Experimental

The cottonseed oil was poured into the first trap E, so that it formed a film on the walls; the second trap F was cooled with dry ice and ether to protect the pumps from water vapor. Under the influence of the active gas from the discharge the oil was almost immediately converted into a solid.

The reaction takes place rapidly and appears to go best on the walls; the product forms as a tightly stretched film or skin. A small piece of iron was placed in the bulk of the oil and by the use of an electromagnet it was possible to stir the mass and so renew the oil surface. With this arrangement it was easy to observe the continued formation of the film.

The product is a white solid, fibrous and resilient. It is insoluble in water and in all of the organic solvents tried and can be washed free of unchanged oil by ether. When the solid is shaken with ether it seems to absorb the ether and swells somewhat. The substance does not melt but chars. Under the same conditions olive oil, linseed oil and castor oil yield white, insoluble substances which have similar properties.

Summary

It has been shown that cottonseed oil is attacked by the active gas from a water vapor discharge tube. Fibrous substances are produced which are insoluble in ether and other organic solvents. Olive oil, linseed oil and castor oil yield similar compounds.

BALTIMORE, MARYLAND

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

THE ACTION OF THE SYSTEM Mg + $MgBr_2$ UPON TRIPHENYLCARBINOL, TRIPHENYLBROMOMETHANE AND UPON TRIPHENYLMETHYL[1]

BY M. GOMBERG AND W. E. BACHMANN

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The method used by Conant[2] for the reduction of carbinols directly to free radicals suggested that a similar reduction, but in non-aqueous solvents, might be accomplished by the system Mg + $MgBr_2$.[3] Triphenylmethyl was actually produced in this manner from triphenylcarbinol, but its formation, we found, was brought about by a secondary reaction, and not by direct reduction of the carbinol.

When a solution of triphenylcarbinol in a mixture of ether and benzene

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[1] From a paper presented before the Division of Organic Chemistry, American Chemical Society, at the third Organic Symposium, Princeton, New Jersey, December, 1929.

[2] Conant, THIS JOURNAL, **45**, 2466 (1923).

[3] From experiments by Dr. F. J. Van Natta, this Laboratory.

is heated with magnesium bromide alone, the basic salt, $MgBr(OH) \cdot (C_2H_5)_2O$, precipitates from the solution, and the reaction proceeds to the extent of 75–80%, as follows

$$(C_6H_5)_3COH + MgBr_2 \longrightarrow (C_6H_5)_3CBr + MgBr(OH) \qquad (1)$$

When, however, the carbinol is heated with a mixture of $MgBr_2$ + Mg, and the reaction product is treated with water in absence of air, there results a mixture, in varying proportions, of triphenylmethyl and triphenylmethane. The former was interpreted as originating from the action of metallic magnesium on carbinol bromide (Equation 2), and the methane as coming from some triphenylmethylmagnesium bromide (Equation 3); triphenylchloromethane is well known to give an analogous Grignard reagent.

$$2(C_6H_5)_3CBr + Mg \longrightarrow 2(C_6H_5)_3C + MgBr_2 \qquad (2)$$

$$(C_6H_5)_3CBr \xrightarrow{Mg} (C_6H_5)_3CMgBr \xrightarrow{HOH} (C_6H_5)_3CH + MgBr(OH) \qquad (3)$$

Our erstwhile interpretation that Reactions 2 and 3 are merely competing reactions became untenable when it was found that the longer the reaction mixture (carbinol + Mg + $MgBr_2$) is heated, the less triphenylmethyl and the more triphenylmethane (*i. e.*, Grignard reagent) is obtainable. Instead of competing, the triphenylmethyl represents, it seemed, an intermediate stage in the formation of the final magnesium compound

$$(C_6H_5)_3CBr \xrightarrow{Mg} (C_6H_5)_3C \xrightarrow[MgBr_2]{Mg} (C_6H_5)_3CMgBr \qquad (4)$$

In order to test this conclusion we studied in detail the reaction between triphenylbromomethane and magnesium.

One gram-mole of the carbinol bromide was found to react with one gram-atom of magnesium, and the Grignard reagent is produced in practically quantitative yield. However, when only one-half that amount of metal is used, no Grignard reagent is present at the end of the reaction and the solution contains only triphenylmethyl and magnesium bromide, as may be represented by Equation 2, although the mechanism may, in reality, be more complex than indicated (see page 2459). If an additional one-half gram-atom of magnesium is now added at this stage, the triphenylmethyl is completely converted into triphenylmethylmagnesium bromide. Obviously, the second part of the process must consist in the reaction

$$2(C_6H_5)_3C + MgBr_2 + Mg = 2(C_6H_5)_3CMgBr \qquad (5)$$

This inference has been verified by experiment. Pure triphenylmethyl has been found to react with the binary system quantitatively in accordance with Equation 5.

The failure to recognize that triphenylmethyl is an *intermediate stage* in the production of triphenylmethylmagnesium halide has been the cause of the many perplexing contradictions in the discussion on this subject by Schmidlin and Chichibabin.[4]

That free radicals with a transitory existence play an important role in the mechanism whereby a Grignard reagent is formed has been previously suggested by us:[5] (a) MgX_2 (activator) + Mg $\rightleftharpoons$ 2MgX, or in absence of activator, RX + Mg = R + MgX; (b) RX + MgX = R + MgX_2; (c) R + R = RR; (d) R + MgX = RMgX, (c) and (d) being two competing reactions. Recently Kinney[6] and Gilman and co-workers[7] have interpreted the formation of the Grignard reagent substantially in accordance with our hypothesis. The latter investigators also remark that "it is possible to prepare triphenylmethylmagnesium iodide from triphenylmethyl and magnesious iodide,"[8] but no experimental details are given.

The results here presented constitute a realization of our surmise—*a Grignard reagent can be produced from a free radical and the system* $MgX_2 + Mg$.

Experimental

Triphenylmethylmagnesium Bromide

Schmidlin, who first prepared triphenylmethylmagnesium chloride, found it necessary to use iodine as an activator and to heat the mixture of the reactants for several hours or, otherwise, instead of the normal "β-modification," there was produced much of the "α-modification," presumably a quinonoid isomer. This so-called α-modification, in our opinion, is largely the ether complex of triphenylmethyl.

We now find that the carbinol bromide reacts far more readily than the chloride. No activator is needed, the reaction proceeds at room temperature, and more rapidly on gentle warming. The triphenylmethylmagnesium bromide is only slightly soluble in ether, but is soluble in a mixture of one part of ether and two parts of benzene, and we used largely such a mixture. For more rapid reaction, magnesium powder or ribbon was employed, but for study of the rate of reaction we used magnesium rods, about 15 × 0.7 cm.; the rods could be quickly removed from the solutions in large test-tubes, weighed and replaced for continuation of the experiment. A number of experiments were carried out, varying the amount of magnesium used and varying the time allowed for the reaction from a few minutes to over a year. It was definitely established that not more than a gram-atom of magnesium enters into the reaction under any conditions (Equation 3).

Triphenylbromomethane, 16.2 g., and 1.34 g. of magnesium ribbon (calcd. 1.22 g.) in a mixture of 25 cc. of ether and 50 cc. of benzene were heated on a steam-bath. The

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[4] Schmidlin, *Ber.*, **39**, 628, 4183 (1906); **40**, 2316 (1907); **41**, 423, 430 (1908). Chichibabin, *ibid.*, **40**, 3965 (1907); **42**, 3469 (1909).

[5] Gomberg and Bachmann, THIS JOURNAL, **49**, 256 (1927).

[6] C. R. Kinney, in a paper before the Division of Organic Chemistry of the American Chemical Society at the meeting in Minneapolis, Minnesota, September, 1929.

[7] Gilman and Fothergill, THIS JOURNAL, **50**, 3334 (1928); Gilman and Kirby, *ibid.*, **51**, 1572 (1929).

[8] Gilman and Fothergill, *ibid.*, **51**, 3152 (1929). The same information, in the same terms, was communicated in a letter to one of us (G.) in February, 1929, when the results described in this paper had been already well established in this Laboratory.

solution was protected against access of air and against light in order to prevent decomposition of the triphenylmethyl. The reaction was apparently completed in less than one hour. The clear solution was filtered from the slight excess of magnesium through a sintered glass funnel and hydrolyzed, all in an atmosphere of nitrogen. The loss in weight of the magnesium was 1.20 g. The $Mg(OH)_2$ in the hydrolyzed mixture required for neutralization 48.7 cc. of N H_2SO_4, calcd. 50.0 cc. The crude triphenylmethane, obtained on evaporation of the ether–benzene solution, was recrystallized from benzene; weight 15.66 g., which is equivalent to 11.74 g. of benzene-free triphenylmethane. The quantity of the latter, the amount of $Mg(OH)_2$ and the weight of metallic magnesium that had dissolved show that the yield of the Grignard reagent was 96–97%.

In another experiment, the triphenylmethylmagnesium bromide was carbonated and the yield of triphenylacetic acid was practically quantitative.

Triphenylmethylmagnesium bromide and iodide can be readily prepared from the chloride. An equivalent amount of the corresponding magnesium halide is added to the solution of the carbinol chloride, whereupon magnesium chloride precipitates. The latter does not interfere with the subsequent course of the reaction. Activation by means of iodine, when the carbinol chloride is employed, is undoubtedly equivalent to adding magnesium iodide.

Isolation of the Grignard Reagent.—When to a concentrated solution of triphenylmethylmagnesium bromide in benzene–ether a further amount of ether is added, the etherate of the Grignard reagent comes down as granular crystals. For purposes of analysis it was prepared as follows. A rod of magnesium was allowed to react at room temperature with a solution of 8 g. of triphenylbromomethane in 75 cc. of ether–benzene (2:1). After one day the rod was coated with a deposit of large colorless transparent prisms. When a sufficiently large crop of these crystals had collected, they were detached from the rod, freed from some triphenylmethyl by washing with ether, and dried in a current of nitrogen. For analysis, a sample was hydrolyzed and the resulting products—triphenylmethane, $Mg(OH)_2$ and bromo ion were determined.

Anal. Subs., 1.592 g. Calcd. for $(C_6H_5)_3CMgBr \cdot 2(C_2H_5)_2O$: $(C_6H_5)_3C$, 49.1; Mg, 4.9; Br, 16.1. Found: $(C_6H_5)_3C$, 48.7; Mg, 4.9; Br, 16.2.

Triphenylmethyl from Triphenylbromomethane and Magnesium

Triphenylbromomethane (1 Mole) + Mg (0.5 Atom).—A mixture of 16.2 g. of triphenylbromomethane and 0.6 g. of magnesium ribbon in 25 cc. of ether and 50 cc. of benzene was heated on the steam-bath. In half an hour all the magnesium disappeared. No magnesium hydroxide was produced when the mixture was hydrolyzed; consequently, no Grignard reagent had been present. Air was passed into the ether–benzene solution, and 10.4 g. of pure triphenylmethyl peroxide was obtained, which, assuming an 80% yield, corresponds to about 12.2 g. of triphenylmethyl, calcd. 12.15. No triphenylmethane was found in the filtrate from the peroxide.

We have represented the formation of triphenylmethyl by Equation 2. Actually, the mechanism may be more complex. Indeed, Schmidlin has shown that triphenylmethylmagnesium chloride can enter into reaction with triphenylchloromethane, giving rise to triphenylmethyl, and he ascribed to this reaction the presence of any triphenylmethyl in admixture with his preparations of the Grignard reagent

$$(C_6H_5)_3CMgX + (C_6H_5)_3CX = 2(C_6H_5)_3C + MgX_2 \qquad (6)$$

With our reagents we find that this reaction proceeds rapidly and completely. When to a solution of triphenylmethylmagnesium bromide an equivalent amount of triphenylbromomethane is added and the mixture is warmed for a few minutes, triphenylmethyl results in quantitative yield.

In view of the rapidity of Reaction 6, it seems quite likely that triphenylmethyl is produced not as represented in Equation 2 but by inter-reaction of Grignard reagent, initially formed, and unchanged triphenylbromomethane, *i. e.*, in two successive steps represented by the equations (3) and (6), respectively.

Triphenylmethyl + Mg + $MgBr_2$ (or MgI_2)

A number of experiments were performed on solutions of the free radical which had been prepared either according to Equation 6 or from triphenylchloromethane by means of silver or zinc. The results were quite satisfactory, but in order to make certain that our solutions of the radical were entirely free from any possible admixture of carbinol halide, the work was repeated with pure triphenylmethyl that had been recrystallized from acetone.

To a solution of 14.3 g. of triphenylmethyl in 60 cc. of benzene was added a solution of 9 g. of anhydrous magnesium bromide (prepared from $HgBr_2$ + Mg)[9] in 40 cc. of benzene and 60 cc. of ether. A small quantity of crystals precipitated, presumably a molecular compound of triphenylmethyl and $MgBr_2$. A coil of magnesium ribbon was introduced into the solution, and the mixture was gently heated on the steam-bath in an atmosphere of nitrogen; the upper end of the reflux condenser was connected to a mercury trap. The reaction started immediately and the mixture was heated for three hours. According to Equation 5, 0.71 g. of metallic magnesium should have reacted; found, 0.66 g., or 93% of the calculated value. The filtered solution was decomposed with water. The magnesium hydroxide so produced required 56.8 cc. of N H_2SO_4, calcd. 58.4 cc., and there were obtained 13.7 g. of pure triphenylmethane and 0.7 g. of triphenylmethyl peroxide.

In another experiment 9.0 g. of triphenylmethyl dissolved 0.445 g. of Mg (calcd. 0.450), and there was obtained on hydrolysis of the reaction product 7.9 g. of triphenylmethane.

Isolation and Analysis of the Triphenylmethylmagnesium Bromide.—Thirteen grams of crystalline triphenylmethyl was added to a solution of 9 g. of $MgBr_2$ in 120 cc. of ether–benzene (2:1), and the solution was heated for several hours with somewhat more than the required amount of magnesium ribbon. To the filtered solution was added a single crystal of triphenylmethylmagnesium bromide (obtained from triphenylbromomethane + magnesium), when sudden crystallization took place and in a short time the solution was half-filled with glistening prisms. The crystals were filtered, washed repeatedly with pure ether, and dried in a stream of nitrogen. The compound was found to be identical with the triphenylmethylmagnesium bromide obtained directly from triphenylbromomethane.

Anal. Subs., 14.56 g. Calcd. for $(C_6H_5)_3CMgBr\cdot 2(C_2H_5)_2O$: $(C_6H_5)_3C$, 49.1; Mg, 4.9; Br, 16.1. Found: $(C_6H_5)_3C$, 49.2; Mg, 4.7; Br, 16.1.

Triphenylmethyl + Mg + $MgBr_2$ at Room Temperature.—Ten and three-tenths grams of triphenylmethyl was added to a solution of 4.6 g. of $MgBr_2$ in 120 cc. of ether–benzene (1:2), containing 0.67 g. of magnesium ribbon. In one week at room temperature there was dissolved 0.50 g. of magnesium, and there was produced a 97% yield of triphenylmethylmagnesium bromide.

Triphenylmethyl + Mg + MgI_2.—A mixture of 12.2 g. of triphenylmethyl, 11 g. of magnesium iodide and 2.5 g. of magnesium ribbon in 150 cc. of ether-benzene (1:2) was heated on the steam-bath for several hours. The magnesium loss was 0.61 g., calcd., 0.608. Hydrolysis of the reaction product yielded 11 g. of triphenylmethane.

Reaction with Carbon Dioxide.—A solution of triphenylmethylmagnesium iodide was prepared from 12.2 g. of triphenylmethyl. A stream of dry carbon dioxide was

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

passed into this solution for three hours; during this time a large amount of light yellow precipitate appeared. Decomposition with dilute acid gave a product from which 12 g. of pure triphenylacetic acid was obtained.

Relative Proportions of $(C_6H_5)_3C$ and $(C_6H_5)_3CMgBr$

It is now obvious that in the process of "grignarding" triphenylbromomethane, no Grignard reagent is present until after one-half of the entire amount of magnesium has reacted. After the half-way mark, generation of Grignard reagent can come about only as a consequence of the reaction between triphenylmethyl and the system Mg + $MgBr_2$. This reaction proceeds to completion in virtue of the fact that Step c (p. 2457) is, in this case, reversible: $R + R \rightleftharpoons RR$. The relative quantities of free radical and of triphenylmethylmagnesium bromide that are present at any time during the reaction may be expressed graphically as in Fig. 1.

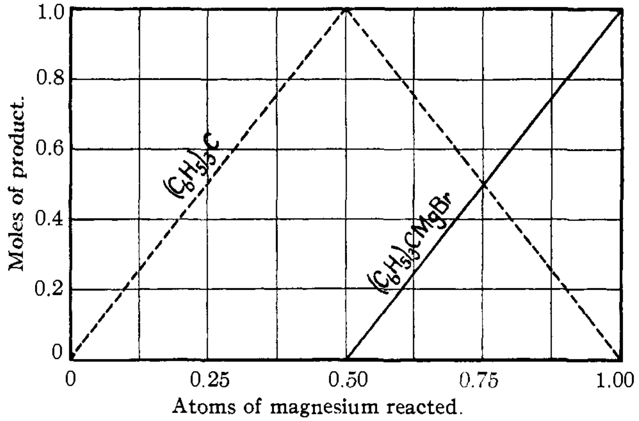

Fig. 1.—Amounts of triphenylmethyl and Grignard reagent in the reaction between triphenylbromomethane and magnesium.

Experiments conducted at room temperature and interrupted before a whole gram-atom of magnesium had reacted gave results which are in accordance with the curves. The following special experiment gave the two components in the ratio as anticipated, 50% each.

Triphenylbromomethane (1 Mole) + Mg (0.75 Atom).—Triphenylbromomethane, 16.2 g., and 0.912 g. of magnesium ribbon were heated together in 75 cc. of ether–benzene. In less than an hour all of the metal disappeared. The magnesium hydroxide produced on hydrolysis required 25.0 cc. of *N* H_2SO_4 for neutralization. This corresponds to a 50% yield of $(C_6H_5)_3CMgBr$ (see Fig. 1). From the benzene solution, after passing air into it, there were obtained 5.88 g. of triphenylmethyl peroxide (calcd. 6.5) and 6.0 g. of triphenylmethane (calcd. 6.1).

Summary

It has been shown that triphenylcarbinol reacts in anhydrous solvents with magnesium bromide and forms triphenylbromomethane.

Triphenylbromomethane reacts with metallic magnesium far more readily than the chloride, and gives rise to triphenylmethylmagnesium bromide. This has been isolated in crystalline state and analyzed.

The formation of triphenylmethylmagnesium bromide takes place in two successive stages: (a) formation of triphenylmethyl; (b) formation, from that, of the magnesium compound, $2\ R_3C + Mg + MgX_2 = 2\ R_3CMgX$. The formation of the triphenylmethyl is in itself most probably the result of two successive reactions: $R_3CX + Mg = R_3CMgX$; $R_3CMgX + R_3CX = 2\ R_3C + MgX_2$.

The formation of triphenylmethylmagnesium halide from triphenylmethyl and the system $Mg + MgX_2$ lends much support to the hypothesis that the action of the binary system is through the intermediate formation of the active compound MgX.

ANN ARBOR, MICHIGAN

[CONTRIBUTION FROM THE INSECTICIDE DIVISION, BUREAU OF CHEMISTRY AND SOILS]

TOXICAROL. A CONSTITUENT OF THE SOUTH AMERICAN FISH POISON CRACCA (TEPHROSIA) TOXICARIA[1]

BY E. P. CLARK

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In connection with a survey of fish poisoning plants as sources of insecticides now in progress in this Laboratory, a chemical examination of the roots of *Cracca* (*Tephrosia*) *toxicaria* was made.[2] It was shown that this plant material contains a crystalline substance which in high dilutions is toxic to fish. The crude crystals had a greenish-yellow color and a melting point of 200–203°. Closer examination revealed that the material was composed of at least two substances. The one that occurs in much the greater proportion is a bright canary yellow, optically inactive compound which has a melting point of 219° (corr.). It has the molecular formula $C_{23}H_{22}O_7$ and has one hydroxyl and two methoxyl groups. The name *toxicarol* has been assigned to it.

The second substance is a pale green crystalline compound which is separated from toxicarol only with difficulty. Owing to the small quantity of the plant available it was impossible to obtain sufficient crystalline material to carry the fractionation of the second substance to a state of certain analytical purity. Its optical properties, however, were readily determined, and from these data it was shown that the substance was identical with an optically inactive dimethoxy compound having the formula $C_{23}H_{22}O_6$ which is found in *Derris* and *Cube* roots.

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[1] The name *Tephrosia* Pers. is antedated by *Cracca* and under the American code of Botanical Nomenclature all species of *Tephrosia* should bear the generic name *Cracca*.

[2] The material was received from the Department of Agriculture, Georgetown, British Guiana, through the American Vice Consul, Harold R. Brown.