[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

THE ACTION OF Mg + MgBr$_2$ ON PHENYLBIPHENYLENEMETHYL. THE FORMATION OF PHENYLBIPHENYLENEMETHYLMAGNESIUM BROMIDE

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Recently it was demonstrated that formation of the Grignard reagent, triphenylmethylmagnesium bromide, takes place through two successive reactions: (a) formation of triphenylmethyl, (b) formation, from that, of the Grignard reagent.[1]

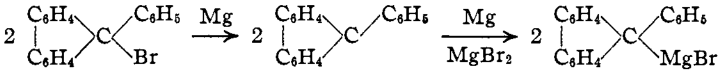
$$2(C_6H_5)_3CBr \xrightarrow{Mg} 2(C_6H_5)_3C + MgBr_2 \qquad (1)$$

$$2(C_6H_5)_3C + Mg + MgBr_2 = 2(C_6H_5)_3CMgBr \qquad (2)$$

Furthermore, it was shown that the free radical itself is quite likely the result of the interaction of Grignard reagent initially produced and unchanged triphenylbromomethane

$$(C_6H_5)_3CMgBr + (C_6H_5)_3CBr = 2(C_6H_5)_3C + MgBr_2 \qquad (3)$$

A similar course is followed by the reaction between phenylbiphenylenebromomethane and magnesium; the rates of reaction in all stages are slower. If a gram atom of magnesium is allowed to react with a gram mole of phenylbiphenylenebromomethane, the Grignard reagent is produced. If, however, only one-half gram atom of metal is employed, phenylbiphenylenemethyl (diphenyl-dibiphenylene-ethane) and magnesium bromide are present at the end of the reaction. If now an additional half atom of magnesium is added to this mixture, the phenylbiphenylenemethyl is converted to the Grignard reagent.



$$2\left.\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\right\rangle C\left\langle\begin{matrix}C_6H_5\\ \\ Br\end{matrix}\right. \xrightarrow{Mg} 2\left.\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\right\rangle C\diagup^{C_6H_5} \xrightarrow[MgBr_2]{Mg} 2\left.\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\right\rangle C\left\langle\begin{matrix}C_6H_5\\ \\ MgBr\end{matrix}\right. \qquad (4)$$

Phenylbiphenylenemethyl, prepared in various ways, reacts with the system Mg + MgBr$_2$ (or MgI$_2$) and gives the Grignard reagent. Although diphenyl-dibiphenylene-ethane dissociates only slightly[2] into phenylbiphenylenemethyl radicals, nevertheless, in virtue of this dissociation, the ethane is completely converted to the Grignard reagent.

Since the Grignard reagent was found to react rapidly with phenylbiphenylenebromomethane and give phenylbiphenylenemethyl, it is considered that this is the process whereby the radical is produced as intermediate product in the formation of the Grignard reagent.

Experimental

Phenylbiphenylenemethylmagnesium Bromide.—The 9-phenylfluorenol was prepared from fluorenone and phenylmagnesium bromide according to the directions of

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[1] Gomberg and Bachmann, THIS JOURNAL, **52**, 2455 (1930).

[2] Schlenk. Herzenstein and Weickel, *Ber.*, **43**, 1754 (1910).

Ullmann and von Wurstemberger.[3] However, a greater yield of product was obtained by hydrolyzing not only the crystalline reaction product but also the solution. In this way from 100 g. of fluorenone there was obtained 140 g. of phenylfluorenol of m. p. 108–109°.

To make the carbinol bromide, 140 g. of carbinol was dissolved in 100 cc. of benzene and 200 g. of acetyl bromide was added. After the solution had been refluxed for twelve hours, most of the solvent was removed under reduced pressure and the residue was treated with an equal volume of petroleum ether. After two recrystallizations from ligroin the phenylbiphenylenebromomethane melted at 99.5–100.5°; yield, 98 g.

Phenylbiphenylenebromomethane (1 Mole) + Magnesium (1 Atom).—Since the Grignard reagent is not very soluble in ethyl ether, the higher boiling *n*-propyl and *n*-butyl ethers, mixed with benzene, were employed. All reactions and all operations were carried out in an atmosphere of dry nitrogen. A mixture of 3.22 g. (0.01 mole) of phenylbiphenylenebromomethane and 0.2432 g. (0.01 atom) of magnesium powder in 30 cc. of *n*-butyl ether and 60 cc. of benzene was heated on a steam-bath. After twelve hours no more magnesium remained and the solution contained glistening crystals of the Grignard reagent. In order to dissolve these crystals an additional 30 cc. of solvent was added. The hot tan-colored solution was filtered and hydrolyzed. The magnesium hydroxide required 9.95 cc. of *N* sulfuric acid for neutralization; calcd., 10.0 cc. From the ether–benzene solution there was isolated 1.8 g. of 9-phenylfluorene, m. p. 146°. It was found to be identical with 9-phenylfluorene prepared by reduction of 9-phenylfluorene.[4] Usually a small amount of phenylbiphenylenemethyl peroxide was also found in the hydrolysis product.

Isolation and Analysis of the Grignard Reagent.—A mixture of 3.22 g. of phenylbiphenylenebromomethane and 0.38 g. of magnesium ribbon in 40 cc. of *n*-butyl ether and 80 cc. of benzene was heated on a steam-bath for twenty-four hours. The clear solution was filtered while hot from the excess of magnesium; 0.235 g. instead of 0.243 g. of magnesium had reacted. On cooling, the filtrate deposited glistening, transparent light yellow plates. These were filtered off, washed with benzene and dried in a stream of nitrogen. For analysis, a half-gram sample was treated with water and the resulting products—phenylfluorene, magnesium hydroxide and brom-ion—were determined. From these results the composition of the compound was calculated on a solvent-free basis.

Anal. Calcd. for $(C_6H_4C_6H_4)(C_6H_5)CMgBr$: $(C_6H_4C_6H_4)(C_6H_5)C$, 69.8; Mg, 7.0; Br, 23.1. Found: $(C_6H_4C_6H_4)(C_6H_5)C$, 69.4; Mg, 7.0; Br, 23.6.

Reaction with Carbon Dioxide.—Dry carbon dioxide was passed for three hours into the Grignard reagent made from 3.22 g. of phenylbiphenylenebromomethane in 45 cc. of ethyl ether–benzene (1:2). At the end of this time a large amount of solid was present. The mixture was hydrolyzed with dilute acid and from the organic solution phenylbiphenylene-acetic acid, $(C_6H_4C_6H_4)(C_6H_5)CCOOH$, was obtained. The product was purified by dissolving it in hot benzene and adding ligroin to the filtered solution. As the solution cooled the acid came out in needles, weight 1.75 g., which represents a 60% yield. As Schlenk and Bergmann[5] report, the phenylbiphenylene-acetic acid readily loses carbon dioxide on being heated and gives phenylfluorene. Because of this decomposition the melting point of the acid varies between 190 and 198°, the value obtained depending upon the rate of heating and the purity of the acid. A sample of the impure acid was converted to phenylfluorene when an attempt was made to recrystallize the acid from glacial acetic acid.

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[3] Ullmann and von Wurstemberger, *Ber.*, **37**, 73 (1904).

[4] Ullmann and von Wurstemberger, *ibid.*, **37**, 74 (1904).

[5] Schlenk and Bergmann, *Ann.*, **463**, 203 (1928).

Phenylbiphenylenemethyl

Phenylbiphenylenebromomethane (1 Mole) + Magnesium (0.5 Atom).—A mixture of 3.22 g. of phenylbiphenylenebromomethane and 0.1216 g. of magnesium powder in 120 cc. of solvent was heated on a steam-bath. After a time colorless crystals of phenylbiphenylenemethyl began to deposit. As soon as all of the metal had disappeared (five hours), water was added to the mixture. One-half cc. of *N* acid was needed for the magnesium hydroxide; this indicated the presence of a small amount of Grignard reagent; in agreement with this 0.3 g. of phenylfluorene was found. The radical formed in the reaction was oxidized to the peroxide by allowing the organic solution to evaporate in an open dish. After recrystallization from benzene the phenylbiphenylenemethyl peroxide weighed 1.5 g. (after benzene of crystallization had been removed); m. p. 197°. The compound was found to be identical with the peroxide prepared by the action of molecular silver on phenylbiphenylenechloromethane in presence of air.[6]

Phenylbiphenylenemethylmagnesium Bromide + Phenylbiphenylenebromomethane.—To a solution of Grignard reagent prepared from 3.22 g. of phenylbiphenylenebromomethane there was added 3.22 g. of the carbinol bromide. Colorless crystals of phenylbiphenylenemethyl began to precipitate immediately (see Equation 3), and after a few minutes a large amount was present. The mixture was warmed for fifteen minutes and then hydrolyzed with dilute acid. The radical was filtered off in a stream of nitrogen, washed well with acetone and dried; weight 2.3 g.; m. p. 253–254° in a sealed tube filled with carbon dioxide. From the filtrate, additional radical in the form of its peroxide was isolated as well as about half a gram of phenylfluorene.

Phenylbiphenylenemethyl + Mg + $\mathbf{MgBr_2}$.—The radical was prepared in various ways: by the reaction represented in Equation 3; by treatment of the carbinol bromide or chloride with molecular silver or with copper powder in benzene solution. A solution of $MgBr_2$ prepared from 0.5 g. of magnesium powder and 3.6 g. of $HgBr_2$[7] in 30 cc. of ether–benzene (2:1) was filtered into a flask containing 2.0 g. of crystalline phenylbiphenylenemethyl, 1.0 g. of magnesium, 20 cc. of *n*-propyl ether and 20 cc. of benzene. The resulting mixture was refluxed for sixteen hours. During this time the crystals of radical disappeared and in their place crystals of Grignard reagent appeared. These crystals were brought into solution by addition of more solvent and the solution was filtered; as the filtrate cooled, the glistening crystals of the Grignard reagent again appeared. The crystals were filtered off and analyzed in the same manner as previously described; they were found to have the composition $(C_6H_4C_6H_4)(C_6H_5)CMgBr$. Hydrolysis of the reaction product yielded 1.54 g. of 9-phenylfluorene.

Phenylbiphenylenemethyl + Mg + $\mathbf{MgI_2}$.—A mixture of Mg + MgI_2 was prepared from 1.5 g. of iodine and 1 g. of magnesium in 30 cc. of *n*-propyl ether and 60 cc. of benzene. To the colorless mixture was added 2.41 g. of crystalline phenylbiphenylenemethyl. On heating, reaction started almost at once. When the reaction was at an end, the solution was filtered from the excess of magnesium; 0.125 g. of metal had reacted, calcd. 0.122 (Equation 2). The Grignard reagent produced in the reaction was treated with carbon dioxide for three hours; from the reaction product 2.48 g. of pure phenylbiphenylene-acetic acid was obtained, which represents a yield of 87%.

9,9-Diphenylfluorene from Phenylmagnesium Bromide and Phenylbiphenylenechloromethane.—An attempt was made to prepare phenylbiphenylenemethyl by the reaction recently described by Schmidt-Nickels,[8] who allowed phenylmagnesium bromide to react with phenylbiphenylenechloromethane. Following his directions, there was obtained 9,9-diphenylfluorene instead of the free radical,

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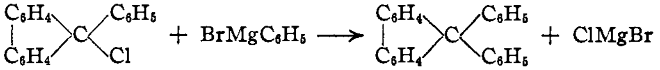
[6] Gomberg and Cone, *Ber.*, **39,** 2969 (1906).

[7] Gomberg and Bachmann, THIS JOURNAL, **49,** 2586 (1927).

[8] Schmidt-Nickels, *Ber.*, **62,** 917 (1929).



$$\begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\!>\!C\!<\!\begin{matrix}C_6H_5\\ Cl\end{matrix} + BrMgC_6H_5 \longrightarrow \begin{matrix}C_6H_4\\ |\\ C_6H_4\end{matrix}\!>\!C\!<\!\begin{matrix}C_6H_5\\ C_6H_5\end{matrix} + ClMgBr \qquad (5)$$

To the Grignard reagent from 12 g. of bromobenzene there was added 15 g. of 9-chloro-9-phenylfluorene. A vigorous reaction took place, with evolution of a considerable amount of heat, and with precipitation of a white solid as Schmidt-Nickels reports. After the mixture was refluxed for an hour, this solid was filtered off, washed with water and with acetone and then dried; weight 3.1 g.; m. p. 215–220°. After recrystallization from benzene it was obtained in the form of large needles melting at 219–220°, which were found to be identical with 9,9-diphenylfluorene prepared from *o*-phenyltriphenylcarbinol by dehydration.[9]

Summary

The system Mg + $MgBr_2$ (or MgI_2) reacts with phenylbiphenylenemethyl and gives the Grignard reagent, phenylbiphenylenemethylmagnesium bromide, $2(C_6H_4C_6H_4)(C_6H_5)C + Mg + MgX_2 = 2(C_6H_4C_6H_4)(C_6H_5)CMgX$.

The same Grignard reagent is formed from the action of magnesium on phenylbiphenylenebromomethane. This reaction was found to take place in two successive stages: (a) formation of phenylbiphenylenemethyl and $MgBr_2$; (b) reaction of the radical with Mg + $MgBr_2$.

The Grignard reagent was isolated in crystalline state and found to have the composition assigned to it. The compound was converted by water into phenylfluorene, by carbon dioxide into phenylbiphenylene-acetic acid.

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THE SUPPOSED EXISTENCE OF TWO STEREOISOMERIC 9-BENZYL-9-PHENYLFLUORENES

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Among the examples of a new kind of stereoisomerism, Schlenk and Bergmann[1] report an isomer of 9-benzyl-9-phenylfluorene. The latter compound was prepared by Gomberg and Cone[2] from benzylmagnesium chloride and 9-chloro-9-phenylfluorene; their product crystallized in prisms and melted at 136°. Schlenk and Bergmann allowed benzyl chloride to react with 9-sodium-9-phenylfluorene and obtained leaflets melting at 125–126°, which they consider to be a stereoisomeric 9-benzyl-9-phenylfluorene. Recently, however, Schmidt, Stein and Bamberger[3] were unable to obtain this isomer when following the directions given for

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[9] Ullmann and von Wurstemberger, *Ber.*, **38,** 4106 (1905); Clarkson and Gomberg, THIS JOURNAL, **52,** 2881 (1930).

[1] Schlenk and Bergmann, *Ber.*, **62,** 745 (1929).

[2] Gomberg and Cone, *ibid.*, **39,** 2968 (1906).

[3] Schmidt, Stein and Bamberger, *ibid.*, **62,** 1890 (1929).