

compound melting at 209°, and having a nitrogen content of 18.48%. This is undoubtedly the symmetrical hexanitrodiphenylethane mentioned by Will<sup>8</sup> as melting at 212° (18.59% N). In spite of repeated attempts to prepare more of this material, none was obtained. It is apparent that this compound is formed in very small amount under even the most favorable conditions.

### Summary

1. Modified methods of preparing 4,4'-dinitro- and 2,4,2',4'-tetranitrodiphenylethane with high yields have been developed. Accurate melting point determinations of these pure compounds, as well as other properties, have been recorded.

2. A new compound has been prepared by the nitration of tetranitrodiphenylethane and identified as  $\alpha$ -2,4,5-trinitro-phenyl- $\beta$ -2,4-dinitro-phenylhydroxyethane. The important properties of this compound have been determined.

3. 2,4,6,2',4',6'-Hexanitrodiphenylethane is formed in very small amount under even the most favorable conditions of nitration.

4. The effects of steric hindrance in the formation of nitro derivatives of diphenylethane have been evaluated.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

## MAGNESIUM DIALKYL. AN HISTORICAL NOTE ON THE FIRST PREPARATION OF AN ALKYL MAGNESIUM HALIDE

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### Introduction

In extension of studies concerned with the preparation of phenylmagnesium chloride in the absence of a solvent,<sup>1</sup> some apparently anomalous reactions were observed when alkyl halides were heated with magnesium. This necessitated an investigation of the related magnesium dialkyls.

Hallwachs and Schafarik<sup>2</sup> were the first to prepare an organomagnesium compound, and this they did by heating ethyl iodide with magnesium. The solid reaction product when heated gave a colorless, volatile liquid which they said contained traces of the magnesium diethyl. Then Cahours,<sup>3</sup> by a like reaction, obtained an entirely volatile product which he considered magnesium diethyl. At a much later time, Löhr<sup>4</sup>

<sup>1</sup> Gilman and Brown, *THIS JOURNAL*, **52**, 3330 (1930).

<sup>2</sup> Hallwachs and Schafarik, *Ann.*, **109**, 206 (1859).

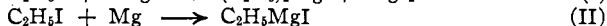
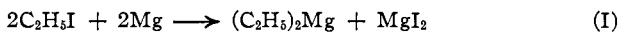
<sup>3</sup> Cahours, *ibid.*, **114**, 227, 240 (1860).

<sup>4</sup> Löhr, *ibid.*, **261**, 48, 72 (1891). See, also, Fleck, *ibid.*, **276**, 129 (1893), who used the mercury diethyl method of preparation described by Löhr. Extensive studies on the direct action of RX compounds and magnesium have been made by Spencer and co-workers. *J. Chem. Soc.*, **93**, 68, 1821 (1908).

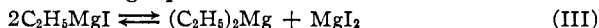
prepared magnesium diethyl by heating ethyl iodide with magnesium and also by heating mercury diethyl with magnesium. In both cases the product was a non-volatile solid. This was subsequently confirmed,<sup>5</sup> and then it was shown, incidental to other studies, that magnesium dimethyl<sup>6</sup> and magnesium di-*n*-butyl<sup>7</sup> were solids. There is a possibility that some higher, possibly branched-chain magnesium dialkyls might be liquids because although beryllium dimethyl is a solid, beryllium di-*n*-butyl is a liquid.<sup>8</sup>

Strictly speaking, the known magnesium dialkyls are volatile to a certain extent, for recent studies<sup>9</sup> have shown that these organomagnesium compounds can not only be sublimed in a high vacuum but also distilled in a stream of ether. Furthermore, the earlier literature<sup>10</sup> on these studies is incorrect in describing the magnesium dialkyls as being essentially insoluble in ether. They are distinctly soluble in ether. Possibly the higher magnesium dialkyls might be found to be sparingly soluble in ether, which is the case with magnesium diphenyl.<sup>11</sup> Other general observations on magnesium dialkyls are contained in the Experimental Part.

Undoubtedly Hallwachs and Schafarik<sup>2</sup> were the first to prepare an organomagnesium compound.<sup>12</sup> They may have been the first to prepare a so-called "individual" or ether-free organomagnesium halide, because either one, or both, of the following reactions can be used to account for their product.



There is not now<sup>13</sup> available a reaction for differentiating between ( $R_2Mg + MgX_2$ ) and  $RMgX$ . Once the reaction product is dissolved, in a solvent such as ether, then the following equilibrium occurs.<sup>14</sup>



In view of this equilibrium it is inconsequential whether Reaction I or Reaction II occurred, because in either case the equivalent of ethyl-magnesium iodide is obtained.<sup>15</sup>

<sup>5</sup> Gilman and Schulze, *THIS JOURNAL*, **49**, 2328 (1927).

<sup>6</sup> Gilman and Brown, *Rec. trav. chim.*, **48**, 1133 (1929).

<sup>7</sup> Gilman and Brown, *ibid.*, **49**, 724 (1930).

<sup>8</sup> Gilman and Schulze, *J. Chem. Soc.*, 2663 (1927).

<sup>9</sup> Gilman and Brown, *THIS JOURNAL*, **52**, 4480 (1930).

<sup>10</sup> Jolibois, *Compt. rend.*, **155**, 353 (1912), who prepared magnesium diethyl in accordance with Löhr's directions from mercury diethyl, described his compound as insoluble in ether but soluble in an ethereal solution of magnesium iodide.

<sup>11</sup> Hilpert and Grüttner, *Ber.*, **46**, 1675 (1913). Gilman and Brown, *Rec. trav. chim.*, **49**, 202 (1930).

<sup>12</sup> We refer here not to carbides or to acetylides, but only to those types having an alkyl or aryl group attached directly to magnesium.

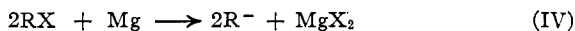
<sup>13</sup> Gilman and Brown, *THIS JOURNAL*, **52**, 1181 (1930). This refers to ether solutions. An x-ray investigation of the crystal structure of these two types should prove of assistance in differentiation.

<sup>14</sup> Leading references to related studies may be traced back from a recent article by Gilman and St. John, *ibid.*, **52**, 5017 (1930).

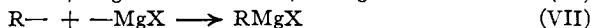
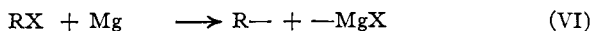
<sup>15</sup> It is interesting to note that it was about forty years later that Grignard first

With the application of heat, the condition used in most of these preparations, the  $\text{RMgX}$  compound might have formed first and then have been converted to the  $\text{R}_2\text{Mg}$  compound, in accordance with Reaction III. It is known that such a transformation does occur on heating.<sup>6,16</sup> Also, it has been generally assumed that in the formation of other organometallic compounds, the organometallic halide ( $\text{RMeX}$ ) is first formed and then is converted to the organometallic compound ( $\text{R}_2\text{Me}$ ): as, for example, in the formation of zinc diethyl from ethyl iodide and zinc through the ethyl zinc iodide stage.

Even though the equilibrium pictured in Reaction III probably applies to a great many, if not all, organometallic combinations it is not necessary to assume that the first stage in the formation of an  $\text{R}_2\text{Metal}$  compound is the  $\text{RMetalX}$  type. The reaction might occur as follows, using magnesium as the metal.<sup>17</sup>



Previously, it was assumed that  $\text{RMgX}$  or ( $\text{R}_2\text{Mg} + \text{MgX}_2$ ) compounds were formed as follows:



This latter interpretation has some objections,<sup>17</sup> not the least of which is its lack of comprehensiveness, as in a reaction between mercury diethyl and a metal, where no halogen is present. Admittedly, both types of reaction might take place concurrently.

### Experimental Part

The technique employed was that described earlier<sup>1</sup> in the preparation of phenylmagnesium chloride, a water pump being used to evacuate the tubes prior to sealing at the vapor pressure of the liquid. The magnesium was freshly ground and of 30–80 mesh. The qualitative color test, quantitative acid titration and characteristic derivatives were those used in other related studies in this Laboratory.

Methyl iodide showed no reaction even after heating at 140–150° for twelve hours. We have no explanation for the vigorous reaction reported by Cahours.<sup>3</sup> However, because he describes his magnesium dimethyl as a volatile, inflammable liquid, we are inclined to the opinion that his magnesium might have contained significant quantities of metallic impurities, such as zinc.

Ethyl iodide reacts at room temperatures, and the yield of organometallic compound at the end of seven days was 46%. When one equivalent of ethyl iodide was heated at 120–130° for four hours with two equivalents of magnesium, the yield was 61%. When two equivalents of ethyl iodide are used with one equivalent of magnesium no prepared ether solutions of  $\text{RMgX}$  compounds. But it was just this operation of Grignard in preparing the  $\text{RMgX}$  compounds in ether which made it possible for these reagents to find their wide application.

<sup>16</sup> Gilman and Fothergill, *THIS JOURNAL*, 51, 3149 (1929).

<sup>17</sup> This interpretation is developed in a paper by Gilman and Brown, *Rec. trav. chim.*, 49 (1930).

organometallic compound results. This is undoubtedly due to a secondary reaction between ethylmagnesium iodide or magnesium diethyl and the excess of ethyl iodide.

*n*-Butyl iodide appears to react more readily than ethyl iodide at room temperature. It is interesting to note that so far we have obtained no reaction under moderate conditions between trimethylene chloro-iodide,  $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{I}$ , and magnesium.

Ethyl bromide did not react at room temperatures in seven days. When heated at  $120\text{--}130^\circ$  for four hours a reaction occurred with the formation of magnesium bromide and gaseous products, but no color test was obtained. Very probably an organometallic compound will be obtained from ethyl bromide under intermediate conditions. Essentially the same results were obtained with *n*-butyl chloride and *n*-butyl bromide.

Methyl<sup>18</sup> and ethyl acetates have pronounced catalytic effects in initiating reaction, particularly with an iodide like ethyl iodide. They have practically no effect with methyl iodide.

Magnesium diethyl and magnesium di-*n*-butyl are very soluble in ether. Magnesium dimethyl is somewhat less soluble than the other two magnesium dialkyls, and a solution of it in ether contained in a sealed tube, deposited fine needle crystals after about six months' standing. The approximate solubility of magnesium dimethyl in ether is 0.08 mole per 100 cc. of solvent. These crystals of magnesium dimethyl (or its etherate) are markedly similar in appearance to the related beryllium dimethyl.<sup>8</sup> The three magnesium dialkyls just described were prepared from the corresponding mercury dialkyls. The product obtained from ethyl iodide and magnesium is only slightly soluble in pure ethyl iodide.

In general, the organomagnesium compounds prepared from magnesium and a mercury dialkyl appear to be more reactive to atmospheric oxygen and moisture than the corresponding compounds prepared from magnesium and an alkyl iodide. Whenever the dry powders, prepared from the mercury dialkyls, are allowed to come in contact with water the mixture almost always takes fire. Ether solutions of the magnesium dialkyls take fire with water, but not so readily as the dry powders. The dry powders sometimes took fire in air, but no definite data are at hand because these compounds were always manipulated in an atmosphere of nitrogen or hydrogen. A high humidity was conducive to such combustion when the powders were exposed to the air.

### Summary

A description is given of some general properties of magnesium dialkyls prepared from magnesium and mercury dialkyls, and organomagnesium compounds prepared from alkyl iodides and magnesium (with no solvent). The first organomagnesium halide, or its equivalent, was prepared by Hallwachs and Schafarik in 1859 *in the absence of ether*, but the use of ether by Grignard first made possible the extensive applications of these compounds.

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<sup>18</sup> Methyl acetate was found by Renshaw and Greenlaw, *THIS JOURNAL*, **42**, 1472 (1920), to be very effective in the preparation of zinc dimethyl.