Summary

1. A new dye, tetraethyldiaminodiphenylfurylmethane hydrochloride, has been prepared and its properties have been determined.
2. The parent compound of the diphenylfurylmethane dyes, diphenylfurylmethane, has been obtained by reduction of the corresponding carbinol.

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THE DISTILLATION OF GRIGNARD REAGENTS

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RECEIVED JULY 21, 1930 PUBLISHED NOVEMBER 5, 1930

Introduction

Solutions of Grignard reagents are mixtures of $RMgX$, R_2Mg, MgX_2, $R—$ and $—MgX$ (or $MgX_2 + Mg$) in a series of equilibria. The following equilibria and dissociation reactions[1] account for the compounds just mentioned.

$$2\ RMgX \rightleftharpoons R_2Mg + MgX_2 \qquad (I)$$

$$RMgX \rightleftharpoons R— + —MgX \qquad (II)$$

In order to lend additional support to these reactions, studies have been made on the sublimation and distillation of organomagnesium compounds. First, in an attempted high vacuum distillation of methylmagnesium chloride, a distillate or sublimate of magnesium dimethyl, free of halogen, was obtained.[2a] The magnesium dimethyl, a solid like magnesium diethyl,[3] owes its formation undoubtedly to a displacement of the equilibrium pictured in Reaction I. Second, a search was made for a liquid organomagnesium compound in order to facilitate a study of Reaction I. The relative stability of the liquid beryllium di-*n*-butyl,[4] suggested that greater success might be had with magnesium di-*n*-butyl. Accordingly, magnesium di-*n*-butyl was prepared,[2b] but unfortunately it also is a solid. Like its homologs, magnesium dimethyl and magnesium diethyl, it can also be sublimed in a high vacuum but less smoothly than the lower members of this series because of its lesser volatility or lesser stability at elevated temperatures or for both of these reasons.

With this partial success, we turned to a method of distillation used earlier[4] in a study of organoberyllium compounds, namely, ether distillation. This method, which was highly successful for the distillation of solid

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[1] Gilman and Fothergill, THIS JOURNAL, 51, 3149 (1929). This article contains leading references to other work.

[2] (a) Gilman and Brown, *Rec. trav. chim.*, 48, 1133 (1929); (b) Gilman and Brown, *ibid.*, 49, 724 (1930).

[3] Gilman and Schulze, THIS JOURNAL, 49, 2328 (1927).

[4] Gilman and Schulze, *J. Chem. Soc.*, 2663 (1927). See also, Gilman and Schulze, THIS JOURNAL, 49, 2904 (1927), for organoberyllium halides.

beryllium dimethyl, was found applicable to the magnesium dialkyls, which are, however, distinctly less volatile than the related beryllium dialkyls. After having demonstrated that magnesium dialkyls can be distilled by this procedure (see Experimental Part), a study was made of the ether distillation of RMgX compounds. When alkylmagnesium halides were treated in this manner, the distillate was found to contain the alkylmagnesium halide. Unfortunately, however, this does not prove that the RMgX compound as such distilled over. This is so because we have shown that under the conditions of our distillation magnesium halide or its etherate also distils. Accordingly we are in no position as yet to state whether the RMgX compound contained in the distillate was due to the separate distillations of R_2Mg and of MgX_2 (see Reaction I), each of which is known to distil, or to the distillation of these two compounds *and* some of the RMgX as such.

If equimolecular parts of R_2Mg and of MgX_2 distilled, then the ratio of Mg:X in the distillate should be one. In two analyses of a distillation of methylmagnesium iodide, the ratio Mg:I was found to be 1.105 and 1.092, respectively. These results merely indicate that almost equimolecular parts of R_2Mg and MgI_2 distil, but they do not tell us whether any RMgI distilled. Even though the ratio agreed with the theoretical for Mg:I, we would still have no compelling evidence of the distillation of RMgX as such. Apart from our primary objective, the results are interesting in showing that RMgX *or its equivalent* ($R_2Mg + MgX_2$) does distil, because a combination of $R_2Mg + MgX_2$ reacts immediately[1] to give RMgX. It may be possible to find a more definite answer with solvents other than ether.

Apparently arylmagnesium halides cannot be distilled in this manner. At least, when phenylmagnesium bromide was used no magnesium diphenyl and no magnesium bromide distilled during the eighteen consecutive full days of distillation. Just why the magnesium bromide which we know to be present in solutions of phenylmagnesium bromide was held back, we do not at present know. From the distillation of this Grignard reagent there was isolated some diphenyl. This indicates that with RMgX compounds of this type it may be possible to remove[5] the radical R– or its coupling or disproportionation product (see Reaction II).

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[5] Experiments with this in view are in progress with RMgX compounds like benzohydrylmagnesium chloride, $(C_6H_5)_2CHMgCl$. See Gilman and Zoellner, THIS JOURNAL, **52**, 3984 (1930). Benzohydrylmagnesium chloride and related types, like triphenylmethylmagnesium chloride,[1] convert benzophenone to benzopinacol (studies by K. E. Marple).

It may prove possible to prepare some R_2Mg compounds from Grignard reagents by distilling off the MgX_2 and leaving the R_2Mg behind. However, an apparently more general and satisfactory method for the preparation of R_2Mg compounds directly from Grignard reagents is that of Schlenk and Schlenk, *Ber.*, **62**, 920 (1929), wherein 1,4-dioxane is used.

Experimental Part

Apparatus.—The apparatus is shown in Fig. 1. It was constructed entirely of glass, and the long neck above the flask A (of about 150 cc. content) was indented to produce good fractionation and to prevent mechanically entrained particles from reaching the receiver B. A ring seal with a sharp edge was also sealed into the upper part of the neck of flask A to prevent any material from creeping out of A. The trap below the water condenser insured a flow of ether and other volatile substances in one direction only. It was found necessary to have the system sealed with a mercury test-tube seal because pressure was gradually built up in the system.[6]

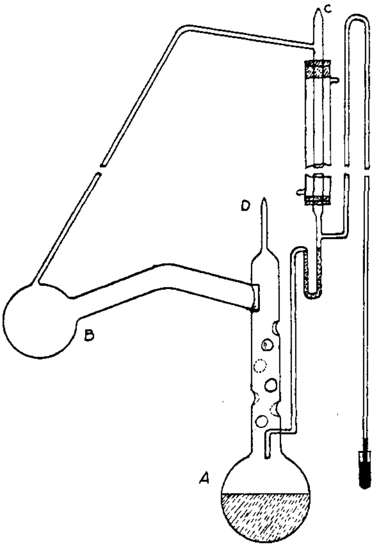

Fig. 1.

The manipulation and operation of the system is as follows. With the tubes C and D open, the apparatus is first thoroughly swept out with dry nitrogen. A solution of the Grignard reagent or MgR_2 compound or MgX_2 compound was then carefully filtered through glass wool into tube C, while the nitrogen continued to flow through D. Tubes C and D were then sealed off. An oil-bath was placed under flask A and the bath was maintained at a temperature of 75–80° by a hot-plate during the course of the experiment. In cool weather a second hot-plate was placed under flask B to drive the ether over into the water condenser and to prevent an undue accumulation of ether in flask B. In warm weather sufficient heat radiated from the plate under A to keep the system in good balance and so make unnecessary a hot-plate under flask B.

At the termination of the experiment, the heating of A was discontinued and the two tubes leading to receiving flask B were sealed off. The smaller of these tubes was next opened to a source of nitrogen, and the contents of B were then investigated. With this apparatus[7] we have found no evidence of creeping, and mechanical entrainment has apparently been annulled. Evidence in support of this is found in the experiment with phenylmagnesium bromide wherein it was shown that the distillate contained neither halogen nor magnesium.

Tests and Analyses.—The R_2Mg and RMgX compounds were tested qualitatively

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[6] Gilman and St. John, *Bull. soc. chim.*, **45**, 1091 (1929), have shown that several typical Grignard reagents can be refluxed at moderately elevated temperatures for several days without any essential impairment in yield of product from the RMgX compound. Possibly the unusually long refluxing used in the present studies may result in a gradual decomposition of the ether or the rate of decomposition of RMgX compound over very long periods may be significant or both of these factors may be involved in the building up of pressure in the system.

[7] This apparatus has some essential improvements over that used in the beryllium dialkyl studies.[4] It is possible to use a simpler type of apparatus for the ether distillation of other organometallic compounds such as zinc dialkyls which, incidentally, can be prepared in satisfactory yields by the reaction between zinc halides and Grignard reagents.

by the color test[8] and quantitatively by the acid titration[9] method of analysis. They were further characterized by the preparation of α-naphthalides as derivatives.[10]

Time Required and Quantities of Distillate in Ether Distillation.—In the ether distillation experiments with magnesium bromide, magnesium iodide, magnesium diethyl, methylmagnesium iodide, ethylmagnesium bromide, ethylmagnesium iodide and phenylmagnesium bromide about 0.1 mole of compound was used in 75–100 cc. of ether.

With methylmagnesium iodide there was slight evidence of distillate (after distilling ether from receiver B) in about one week from the start of distillation. With ethylmagnesium bromide and iodide there was no evidence of distillate until about the tenth day. Each distillation was run for eighteen full days, and the distillation when once started required practically no attention. This time was arbitrarily selected because it gave a quantity of distillate which though quite small could nevertheless be analyzed. Duplicate distillations were made with practically every compound investigated.

The acid titration of one distillate from methylmagnesium iodide indicated approximately 0.15 g. of distillate calculated as methylmagnesium iodide. The distillates from ethylmagnesium bromide and iodide were not titrated, but they appeared to be somewhat smaller. In the phenylmagnesium bromide experiments the quantity of diphenyl isolated in each distillation was about 0.2 g. Its identity was confirmed by mixed melting point determinations with an authentic specimen.

The apparently inordinate time required for the ether distillation of appreciable quantities of compounds can probably be reduced by the use of other solvents or combinations of solvents.

High Vacuum Sublimation.—The technique used for the high vacuum sublimation was that described earlier. Of the three magnesium dialkyls which were sublimed in a high vacuum, magnesium dimethyl was most volatile. Magnesium di-*n*-butyl was less volatile than magnesium diethyl. The same order applies to the relative thermal stability of these compounds, magnesium dimethyl being most stable. A free flame was used in the distillation of the magnesium dialkyls, and methylmagnesium chloride was heated in an oil-bath. We have also shown that it is possible to sublime magnesium acetylacetone in a high vacuum.

Summary

In connection with studies on the following systems present in solutions of Grignard reagents

$$\begin{aligned} 2\mathrm{RMgX} &\rightleftarrows \mathrm{R_2Mg} + \mathrm{MgX_2}, \text{ and} \\ \mathrm{RMgX} &\rightleftarrows \mathrm{R{-}} + \mathrm{{-}MgX} \end{aligned}$$

it has been shown that some RMgX compounds, or their equivalents, can be distilled in a stream of ether. The high vacuum sublimation of RMgX compounds gives R_2Mg compounds.

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[8] Gilman, Sweeney and Heck, THIS JOURNAL, **52**, 1604 (1930). This article contains leading references to earlier studies on the color test.

[9] Gilman, Wilkinson, Fishel and Meyers, *ibid.*, **45**, 150 (1923); also Gilman, Zoellner and Dickey, *ibid.*, **51**, 1576 (1929).

[10] Gilman and Furry, *ibid.*, **50**, 1214 (1928).