryls with halogens.

Of the several methods available for the synthesis of met-tallic alkyls or aryls, only two need by considered here.

    I. Action of the metal on the metal alkyl of a less posi-tive metal.

    II. Action of the metal salt on the metal alkyl of a more positive metal.

The first method was used in the present study where the metals were treated with several mercury alkyls and aryls. The second method is hardly available for the present purpose due to the scarcity of alkyls of metals which are more positive than the alkaline earth metals. It is probable that the sodium and potassium alkyls and aryls would be the only practical com-pounds to use for this purpose.

It is suggested that the reactions of the free alkaline earth metals, and their halogen salts, with (1) zinc alkyls and aryls and (2) sodium or potassium alkyls and aryls be investi-gated as future lines of work on this problem.

EXPERIMENTAL

Metallic calcium, strontium, and barium were treated with mercury diethyl, di n-butyl, diphenyl, and di p-tolyl under a variety of conditions. The metal and mercury compound were sealed in small test tubes and allowed to stand at various temperatures for different lengths of time. Although it appeared that reaction had taken place in a number of instances, there was no definite evidence that organometallic derivatives had been formed.

Electrolytic strontium and barium appeared to have reacted with mercury diethyl and dibutyl after standing together several days at room temperature. However the products gave negative color tests. Heating at 90 for several days caused reaction to take place between calcium, strontium, and barium, and strontium and barium amalgam and mercury diethyl and dibutyl but none of the products would give a positive test. When the same materials were heated to 200° for 2 hours the contents of the tubes were dark, much pressure was produced in the tubes, and the contents gave negative tests.

Similiar results were obtained with mercury diphenyl and di p-tolyl. No reaction took place at low temperatures and at elevated temperatures there was much decomposition of the products. Slight positive tests were given in several instances but these may have been given by traces of free metals reducing Michler's ketone during the hydrolysis of the mixtures.

A summary of the work on these compounds is given in Tables III, IV and V.

TABLE III

Metal	HgR$_2$	Time & Temp.	Reaction	Test
Ca Electrolytic	Hg(C$_2$H$_5$)$_2$	2 hours 200° C.	Metal converted to brown powder	Slight test which may have due to free Ca
" " "	Hg(C$_6$H$_5$)$_2$	4 hours 210° C.	Superficial action on Ca. Mixture brown	Slight + test
" " "	Hg(C$_2$H$_5$)$_2$	Over night Room temp.	No action	Negative
" " "	Hg(nC$_4$H$_9$)$_2$	" " "	" " "	"
" " "	Hg(C$_6$H$_5$)$_2$	One week 90° C.	" " "	"
" " "	Hg(C$_6$H$_4$CH$_3$)$_2$	" " "	" " "	"
" " "	Hg(C$_2$H$_5$)$_2$	Three days 90° C.	Light brown crust on metal small amt free Hg visible	"
" " "	Hg(nC$_4$H$_9$)$_2$	Three days 90° C.	Same as above	"
" " "	Hg(C$_2$H$_5$)$_2$	Six hours at 180°	Contents dark, much pressure	"

TABLE III (CONTINUED)

Metal	HgR₂	Time & Temp.	Reaction	Test
Ca Electrolytic	Hg(C₄H₉)₂	Six hours at 180° C.	Same as above	Negative
" " "	Hg(C₆H₅)₂	Three days 225° C.	Black resinous solid, free Hg.	"
" " "	Hg(C₆H₄CH₃)₂	" " "	Brown solid: free Hg	"
" " "	Hg(C₆H₅)₂	Six hours 225° C.	Black free Hg, C₆H₆	Very slight test, probably due to free Ca
" " "	Hg(C₆H₄CH₃)₂	Six hours 225° C.	Black free Hg, C₆H₅CH₃	Negative

TABLE IV.

Metal	HgR_2	Time & Temp.	Reaction	Test
Sr. Electrolytic	$Hg(C_2H_5)_2$	Two hours 200° C.	Metal converted to brown powder Tube exploded	Slight + test may have been due to free Sr.
" " " Frankel & Landau	$Hg(C_2H_5)_2$	Several days Room temp.	Slight brown crust on metal	Negative
" " "	$Hg(nC_4H_9)_2$	" " "	" " "	"
" " "	$Hg(C_2H_5)_2$	Three days 90° C.	Yellow material formed trace of free Hg.	"
" " "	$Hg(nC_4H_9)_2$	" " "	" " "	"
Sr. amalgam	$Hg(C_2H_5)_2$	" " "	Slight evidence of reaction	"
" " "	$Hg(nC_4H_9)_2$	" " "	" " "	"
Sr. Electrolytic	$Hg(C_6H_5)_2$	" " "	No action	
" " "	$Hg(C_6H_4CH_3)_2$	" " "	No action	
" " "	$Hg(C_6H_5)_2$	Three days 225° C.	Black resinous solid, free Hg	Negative

TABLE IV CONTINUED

Metal	HgR_2	Time & Temp.	Reaction	Test
Sr. Electrolytic	$Hg(C_6H_4CH_3)_2$	Three days 225° C.	Black solid Free Hg	Negative
Sr. amalgam	$Hg(C_6H_5)_2$	" " "	Black powder Free Hg	"
" " "	$Hg(C_6H_4CH_3)_2$	" " "	Brown powder Free Hg.	"
" " "	$Hg(C_6H_5)_2$	Six hours 225° C.	Dark solid Free Hg.	"
" " "	$Hg(C_6H_4CH_3)_2$	Six hours 225° C.	" " "	"
Sr. Electrolytic	$Hg(C_6H_5)_2$	" " "	" " "	"
" " "	$Hg(C_6H_4CH_3)_2$	" " "	" " "	"

TABLE V.

Metal	HgR_2	Time & Temp.	Reaction	Test
Ba Electrolytic	$Hg(C_2H_5)_2$	Two hours to 200° C.	Metal converted to brown powder. Free Hg visible	Slight + test may be due to free Ca
" " "	$Hg(C_2H_5)_2$	Several days Room templ	Slight brown crust on metal	Negative
" " "	$Hg(nC_4H_9)_2$	" " "	" " "	"
" " "	$Hg(C_2H_5)_2$	Three days at 90° C.	Brownish yellow material formed. Free Hg.	"
" " "	$Hg(nC_4H_9)_2$	" " "	" " "	"
Ba amalgam	$Hg(C_2H_5)_2$	" " "	Slight appearance of reaction	"
" " "	$Hg(nC_4H_9)_2$	" " "	" " "	"
Ba Electrolytic	$Hg(C_6H_5)_2$	" " "	No action	
" " "	$Hg(C_6H_4CH_3)_2$	" " "	No action	

TABLE V. (CONTINUED)

Metal	HgR$_2$	Time & Temp.	Reaction	Test
Ba Electrolytic	Hg(C$_6$H$_5$)$_2$	Three days at 225° C.	Dark solid Free Hg.	Negative
" " "	Hg(C$_6$H$_4$CH$_3$)$_2$	" " "	" " "	"
Ba amalgam	Hg(C$_6$H$_5$)$_2$	" " "	Black resin. Free Hg	"
" " "	Hg(C$_6$H$_4$CH$_3$)$_2$	" " "	Light brown Powder	"
" " "	Hg(C$_6$H$_5$)$_2$	Six hours 225° C.	Dark solid C$_6$H$_6$, Free Hg	Very slight test. Probably due to free Ba.
" " "	Hg(C$_6$H$_4$CH$_3$)$_2$	" " "	Dark solid C$_6$H$_5$CH$_3$. Free Hg	" " "
Ba Electrolytic	Hg(C$_6$H$_5$)$_2$	" " "	Brown solid Free Hg	" " "
" " "	Hg(C$_6$H$_4$CH$_3$)$_2$	" " "	Not much evidence of reaction. Free Hg.	" " "

SUMMARY

There is not sufficient evidence that the organometallic derivatives of calcium, strontium, and barium were actually obtained in this work.

Suggestions have been made for future lines of work on this problem.

PART V.

ORGANOBERYLLIUM HALIDES

INTRODUCTION

Several unsuccessful attempts have been made to prepare organoberyllium halides[9]. Recently Durand[10] claimed to have prepared methylberyllium iodide from the reaction between finely divided beryllium and methyl iodide in ether using a trace of mercuric chloride as a catalyst. After the first unsuccessful experiments on the direct preparation of organoberyllium halides[9], a study was made of beryllium dialkyls[11] in order to prepare the organoberyllium halides by indirect methods. The indirect methods yielded these new organometallic halides.

As a result of both the indirect and direct methods of preparation sufficient information is available to warrant the conclusion that Durand very probably did not have methylberyllium iodide. The information given by Durand appears to be quite convincing. He described his methylberyllium iodide as a solid which when analyzed after hydrolysis for methane and iodine gave excellent values for this compound. However, we have found it impossible to get methylberyllium iodide when his directions were followed explicitly. The methylberyllium iodide we obtained was, contrary to Durand's experiences, very soluble in ether. His method of purification, by ether washing, should have completely

9. Gilman, J. Am. Chem. Soc., 45, 2693 (1923)
10. Durand, Compt. rend., 182, 1162 (1926).
11. See PART VI of this thesis.

removed the compound leaving no organoberyllium iodide for analysis. Furthermore, it appears that the gas he obtained by hydrolysis was hydrogen from unused beryllium and not methane from methylberyllium iodide. 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[12].

EXPERIMENTAL

When Durand's directions for the preparation of methylberyllium iodide were carried out in detail, 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 analysed after displacing all the air by carbon dioxide. Hydrolysis by dil. hydrochloric acid gave a gas that was pure hydrogen.

In a second experiment, 0.091 g. (0.01 mole) of beryllium and corresponding amounts of methyl iodide, mercuric chloride and ether were treated according to Durand's directions. The gas analysis gave 216.5 cc., instead of the calculated 224 cc. 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".

12. Gilman and Schulze, J. Am. Chem. Soc., 49, 2328 (1927).
    This paper contains 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 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. His gas analysis and ours, made under corresponding conditions, emphasize this point. But we showed that hydrogen and not methane was evolved.

TEMPERATURE

No methylberyllium iodide is formed when 0.091 g. (0.01 mole) of finely divided beryllium[13] 1.4 g. (0.01 mole) of methyl iodide

13. 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.

15 cc. of ether and a trace of mercuric chloride are shaken in a sealed test tube at room temperature for one week.

The orienting experiments at elevated temperatures were carried out in the same sealed test tubes, prepared by drawing out a glass test tube of about one-half inch diameter so that the length, exclusive of the capillary, was about 2.5 inches. These tubes were placed in a short length of iron pipe, closed at one end, and the heating was effected by placing the iron pipe either on a steam hot plate or in an oil bath. Heating at 80-90° for 15 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 invariable 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. Reaction at elevated temperatures was always accompanied by considerable pressure in the tubes.

In many experiments the reagents were heated at 80-90° for periods in excess of 15 hours and up to one week. Judging by the depth of the color test recommended by Gilman and Schulze[4] for RMgX and some ether organometallic compounds, there was no appreciable increase in yield with these extended periods of heating. Incident-

ally 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

Durand must be credited for using the best catalyst: namely, mercuric chloride. This 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 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.

Room temperature experiments were made with methyl and ethyl iodides, ethyl bromide, tert.--butyl iodide and triphenylchloromethane and a variety of catalysts. The catalyst or activator usually reacted at once with the metal, but no pressure was evident when the tubes were opened, and the solutions gave no positive color test. The yellow color produced on the addition of Michler's ketone[4] was probably due to the beryllium halide.

With triphenylchloromethane, the solutions turned yellow soon after the tubes were sealed, but the color appeared to be of a lesser depth than that observed with some other metals like mercury. Also, the beryllium-copper alloy gave a slightly deeper color than pure beryllium.

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. Methylberyllium iodide gives a positive color test when the solution is allowed to stand for 10-15 minutes with Michler's ketone before hydrolysis and the addition of the iodine-glacial acetic acid solution. 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 5 minutes standing before a satisfactory color test is obtained.[14] One experiment under like conditions with ethyl iodide gave no positive test.

No reaction occurs when methyl and ethyl iodides are treated as above, but heated only for 15 hours. Furthermore, beryllium with methyl or ethyl iodide, but no catalyst, showed no signs of having reacted after heating to 80-90° for several days. This is of interest in connection with Cahours' early work[15].

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 volums of ether in sealed tubes. Convenient reaction vessels may be prepared from the commercially available

14. Gilman and Schulze, Bull. soc. chim., (1927 or 1928)
15. Cahours, Ann. chim. phys., (3) 58, 5 (1860)

small, heavy sealed bottles used for the shipment of low boiling liquids.

About 0.5 g. of powdered beryllium, 0.2-0.5 g. 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 15 hours, the bottle is cooled, and its capillary end is first inserted in a 50 cc. 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 was 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 15 hours.

n-Butylberyllium iodide was prepared in the presence of ether and mercuric chloride after heating for 15 hours at 80-90°.

Phenylberyllium iodide gave a positive test when prepared in the presence of mercuric chloride after heating at 80-90° for

15 hours. This experiment was not duplicated in another run.
However, the phenylberyllium iodide was readily prepared by
heating at a more elevated temperature (110°, 150° or 175°) with
either mercuric chloride or beryllium chloride as a catalyst.

Tert.-butyl chloride and bromide appeared to have reacted
when heated to $80-90^o$ for 15 hours with mercuric chloride as a cata-
lyst. However, the products in both cases gave negative tests.
Under like conditions, benzyl bromide and n-butyl chloride show-
ed no evidence of reaction. The experiments with triphenylchloro-
methane, previously mentioned, were carried out at room tempera-
ture.

REACTIONS OF ALKYLBERYLLIUM HALIDES

All of them are decomposed by water, with the general forma-
tion 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 fur-
ther 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 di-
methyl was definitely identified in this manner when methylberyl-
lium iodide was heated. The following equilibrium is quite probable

$$2RBeX \longleftrightarrow BeR_2 + BeX_2$$
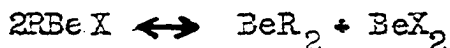
inasmuch as alkylberyllium halides are formed when beryllium di-
alkyls are treated with a beryllium halide. Some experiments on
the heating of RMgX compounds indicate that the same may be true
with organomagnesium compounds.

When carbon dioxide was bubbled through an ethereal solution

of methylberyllium iodide for 3 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 10-15 minutes standing prior to hydrolysis. Beryllium dialkyls give the test at once.

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

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

SUMMARY

A study has been made of the preparation and properties of several organoberyllium halides.

PART VI

BERYLLIUM DIALKYLS

In continuation of studies concerned with the preparation
of organoberyllium halides[16] it was necessary to prepare some ber-
yllium dialkyls for comparative purposes inasmuch as the two classes
of compounds appear to be interconvertible.

Cahours[17] claimed the preparation of beryllium diethyl by
heating the metal with ethyl iodide in a sealed tube. Later[18] he
reported the preparation of beryllium diethyl and beryllium dipro-
pyl by heating the metal with the corresponding mercury dialkyls
in a sealed tube at 130°. It is highly probable that Cahours' work
on beryllium diethyl is incorrect. His beryllium diethyl was dis-
tilled in an atmosphere of carbon dioxide and boiled at $185-188^{\circ}$.
We have found that beryllium diethyl not only reacts with carbon
dioxide, but also boils at a much higher temperature (with decomp-
osition) than that reported by Cahours. Furthermore, we had no
success in the preparation of beryllium diethyl and beryllium di-
n-butyl by heating beryllium with the appropriate mercury dialkyl
under the conditions recommended by Cahours. Incidentally, Cahours
incorrectly described magnesium diethyl as a liquid, inasmuch as
it is a solid.[12]

Lavroff[19] in a protocol of 1884 very briefly mentioned the
preparation of beryllium dimethyl by the action of beryllium on
mercury dimethyl in a sealed tube at 120°. We have found no fur-

16. See PART V of this thesis.
17. Cahours, Ann. chim. phys., (3) 58, 22 (1860).
18. Cahours, Compt. rend., 76, 1383 (1873). Cahours work on bery-
    llium dialkyls has been discussed by Frankland, J. Chem. Soc.,
    13, 181, 194 (1861).
19. Lavroff, J. Russ. Phys. Chem. Soc., 16, 93 (1884). Also Bull.
    soc. chim., (2) 41, 548 (1884).

ther mention of his work. Despite the very meager detail in his preliminary communication, it is quite probable that Lavroff did have beryllium dimethyl, as subsequent experimental work in the present investigation proved.

Krause and Wendt[20] in a footnote to a paper on aluminum alkyls, state that beryllium dialkyls may be prepared by the reaction between beryllium chloride and an excess of Grignard reagent.

EXPERIMENTAL

Several unsuccessful experiments were carried out in an endeavor to prepare beryllium diethyl and beryllium di-n-butyl by heating beryllium with the corresponding mercury dialkyl, with or without the use of mercuric chloride as a catalyst. The finely crushed metal showed no evidence of reaction when allowed to remain in sealed tubes for 3 weeks at room temperature with equivalent quantities of mercury diethyl and mercury di-n-butyl. When heated for the same extended period at 90° some free mercury was formed, but qualitative tests showed the absence of beryllium dialkyls. On heating several tubes for 15 hours at 130°, 175°, 200°, and 225° the only apparent reaction induced was decomposition of the mercury dialkyls, and there was no evidence of the formation of beryllium dialkyls.

Beryllium diphenyl and beryllium di-p-tolyl may be readily prepared by heating equivalent quantities of beryllium with mercury diphenyl and mercury di-p-tolyl and a trace of mercuric chloride in sealed tubes at 225° for six hours.

20. Krause and Wendt, Ber., **56**, 467 (1923, footnote 2.).

In the experiments with mercury dialkyls, mercuric chloride was sometimes added. Other studies[13] have shown that mercuric chloride is an almost indispensable catalyst in the preparation of some metallic dialkyls, like magnesium diethyl. When beryllium was heated to $130°$ for 6 hours with mercury dimethyl, which contained some methyl mercuric iodide, beryllium dimethyl was formed. It is quite reasonable to assume that traces of some mercuric halide were contained in the materials used by Lavroff. The beryllium used in the present studies was obtained from the Beryllium Corporation of America and contained more than 99.5% beryllium.

It is possible to prepare beryllium dialkyls by heating beryllium with the appropriate alkyl halides. The intermediate compound formed in this reaction is an alkylberyllium halide. Here again, mercuric chloride is a very helpful catalyst.

However, it appears that the most convenient method for the preparation of beryllium dialkyls is the reaction between anhydrous beryllium chloride and the appropriate Grignard reagent. By means of this method we have prepared beryllium dimethyl, diethyl and di-n-butyl.

PREPARATION OF BERYLLIUM DIALKYLS

Plate I is the photograph of the apparatus used in the preparation of beryllium dialkyls from the Grignard reagent.

Because of the highly hygroscopic nature of anhydrous beryllium chloride and the ready decomposability of beryllium alkyls and the Grignard reagent by atmosphere, all operations were carried out in pure and dry hydrogen or nitrogen. 8 g. (0.1 mole)

of anhydrous beryllium chloride was dissolved in 50 cc. of anhydrous ether. The considerable heat of solution necessitates external cooling by means of tap water. The filtered solution of the chloride has an oily appearance and may be either colorless or pale yellow. It separates into two layers, a lower layer of beryllium chloride etherate and an upper lower consisting largely of ether.

The beryllium chloride is filtered directly into a solution of 75 cc. of 4 molar (0.3 mole) methylmagnesium iodide contained in a 250 cc. reaction flask (A). It is advisable to gently shake the Grignard solution during the addition of the chloride. There is little heat of reaction if the beryllium chloride solution is pure and anhydrous. The formation of white clouds of the surface of the reaction mixture is indicative of the presence of air or oxygen.

Excess ether is removed by stopping the circulation of water in condenser (B) until the oil bath attains a temperature of 150°. The water is then turned on slowly in order to minimize a too sudden contraction (due to the condensation of ether) that might draw air into the condenser and receiving flask. The temperature of the oil bath is permitted to exceed 150° but not 200°, and the distillation is continued for 6 to 15 hours during which time an ethereal solution of the beryllium dimethyl collects in the receiving flask (C). Heat radiating from the oil bath is sufficient to keep the receiver above the boil-

ing point of ether and thereby prevent the condensation of more ether than is necessary to hold the beryllium dimethyl in solution.

Unfortunately it is difficult to determine sharply the end of the distillation except by an experience that comes with several observations. This is, however, not a serious matter, for in this work the distillation was continued over-night in many cases because the operation requires no attention. A certain method for determining the end of the distillation consists in replacing the receiver by another and noting if any more beryllium dimethyl distils over. Should the ether be driven out completely from the distilling flask (A) so that no more ether vapor circulates, it is necessary merely to gently heat the receiver to return the ether to flask (A). Such heating should be moderate, otherwise some of the beryllium dimethyl will be driven back into (A) and so extend the time of recovery of the compound.

The ethereal solution of beryllium dimethyl obtained in this manner is clear and colorless (when care has been taken to exclude air), and it may be used directly in a study of the reactions of the compound. When not in use it is kept preferable in sealed glass containers. Pure, ether free beryllium dimethyl is obtained by heating the distillate. At about $100-125^{\circ}$, most of the ether is expelled and the whole solution suddenly turns to a mass of white needles. Analysis showed these crystals to have some ether. All of the ether can be removed by

PLATE   I
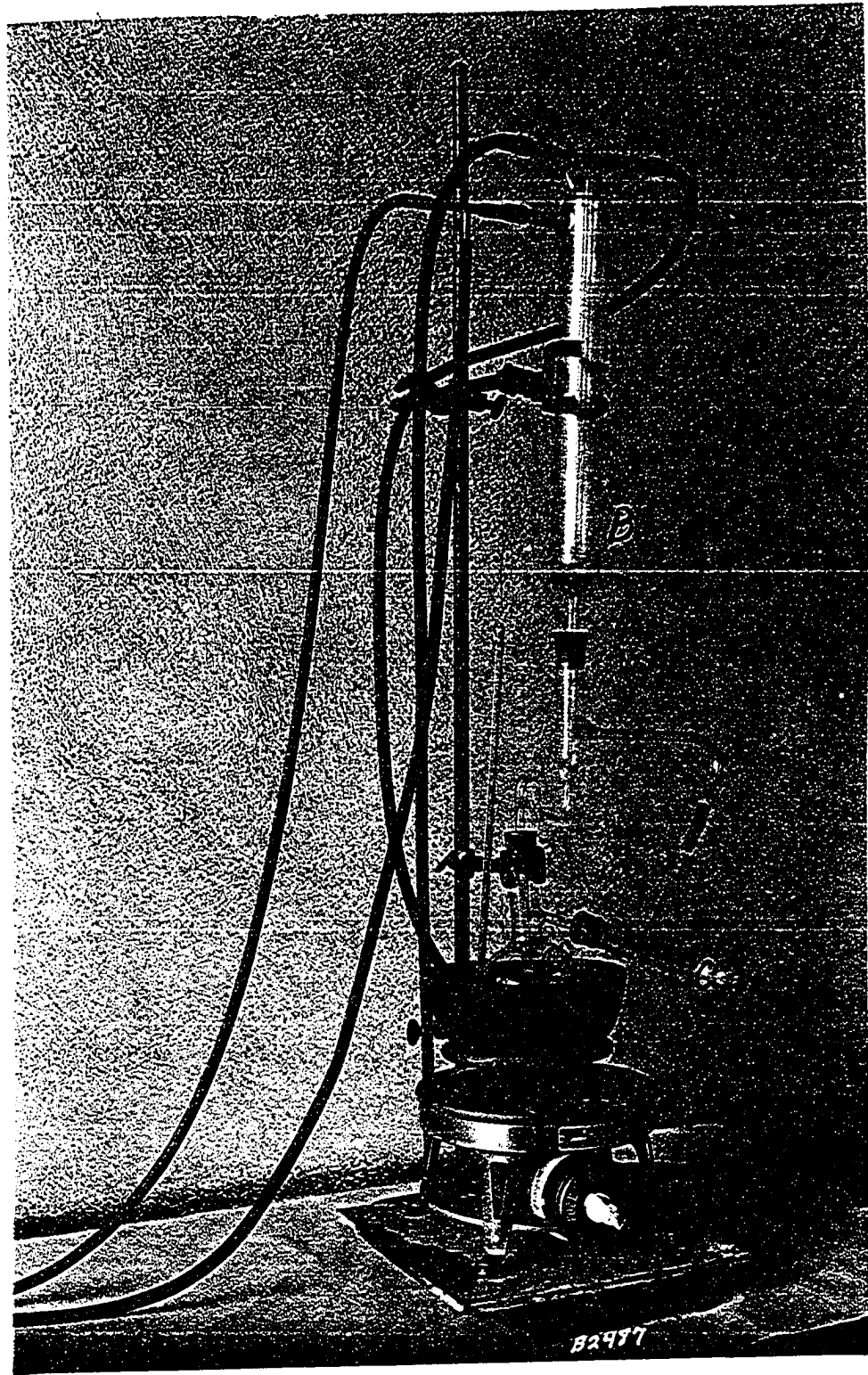
heating to 200°. When the temperature of the external bath reaches 200°, the compound commences to sublime rapidly, and part of it collects in the capillary when a constricted test tube is used for the preparation of ether free samples. However, the capillary can be kept open prior to sealing by applying a small luminous flame. A repetition of this process of distillation in a sealed U-tube arrangement originally filled with ether vapor, makes it possible to obtain material free of oxide or methoxide, by alternately heating and cooling each part of the U-tube. The samples used for analysis were prepared in this manner.

3.5 g. or a 90% yield of beryllium dimethyl was obtained in a 0.1 mole experiment. In a 0.3 mole experiment the yield was 84.7%.

Beryllium diethyl and di-n-butyl were also prepared in a manner essentially like that just described for the preparation of beryllium dimethyl. However, it is possible to distil beryllium diethyl and di-n-butyl directly in a vacuum. Because of the lower vapor pressure of beryllium di-n-butyl it would probable be more advantageous to use a vacuum distillation rather than the ether distillation or ether sublimation process used for the dimethyl compound. .

ANALYSIS OF BERYLLIUM DIMETHYL.

The samples prepared by distillation at 200° were analysed for methane and beryllium oxide after decomposition of water.

In the analysis for methane, one of the sealed tubes containing beryllium dimethyl was weighed; then broken in a container filled with dry ether; and, the volume of methane liberated on the addition of water and then dil. hydrochlorid acid, was measured in a special eudiometer containing conc. sulfuric acid. An aliquot of the evolved gas when exploded with a measured volume of oxygen was shown to consist of pure methane.

The beryllium was analyzed as beryllium oxide after carefully filtering the glass which was weighed to determine the weight of beryllium dimethyl originally present in the sealed container.

Analysis.---0.1501 g. of beryllium dimethyl gave 173.2 cc. of methane (corrected). The calculated volume for this weight is 171.4 cc. Another sample containing 0.1771 g. gave 200.7 cc. of methane instead of the calculated 202.3 cc.

The 0.1501 g. sample of beryllium dimethyl (analyzed above) gave 23.33% beryllium, and the calculated value is 23.25%. The other sample gave but 21.35% of beryllium due to partial loss resulting from the breaking of the crucible.

PROPERTIES OF BERYLLIUM DIALKYLS.

Beryllium dimethyl is a solid, and crystallizes from hot concentrated ether solution in snow white needles. (See PREPARATION OF BERYLLIUM DIMETHYL). It also deposits in the same form when it sublimes, without melting, at about 200°. The method of preparation is based on its high volatility in ether, and these ethereal solutions fume strongly when exposed to the

atmosphere. When suddenly overheated it undergoes partial decomposition leaving a brown or gray mirror.

Beryllium diethyl is a colorless liquid, boiling at 93-95°/ 4 mm., and 110°/15 mm. It distils between 180-240° at atmospheric pressure with considerable decomposition. The compound is only distilled with difficulty because of its pronounced tendency to become superheated and then break suddenly into foam. This may be due to the decomposition of an etherate. A part of the purest material solidified, in a carbon dioxide-ether freezing mixture, to white crystals which on warming melted at -13 to -11°.

Beryllium di-n-butyl is a clear, colorless liquid having a mercaptan-like odor. The boiling point, 170°/25 mm., was determined with a rather small quantity of material and so may not be taken with too much credence.

Both beryllium dimethyl and diethyl are spontaneously inflammable in the air, and especially so in a humid atmosphere. Even concentrated ethereal solutions are inflammable spontaneously in the presence of moist air. The compounds burn with luminous flames, evolving dense white fumes of beryllium oxide. Their very high sensitivity to oxygen made it difficult, at first, to purify the hydrogen or nitrogen to an extent that they would not give a white cloud of beryllium oxide when passed over the ethereal solutions of the dialkyls. For this reason, a phenylmagnesium bromide solution was inserted in the drying and purifying train in order to remove a residuum of oxygen. Beryl-

lium di-n-butyl is not spontaneously inflammable when exposed to the air, but it does oxidize rapidly, when so exposed, with the evolution of heat. Very probably, beryllium butylate is a product of such oxidation inasmuch as the odor of n-butyl alcohol becomes quite pronounced after a short air exposure.

The reaction of the dialkyls with water is violent, and in the presence of small amounts of water the materials frequently inflame. It was shown that methane and ethane are evolved when the corresponding dialkyls are decomposed by water.

Beryllium dimethyl in the solid state inflames when treated with carbon dioxide. With an ethereal solution, however, the reaction is quite mild and acetic acid is formed. An ethereal solution of beryllium diethyl reacts with carbon dioxide to give triethyl carbinol.

Phenyl isocyanate in ethereal solution reacts with extreme violence with the three dialkyls studied. In each case a white solid separated at first, and then dissolved in the excess of beryllium dialkyl. The expected anilides were obtained from beryllium dimethyl and diethyl, but the valeranilide from beryllium di-n-butyl came out as an oil. This anilide is known to crystallize with difficulty so that its identity has not been confirmed, as was done with the other two anilides, by a mixed melting point determination with an authentic specimen. Acet-α-naphthalide was obtained from beryllium dimethyl and α-naphthyl isocyanate.

The three dialkyls give an immediate positive color reaction with Michler's ketone according to the test described by Gilman and Schulze[4] for RMgX and some other organometallic compounds. The blue instead of green color given by beryllium di-n-butyl indicates that this dialkyl probably reduced the ketone to Michler's hydrol.

Beryllium dimethyl with benzophenone gave diphenyl methyl carbinol which was identified as α,α-diphenylethylene. Beryllium diethyl, on the other hand, reduced benzophenone to benzohydrol. In this latter reaction, a bright orange red color was present transitorily at the junction of the two liquids. This may be indicative of the intermediate formation of a free radical.

Beryllium dimethyl with benzoyl chloride gave dimethyl phenyl carbinol, and this was identified by the formation of isopropenyl benzene when the carbinol was distilled. The reaction product was probably free of acetophenone as indicated by a test with semicarbazide.

The beryllium dialkyls appear to have high solvent characteristics, for all the intermediate reaction products dissolved in an excess of the dialkyl. Equally striking is the fact that beryllium diethyl dissolved the beryllium oxide and ethoxide formed by partial decomposition of the dialkyl, as well as the brown or gray mirror formed by the high temperature decomposition of the dialkyl.

Beryllium dimethyl and diethyl react vigorously with iodine. When 1.343 g. of beryllium dimethyl was treated with one equivalent (4.353 g.) of iodine, the solution still contained some dialkyl as was evidenced by the fuming on air exposure and by a slight positive test. After standing for several days in a cork stoppered flask, the solution no longer fumed and gave a negative test. Very probably methylberyllium iodide was formed as a result of the iodine reaction because the solution gave acetanilide with phenyl isocyanate, and when heated it fumed and gave a positive test. These are among the criteria included for the characterization of alkylberyllium halides.

Beryllium diethyl reacts with an excess of an ethereal solution of beryllium chloride to give a solution with the characteristics of ethylberyllium chloride. In view of these latter experiments the following equilibrium is probable.

$$BeR_2 + BeX_2 \rightleftarrows 2RBeX$$
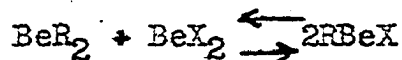
In general, the alkylberyllium halides are less active than the beryllium dialkyls, and the beryllium dialkyls are at least equal in activity to the Grignard reagents.

SUMMARY

A study has been made of the preparation and properties of several beryllium dialkyls.

PART VII

ORGANOMETALLIC ANTI-KNOCK COMPOUNDS

Preparation of Organic Antimony Derivatives

INTRODUCTION

In connection with studies concerned with the preparation of new organometallic anti-knock compounds, the synthesis of tri p-bromophenyl stibine and tri p-dimethylamino-phenyl stibine was undertaken. An attempt was also made to prepare diphenyl stibinous chloride and phenylstibinous chloride. By treating these compounds with a variety of Grignard reagents it was hoped that a number of new mixed stibines could be prepared.

Several methods for the preparation of aromatic stibines are available.

I. Reaction of antimony trichloride with aryl halides in the presence of an excess of sodium[21].

II. Treatment of an organic halide with an alloy of sodium and antimony.

III. Reaction of antimony trichloride with the Grignard reagent[22].

The first and second methods would obviously not apply to the synthesis of tri p-bromophenyl stibine, inasmuch as mixtures of compounds would form due to reaction with both halogens of p-dibromobenzene. p-Dibromobenzene reacts with magnesium to give a good yield of p-bromophenylmagnesium bromide, and this in turn should react with antimony trichloride, thus giving a reli-

21. Michaelis and Reese, (a) Ber. 15, 2877, (1882); (b) Ann 223, 39, (1886).
22. Pfeiffer and Pietsch, Ber. 37, 4620, (1904).

able reaction for the preparation of p-bromophenyl stibine.

Tri p-dimethylaminophenyl stibine could be prepared by any of the methods given above. Of these, the reaction involving the intermediate formation of the Grignard reagent is to be preferred. There is a possibility that this compound might also be formed by a reaction not emmerated above, namely, by a condensation between antimony trichloride and dimethylaniline, involving the elimination of hydrogen chloride. No condensation of this type is given in the literature, and on the basis of experimental work, the reaction does not take place readily.

All attempts at preparing diphenylstibinous chloride and phenylstibinous chloride by methods given in the literature were unsuccessful, therefore the proposed preparation of mixed stibines was abandoned.

EXPERIMENTAL

PREPARATION OF TRI P-BROMOPHENYL STIBINE

p-Bromophenylmagnesium bromide was prepared from 17 g. (0.7 mole) magnesium and 165 g. (0.7 mole) dibromobenzene. A solution of 45 g. (9.2 mole) freshly distilled antimony trichloride in 100 cc. ether was slowly added to the Grignard reagent. The reaction between the Grignard reagent and antimony trichloride solution is vigorous and it is necessary to add the solution very slowly. After standing over night the mixture still contained some unaltered Grignard reagent, as indicated by a positive test. The reaction mixture was hydrolysed by

adding ice and ammonium chloride solution. The ethereal
layer was separated and filtered to free it of a small amount
of tarry material. After evaporation of the ether there was
obtained 106 g. of viscous yellow oil. Assuming it to be all
tri p-bromophenyl stibine this amount would correspond to a
90.6% yield, based on antimony trichloride.

All attempts to induce the material to crystallize fail-
ed. The material was steam distilled to remove a small amount
of dibromobenzene. The residual stibine was taken up in low
boiling petroleum ether but showed no tendency to crystallize
even after the solution had been seeded with small crystals of
triphenyl stibine. Vacuum distillation appeared to be impract-
ical, since the material decomposed when heated under low pres-
sure. After long standing the material would set to a light
yellow, transparent, amorphous semisolid.

Since the material resisted all efforts at purification,
several attempts were made to convert it to derivatives which
would show more desirable properties. Triphenyl stibine re-
acts with iodine, in various solvents, to give triphenyl sti-
binic iodide, a solid which may be easily crystallized. Like-
wise, on oxidation with sodium peroxide in a water suspension
it yields triphenyl stibinic hydroxide, which may be crystal-
lized readily, and posesses a high melting point.

With iodine, tri p-bromophenyl stibine yielded a brown,
varnish-like material which could not be crystallized. Oxi-

dation with sodium peroxide in water appeared to yield a solid derivative but on standing this reverted to an oil resembling the original stibine.

In view of the practical impossibility of obtaining the material absolutely pure it was not analysed. However, qualitative tests showed the presence of antimony and bromine, which, when considered with the method of preparation indicated that the material is undoubtedly the expected tri p-bromophenyl stibine. Furthermore, it has been found that the p-bromophenyl derivatives of lead and tin are also inclined to be oils and are difficult to obtain the crystalline condition.

Preparation of tri p-dimethylaminophenyl stibine.

Activated magnesium copper alloy, 88% Mg. -12% Cu, was treated with an ethereal solution of p-bromodimethyl aniline. It was necessary to add a small amount of ethyl bromide to start the reaction. A slow current of dry nitrogen was passed through the apparatus in order to protect the RMgX compound from the action of the air. The yield of p-dimethylaminophenylmagnesium bromide appeared to be poor.

An ethereal solution of antimony trichloride was added and a brisk reaction ensued. The mixture was hydrolysed with ammonium chloride solution. The ethereal solution was steam distilled to separate p-bromodimethyl aniline and dimethylaniline from the reaction product. The dark residue was taken up in ether and the solution was allowed to evaporate slowly.

A dark brown tarry material remained which would not crystal-
lize after standing several months at low temperature. The mater-
ial was extracted with alcohol and the resultant solution was
allowed to evaporate. The residue was taken up in benzene. The
alcohol solution yielded a brown tar while the benzene solution
gave a hard varnish like material. It was not possible to iso-
late any definite compound from these fractions.

<u>Condensation of dimethyl aniline with antimony tri-
chloride</u>

0.1 mole antimony trichloride was dissolved in 0.3 mole
dimethyl aniline. There was a slight elevation in temperature
of the mixture when the solid went into solution. The solu-
tion was then heated on a steam plate over night. The product
was a dark blue viscous liquid. It was poured into cold water
and much antimony oxychloride separated out. The mixture was
extracted with ether but only dimethyl aniline was recovered,
and the residual solid contained no organic materials.

SUMMARY

Tri p-bromophenyl stibine has been prepared in good yield
by the reaction between antimony trichloride and an excess of
p-bromophenylmagnesium bromide. The material is a light yellow,
transparent semi-solid which cannot be completely purified.

Tri p-dimethylaminophenyl stibine could not be prepared
by treating antimony trichloride with p-dimethylaminophenyl-
magnesium bromide. The product of this reaction was a brown,
varnish-like material from which no definite compound could be

isolated. Antimony trichloride does not condense with dimethyl aniline to give the desired tri p-dimethylaminophenyl stibine.