Action of Alkalies.—The dibromide is comparatively insensitive to bases but it slowly reacts with hot alkalies. Thus when 1.5 g. of the substance was boiled with excess of concentrated alcoholic potassium hydroxide it slowly dissolved and when the resulting dark colored solution was acidified it deposited a good yield of the cyclopropene di-acid. Toward concentrated alkalies, therefore, the dibromide behaves essentially like the cyclopropene dibromide discovered by Feist.[4]

The dibromide is also attacked slowly by dilute alkalies but the reaction, which is much more involved, has not yet been cleared up.

Summary

1. It is shown that cyclopropene derivatives can be obtained by eliminating nitrous acid from properly constituted nitro cyclopropane derivatives.

2. A method is described for preparing cyclopropene derivatives which differ from the few known heretofore in that they contain neither a conjugated system nor any hydrogen which by shifting could generate such a system.

3. It is found that the stability of cyclopropene derivatives is not dependent on the presence of a mobile hydrogen atom.

Converse Memorial Laboratory
Cambridge, Massachusetts

[Contribution from the Chemical Laboratory of Iowa State College]

THE REACTION BETWEEN MAGNESIUM DIPHENYL AND BROMINE. AN HISTORICAL NOTE ON THE FIRST PREPARATION OF PHENYLMAGNESIUM BROMIDE

By Henry Gilman and Robert E. Brown

Received November 4, 1929 Published March 6, 1930

Introduction

Long years ago Frankland[1] and Fleck[2] publicly called attention to the absence of organomagnesium halides. Fleck[2] purposefully set out to prepare phenylmagnesium bromide (by the *slow* addition of bromine to dry magnesium diphenyl covered with anhydrous ether) by the following reaction written by him

$$(C_6H_5)_2Mg + Br_2 \longrightarrow C_6H_5MgBr + C_6H_5Br \qquad (I)$$

However, because he obtained only bromobenzene and magnesium bromide he pictured the course of reaction as follows

$$(C_6H_5)_2Mg + 2Br_2 \longrightarrow 2C_6H_5Br + MgBr_2 \qquad (II)$$

and wrote, "One may assume that the latter reaction took place and that

---

[4] Feist, *Ber.*, **26**, 750 (1893).

[1] Frankland, *J. Chem. Soc.*, **13**, 194 (1861).

[2] Fleck, *Ann.*, **276**, 129 (1893). The results of these studies by Herman Fleck of Philadelphia, working in the laboratory of Lothar Meyer, were published in a dissertation at Tübingen in 1892.

a stable compound corresponding with the formula C_6H_5MgBr was not formed."

Incidental to studies on magnesium dialkyls and diaryls, we were curious to learn whether Fleck actually did have phenylmagnesium bromide in hand. Solely by analogy with other investigations in this Laboratory on organometallic compounds, it appeared altogether reasonable that phenylmagnesium bromide was an intermediate compound. However, it is an uncommonly difficult matter to make any chemical differentiation between phenylmagnesium bromide and a solution or mixture of magnesium diphenyl and magnesium bromide. This is so because we have not as yet come upon any chemical reaction of either of these compounds that is not shown by the other.

However, we believe that we have shown by a series of indirect proofs that Fleck actually did synthesize phenylmagnesium bromide as an intermediate step in his reaction.[3] As previously stated, there is not available at present any chemical reaction which can serve to differentiate unambiguously magnesium diphenyl from phenylmagnesium bromide. For example, after adding to magnesium diphenyl a quantity of bromine equivalent to that indicated in Reaction I, a simple but reliable test like the color test of Gilman, Schulze and Heck[4] is obtained. But there is no way of telling whether the positive color test obtained under such conditions is due to either one or both of the organomagnesium compounds, inasmuch as some of the *one* molecule of bromine may have reacted in accordance with *both* Reactions I and II, forming phenylmagnesium bromide and leaving some unaltered magnesium diphenyl—and each of these compounds gives the color test. In all this discussion it must be remembered that Fleck added an excess of bromine to the magnesium diphenyl, but he added it *slowly*, and sometimes in the course of the addition there was present in the reaction mixture one molecule or one equivalent of bromine in accordance with his Reaction I.

Two experiments served to prove that when *one* molecule of bromine is added, phenylmagnesium bromide is formed, and formed in accordance with Reaction I, to the probable exclusion of any unaltered magnesium diphenyl. First, it was shown that phenylmagnesium bromide reacts

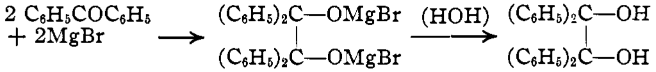
---

[3] We are not concerned here with any consideration of Fleck's priority. Fleck actually synthesized unknowingly the first organomagnesium halide; he knowingly set out to do so; but he equally definitely stated that a stable organomagnesium halide had not formed. Some credit is due Fleck for his early work. Whatever earlier work was done by others does not detract from the splendid and comprehensive studies by Professor Grignard. One of us (H. G.) in April, 1923, at the spring meeting of the American Chemical Society at New Haven, Connecticut, read a paper on this particular subject entitled "What Constitutes Discovery?"

[4] Gilman and Schulze, THIS JOURNAL, **47**, 2002 (1925); *Bull. soc. chim.*, **41**, 1479 (1927); Gilman and Heck, *Rec. trav. chim.*, **48**, 193 (1929); *Ber.*, **62**, 1379 (1929).

much more readily with *n*-valeronitrile than does an equivalent solution of magnesium diphenyl.[5] With this as a basis, one molecule of bromine was added to magnesium diphenyl and a determination made of the rate of reaction of the resulting solution with *n*-valeronitrile. It was found that the solution formed in this way reacted almost exactly at the same rate as an equivalent solution of phenylmagnesium bromide (see Reaction I).

Second, if on the addition of *one* molecule of bromine a transformation occurs in accordance with Reaction I (but not in accordance with Reaction II), then no magnesium bromide should be present. Fortunately, the recent studies by Gomberg and co-workers[6] make it possible to ascertain the presence of magnesium bromide. They showed that a mixture of magnesium bromide and magnesium behaves as though it were magnesious bromide (–MgBr), and that such an abnormally valenced complex reduces benzophenone to benzopinacol, as follows



$$\begin{array}{l}2\,C_6H_5COC_6H_5\\+\,2MgBr\end{array}\longrightarrow\begin{array}{l}(C_6H_5)_2C{-}OMgBr\\\qquad|\\(C_6H_5)_2C{-}OMgBr\end{array}\xrightarrow{(HOH)}\begin{array}{l}(C_6H_5)_2C{-}OH\\\qquad|\\(C_6H_5)_2C{-}OH\end{array}\qquad\text{(III)}$$

Accordingly if an excess of benzophenone and magnesium were added to a solution resulting from one molecule of magnesium diphenyl and one molecule of bromine, benzopinacol should form if any magnesium bromide were present. This is probably so even if three reagents (the magnesious bromide, magnesium diphenyl and phenylmagnesium bromide) were competing for but one molecule of benzophenone and not the excess we used. The reason for this is that Gomberg and Bachmann[6] have shown that magnesious iodide reacts more rapidly with benzophenone than does phenylmagnesium iodide, and our present studies show that phenylmagnesium bromide reacts more readily than magnesium diphenyl.[7]

The absence of magnesium bromide was established in an indirect manner. Even though one molecule of bromine might have reacted to some degree in accordance with Reaction II to give magnesium bromide, it is quite certain that the magnesium bromide so formed would react in turn with unaltered magnesium diphenyl, in accordance with the following reaction, to give phenylmagnesium bromide

---

[5] This is one of a number of semi-quantitative studies on the reaction rates of a variety of organometallic compounds. A preliminary account of these studies was read at the April, 1929, Meeting of the Iowa Academy of Science held at Fairfield, Iowa, and at the September, 1929, Meeting of the American Chemical Society held at Minneapolis, Minnesota. The difference in time of action illustrates the possibility of getting preferential reactions with magnesium diphenyl.

[6] See Gomberg and Bachmann, THIS JOURNAL, **49**, 236 (1927), and subsequent papers by Gomberg and co-workers.

[7] We should emphasize here that the more rapid reaction of phenylmagnesium bromide with *n*-valeronitrile does not justify any sweeping generalization to the effect that phenylmagnesium bromide will react more rapidly than magnesium diphenyl with *any* reagent.

$$(C_6H_5)_2Mg + MgBr_2 \longrightarrow 2\ C_6H_5MgBr \qquad \text{(IV)}$$

The correctness of Reaction IV was established by adding one molecule of magnesium bromide to one molecule of magnesium diphenyl and noting that the resulting solution when treated with magnesium and benzophenone gave no benzopinacol, thereby proving the absence or the disappearance of the magnesium bromide.[8] A like result was obtained with magnesium diphenyl and magnesium iodide. These experiments confirm earlier work by Gilman and Fothergill[9] on the constitution and dissociation of the Grignard reagent in which it was shown that magnesium diethyl reacts with magnesium iodide to give ethylmagnesium iodide, and that the transformation represented in Reaction IV is probably an equilibrium, with the equilibrium displaced almost completely to the right.

We have also shown that Fleck's Reaction II is correct when an *excess* of bromine is added, inasmuch as almost exactly *two* molecules of bromine react with one molecule of magnesium diphenyl to give a solution that contains neither magnesium diphenyl nor phenylmagnesium bromide. What Fleck did, therefore, was to first form phenylmagnesium bromide and then destroy it by continuing the addition of bromine to an excess.

Experimental Part

The magnesium diphenyl was prepared in accordance with the directions of Gilman and Brown,[10] and was free of mercury diphenyl, diphenyl and halogen. All operations were carried out in an atmosphere of dry nitrogen. Aliquots of the magnesium diphenyl in a mixture of ether and benzene were used for the several experiments. The concentration of magnesium diphenyl was determined quantitatively by the method of Gilman, Wilkinson, Fishel and Meyers.[11]

Rate of Reaction with *n*-Valeronitrile.—The time required for the disappearance of a positive color test[4] when 0.01 mole of phenylmagnesium bromide was treated with 2 cc. (2 g. or 0.024 mole) of *n*-valeronitrile in a total of 40 cc. of ether–benzene solution was between five and six minutes.[12]

---

[8] There is, of course, the possibility that the magnesium bromide might combine in some loose manner with the magnesium diphenyl to give a complex like $(C_6H_5)_2Mg\cdot MgBr_2$. Such a complex might at the same time show all of the reactions of magnesium diphenyl and yet hold the magnesium bromide with a sufficient tenacity to prevent its reaction with magnesium and benzophenone to give benzopinacol. This we consider unlikely because the addition compound of benzophenone and magnesium bromide[6] can react with magnesium to give benzopinacol. Also, studies on the structure of RCOOMgX, and ROMgX and HOMgX compounds show that all of them at moderate temperature react with magnesium and benzophenone to give benzopinacol. The same is true of the pyridine complex with magnesium iodide.

[9] Gilman and Fothergill, THIS JOURNAL, **51,** 3149 (1929).

[10] Gilman and Brown, *Rec. trav. chim.*, **49,** (March, 1930).

[11] Gilman, Wilkinson, Fishel and Meyers, THIS JOURNAL, **45,** 150 (1923). See also Gilman, Zoellner and Dickey, *ibid.*, **51,** 1576 (1929), for improvements in this method of titration for the quantitative estimation of reactive organometallic compounds.

[12] In this procedure a small part of the reaction mixture is removed at stated intervals for the color test. For a general idea of the sensitiveness of this method see Gilman and Vanderwal, *Bull. soc. chim.*, **45,** 344 (1929).

To a well-cooled solution of 0.01 mole of magnesium diphenyl was added 1.6 g. (0.01 mole) of bromine in an ether–benzene solution. After the mixture had cooled to room temperature, 2 cc. of *n*-valeronitrile was added. The total volume of solution was again 40 cc. This reaction was complete in five minutes.

An ether–benzene mixture was added to a solution of 0.01 mole of magnesium diphenyl until the volume was 36 cc. Then 4 cc. of *n*-valeronitrile was added with rapid stirring, a procedure followed in the other rate experiments. The reaction was complete after about two *hours*. In order to make certain that the bromobenzene formed in accordance with Reaction I was without effect on the rate in the magnesium diphenyl experiment, 3.2 g. (0.02 mole) of bromobenzene was added to a magnesium diphenyl solution and the rate of reaction with *n*-valeronitrile measured as before. The time required for the disappearance of magnesium diphenyl was the same as that when no bromobenzene was present. Bromobenzene is also without effect on the rate of reaction between phenylmagnesium bromide and *n*-valeronitrile.

Magnesium Diphenyl with Magnesium Bromide and Magnesium Iodide.—There appeared to be no heat of reaction when 0.01 mole of magnesium iodide in an ether–benzene solution was added to 0.01 mole of magnesium diphenyl. On the subsequent addition of 0.3 g. (0.0125 atom) of powdered magnesium and 7.3 g. (0.04 mole) of benzophenone in 25 cc. of benzene, the solution became warm, and after about ten minutes the mixture cooled somewhat and a whitish-yellow precipitate formed in considerable quantity. The mixture was allowed to stand for several hours with frequent shaking. On the following day the contents of the flask had not changed in appearance. On working up the reaction mixture in a customary manner,[9] there was obtained 3.8 g. or 73% of triphenylcarbinol. No benzopinacol was found. In a corresponding experiment in which the magnesium iodide was replaced by magnesium bromide, the yield of triphenylcarbinol was 65%. Again no benzopinacol was found.[13]

Magnesium Diphenyl and Bromine.—A solution resulting from the reaction between 0.01 mole of bromine and 0.01 mole of magnesium diphenyl was carbonated after the procedure of Gilman and Parker.[14] The yield of benzoic acid obtained in this manner was 0.65 g. or 53%, which compares favorably with larger-sized runs with phenylmagnesium bromide.

A solution containing 3.2 g. (0.02 mole) of bromine in 50 cc. of an ether–benzene mixture was added to 0.01 mole of a magnesium diphenyl solution. After the addition of 45 cc. of the bromine solution, the reaction mixture still gave a positive color test.[4] However, when all (50 cc. or 0.02 mole) of the bromine solution was added, there was no color test.

Summary

When bromine is added to magnesium diphenyl, phenylmagnesium bromide is first formed. This is probably the first reported reaction in which an organomagnesium halide is formed in ether. However, Fleck, who originally carried out this reaction, overlooked the intermediate formation of phenylmagnesium bromide.

AMES, IOWA

---

[13] The experiments with magnesium bromide and magnesium iodide were checked. The same was done with the rate determinations in the *n*-valeronitrile reaction with magnesium diphenyl and phenylmagnesium bromide, respectively.

[14] Gilman and Parker, THIS JOURNAL, **46**, 2816 (1924).