[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

THE FORMATION OF DI-PARA-TOLYL INCIDENTAL TO THE PREPARATION OF BENZYLMAGNESIUM CHLORIDE. THE PROBABLE PRELIMINARY FORMATION OF FREE RADICALS IN THE PREPARATION OF GRIGNARD REAGENTS

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Introduction

In the course of some studies on the reaction between alkyl *p*-toluenesulfonates and RMgX compounds, Gilman and Beaber[1] obtained very small quantities of an unidentified hydrocarbon melting at 119–120° in all cases where benzylmagnesium chloride was used. Later Gilman and McCracken[2] isolated the same compound, again in very small amounts, from the reaction products of nitrobenzene and benzylmagnesium chloride. More recently, in connection with an investigation of the rearrangements[3] of some Grignard reagents like benzylmagnesium chloride, the same hydrocarbon was obtained as an extremely minor product of the reaction between formaldehyde and benzylmagnesium chloride.

Inasmuch as the hydrocarbon was obtained in three widely different reactions of benzylmagnesium chloride, it appeared probable that the compound was formed independently of the reagent brought into reaction with the benzylmagnesium chloride, and must have formed during the preparation of benzylmagnesium chloride. Several check experiments soon confirmed this, for the compound was obtained, again in very small quantities, when benzylmagnesium chloride was hydrolyzed. The compound was finally shown to be di-*p*-tolyl. Its identity was confirmed by a series of mixed melting-point determinations between the product of the several reactions[4] and with each of these compounds and an authentic specimen of di-*p*-tolyl.

The most reasonable explanation, at present, for the formation of di-*p*-tolyl is the preliminary formation of free radicals in the preparation of Grignard reagents. This idea finds support in some experimental work presented recently by Gilman and Fothergill[5] on the disproportionation of free alkyl radicals probably formed incidental to the preparation of some alkylmagnesium halides. These two independent series of observations

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[1] Gilman and Beaber, THIS JOURNAL, **47**, 518 (1925).

[2] Gilman and McCracken, *ibid.*, **51**, 821 (1929).

[3] See p. 1826 of an article by Gilman and Harris, *ibid.*, **49**, 1825 (1927).

[4] The Experimental Part describes other reactions from which the di-*p*-tolyl was subsequently isolated in connection with studies on the course of the reaction.

[5] Gilman and Fothergill, THIS JOURNAL, **50**, 3334 (1928). This article contains leading references to other related studies.

have set us in pursuit of the free radicals with the hope of capturing them before they have had an opportunity to couple or to disproportionate.[6] With such capture by so-called reliable reactions to give readily identifiable compounds, we would have unequivocable proof for the prior formation of radicals in the preparation of organomagnesium halides.[7]

The following reactions might account for the formation of di-*p*-tolyl and other products.

$$C_6H_5CH_2Cl + Mg \longrightarrow C_6H_5CH_2\text{—} + \text{—}MgCl \qquad (I)$$
$$C_6H_5CH_2\text{—} + \text{—}MgCl \longrightarrow C_6H_5CH_2MgCl \qquad (II)$$
$$C_6H_5CH_2\text{—} + C_6H_5CH_2\text{—} \longrightarrow C_6H_5CH_2CH_2C_6H_5 \qquad (III)$$
$$C_6H_5CH_2\text{—} \longrightarrow p\text{-}CH_3C_6H_4\text{—} \qquad (IV)$$
$$p\text{-}CH_3C_6H_4\text{—} + p\text{-}CH_3C_6H_4 \longrightarrow p\text{-}CH_3C_6H_4\cdot C_6H_4CH_3\text{-}p \qquad (V)$$

The free radicals[8] formed in accordance with Reaction I combine to a very large extent to give benzylmagnesium chloride (Reaction II). Gilman, Zoellner and Dickey[9] have just shown that the yield of benzylmagnesium chloride is about 95%, and that this yield is independent of the rate of addition of benzyl chloride to magnesium and ether. The yield of dibenzyl formed in accordance with Reaction III is about 3 to 5%, and the yield of di-*p*-tolyl (see Reactions IV and V) is about 0.2 to 0.3%.

Reaction IV is illustrative of the rearrangement of the benzyl radical to a *p*-tolyl radical. It is highly improbable that the benzyl radical would rearrange to any appreciable extent to a *m*-tolyl radical. However, it is reasonable to expect that if a free benzyl radical is formed it should rearrange to an *o*-tolyl radical, and to an extent probably less than that of its rearrangement to a *p*-tolyl radical. Should the benzyl radical rearrange not only to the *p*-tolyl radical but also to the *o*-tolyl radical, then one might expect, in addition to di-*p*-tolyl, compounds like the following: *o*- and *p*-methyldiphenylmethane, 2,2′-dimethyldiphenyl and 2,4′-dimethyldiphenyl. The presence of an *o*-tolyl linkage should reveal itself in the formation of phthalic acid when the very small quantities of oils were oxidized. Evidence, in this manner, for the presence of an *o*-tolyl linkage was obtained by the characteristic sensitive fluorescein test with a quantity of material that was too minute for isolation. It is obvious from the

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[6] A preliminary report of these studies was read by Gilman, Fothergill, Kirby and McGlumphy at the September, 1928, meeting of the American Chemical Society held at Swampscott, Massachusetts.

[7] A recent, very interesting, article by Bachmann and Clarke, THIS JOURNAL, **49**, 2089 (1927), on the mechanism of the Wurtz–Fittig reaction may be conveniently interpreted by assuming the intermediate formation of free radicals. They give references to other related studies on the Wurtz–Fittig reaction.

[8] The excellent work of Gomberg and Bachmann, *ibid.*, **49**, 2584 (1927), on magnesious halides has definitely added these abnormally valenced complexes to the growing series of free radicals.

[9] Gilman, Zoellner and Dickey, *ibid.*, **51**, 1576, 1583 (1929).

very large yield of Grignard reagent and the appreciable yield of dibenzyl that very little of the benzyl chloride remained to form other products.[10]

The very small percentage of di-*p*-tolyl made it desirable to study other possible explanations for the origin of this compound in the preparation of benzylmagnesium chloride. Quite naturally, a first consideration turns on the purity of the benzyl chloride. There is the possibility that our benzyl chloride, even though of high purity, might contain some *p*-chlorotoluene. If such *p*-chlorotoluene were present, it might react with the magnesium[11] to form *p*-tolylmagnesium chloride and a small quantity of the normal[5] coupling product, di-*p*-tolyl. However, the possibility of the benzyl chloride being contaminated with a small amount of *p*-chlorotoluene was ruled out by two experiments. First, when a mixture of equivalent quantities of benzyl chloride and *p*-chlorotoluene was added to sufficient magnesium in ether to react with both halides, no *p*-tolylmagnesium chloride was formed[12] and, also, there was practically no di-*p*-tolyl. Second, the oxidation of our benzyl chloride gave benzoic acid, and none of the *p*-chlorobenzoic acid that might have been expected if *p*-chlorotoluene were present as an impurity.[13]

We would not have it understood that there is an inflexible ratio between the yields of dibenzyl and di-*p*-tolyl formed from the benzyl radical. Variations were noted in the several hydrolysis experiments. Furthermore, in two experiments that were purposely selected to give large quantities of coupling products, we found that the customary small amounts of di-*p*-tolyl were formed along with comparatively extremely large quantities of dibenzyl. These two experiments were the reactions with benzyl-

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[10] We have little doubt that extremely large-sized preparations of benzylmagnesium chloride would reveal coupling products, in workable amounts, of compounds other than dibenzyl and di-*p*-tolyl. It is not a particularly inviting procedure for us to prepare very large quantities of any RMgX compound and then decompose it by hydrolysis. On p. 159 of Vol. 3 of the "Annual Survey of American Chemistry" we directed attention, in connection to the work of Bachmann and Clarke (see ref. 7 of this paper), to the special contributions to organic chemistry by manufacturers and dealers in research chemicals. For the immediate purposes of the present study, there is no imperative need for the isolation and identification of the several other possible compounds already mentioned, and which would be formed to a very small extent.

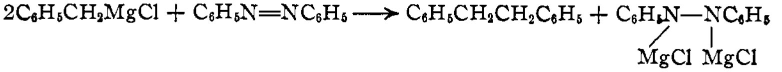
[11] Such reaction would be highly favored by the strong positive catalytic effect of benzylmagnesium chloride, a Grignard reagent that forms with great ease. See Gilman, Peterson and Schulze, *Rec. trav. chim.*, **47**, 19 (1928), for a comparative study of various catalysts. Aryl chlorides form the corresponding Grignard reagents with great difficulty.

[12] This was shown by the absence of any *p*-toluic acid when the reaction mixture was treated with carbon dioxide prior to hydrolysis.

[13] See the Experimental Part for a discussion of the Beilstein flame test for our benzoic acid and that of several samples of "halogen-free benzoic acid" kindly supplied us by others.

magnesium chloride and cupric chloride[14] and azobenzene,[15] respectively. The following are typical reactions

$$2C_6H_5CH_2MgCl + 2CuCl_2 \longrightarrow C_6H_5CH_2CH_2C_6H_5 + Cu_2Cl_2 + 2MgCl_2 \qquad (VI)$$



$$2C_6H_5CH_2MgCl + C_6H_5N{=}NC_6H_5 \longrightarrow C_6H_5CH_2CH_2C_6H_5 + C_6H_5\underset{MgCl}{N}-\underset{MgCl}{N}C_6H_5 \qquad (VII)$$

Attention should also be directed to the possibility of the free radicals forming only with the hydrolysis of the benzylmagnesium chloride, and not being present prior to the formation of the Grignard reagent. For example, Gilman and Fothergill[5] obtained evidence for disproportionation and therefore for free radicals when they hydrolyzed some of the *alkyl*-magnesium halides studied by them. But they also showed that the same disproportionation took place to a greater extent *before* hydrolysis. By analogy, therefore, the greater part of the coupling products from benzylmagnesium chloride were formed prior to hydrolysis. Unlike the gaseous products of coupling and disproportionation that result from the preparation of *alkyl*magnesium halides having an R group of low molecular weight, it would be difficult to isolate the essentially non-volatile products like dibenzyl and di-*p*-tolyl without destroying the benzylmagnesium chloride, in whole or in part.[16]

Experimental Part

Hydrolysis of Benzylmagnesium Chloride.—A one-mole preparation of benzylmagnesium chloride was hydrolyzed by iced hydrochloric acid and the resulting mixture was steam distilled. The forerun of this steam distillate when separated, dried and distilled at atmospheric pressure gave 66.3 g. or a 72.1% yield of toluene. As soon as a sample of the original steam distillate gave crystals on cooling, the receiver was changed and the next liter of steam distillate gave 2.8 g. or a 3.1% yield of pure dibenzyl. The succeeding 550 cc. of steam distillate gave 0.25 g. (or 0.3%) of a crystalline solid melting unsharply between 85 and 90°. After 3 crystallizations of this solid from 95% alcohol, the compound melted at 119–120° and was identified as di-*p*-tolyl. A careful fractionation by crystallization of the dibenzyl mentioned above gave no di-*p*-tolyl. The 2.4 g. of dark brown non-steam distillable oil was oxidized by potassium dichromate in dilute sulfuric acid to give benzoic acid, no other carbonyl-containing compound and an oil. Oxidation of this oil by alkaline permanganate gave benzoic acid.

In a second one-mole run, the toluene fraction was distilled under reduced pressure in order to avoid the possible formation of *p*-benzyldibenzyl, inasmuch as Fuson[17] has shown that dibenzyl and benzyl chloride combine under the influence of heat to form

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[14] Gilman and Parker, THIS JOURNAL, **46**, 2823 (1924). This article contains leading references to earlier work on this coupling reaction.

[15] Gilman and Pickens, *ibid.*, **47**, 2406 (1925). Gilman and Fothergill, *ibid.*, **50**, 867 (1928) (see footnote 5 on p. 868 of this article by G. and F.). Also, Rheinboldt and Kirberg, *J. prakt. Chem.*, **118**, 1(1928).

[16] In this connection it is interesting to note that ethylmagnesium bromide can be refluxed in a *p*-cymene solution (b. p. 175°) without decomposition [see Gilman and Peterson, *Rec. trav. chim.*, **48**, 247 (1929)]. Also, it is possible to prepare some ether-free Grignard reagents by the direct application of heat.

[17] Fuson, THIS JOURNAL, **48**, 2937 (1926).

p-benzyldibenzyl. We wished to avoid the formation of this compound in order to restrict the origin of any terephthalic acid (resulting from oxidation of the small residues) to such coupling products as di-*p*-tolyl and *p*-benzyltoluene. From this run there was obtained 66.3% of toluene, 5.4% of dibenzyl and 0.2% of di-*p*-tolyl. Oxidation of the residues gave benzoic acid but no phthalic and no terephthalic acids. In a search for carbonyl compounds that might have resulted from such oxidation, a few drops of a light yellowish oily oxime was obtained; this showed no tendency to crystallize.

From a third one-mole run prepared by the very rapid[18] addition of benzyl chloride there was obtained 60.7% of toluene, 3.85% of dibenzyl and 0.2% of di-*p*-tolyl. The 1.9 g. of non-volatile oil resulting from the steam distillation was oxidized by alkaline permanganate. When the filtered oxidation mixture was acidified a slight cloudiness indicative of a trace of terephthalic acid[19] appeared. However, the quantity was altogether too small to permit of isolation. The resulting water solution was thrice extracted with ether and the ether solution, after drying, was evaporated to dryness. The solid acids were extracted with chloroform in order to isolate any phthalic acid. Only a trace remained undissolved and this appeared to be phthalic acid, inasmuch as it gave a good fluorescein test when warmed with resorcinol and sulfuric acid. Evaporation of the chloroform extracts gave 0.13 g. of benzoic acid. It should be mentioned here that oxidations in search of acids were regularly carried out with all fractions, both of steam distillates and residues, that were not definitely shown to be toluene, dibenzyl or di-*p*-tolyl.

Benzylmagnesium Chloride, *p*-Chlorotoluene and Carbon Dioxide.—A mixture of 0.1 mole of benzyl chloride and 0.1 mole of *p*-chlorotoluene was added to 0.2 atom of magnesium in ether. The resulting solution of RMgCl compound or compounds was treated with carbon dioxide in the customary manner and then hydrolyzed. The phenylacetic acid (7.0 g. or 51%) melted sharply at 76–77°, and fractional crystallization of it yielded no *p*-toluic acid. The yield of recovered *p*-chlorotoluene was 87.3%.

Oxidation of Benzyl Chloride.—The benzoic acid obtained by the alkaline permanganate oxidation of 0.1 mole of the benzyl chloride used in these studies gave no positive sodium fusion test for halogen. However, it did give a weak Beilstein copper wire color test. The faint green flame test appeared momentarily and without excessive heating of the wire. Because of the very critical nature of this test (a positive test would indicate the presence of *p*-chlorotoluene in our benzyl chloride) it was also carried out with several samples of halogen-free benzoic acid.[20] To our great surprise all four samples of such halogen-free benzoic acid (which showed no halogen after a sodium fusion test) gave a slight positive Beilstein test.

The weak Beilstein test with our several samples of benzoic acid prompted a like test with other supposedly pure carboxylic acids. The faint Beilstein test is not shown by all carboxylic acids, for among the 9 acids tested there was no positive flame test with salicylic, diphenylacetic and terephthalic acids. Should our "halogen-free benzoic acids" actually contain a trace of halogen sufficient to give this very delicate flame test

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[18] This was carried out prior to the experiments (see ref. 9) on the effect of rapid addition of halide on the yield of RMgX compound. At that time it was believed that a rapid addition would favor the formation of coupling products and so improve the opportunity of obtaining coupling products in addition to the dibenzyl and di-*p*-tolyl previously isolated.

[19] At the time these studies were carried out a technique had been acquired for the isolation and identification of small quantities of the phthalic and other acids. See ref. 3 of this paper.

[20] In this connection the authors wish to express their appreciation for samples provided by Dr. H. T. Clarke and Dr. E. K. Bolton.

it still would not affect seriously our conclusions in view of the experiment (described above) on benzylmagnesium chloride, *p*-chlorotoluene and carbon dioxide. The tests with the several benzoic acids are sufficiently important to warrant further study, and we are collecting samples of benzoic acid which (as well as we can determine) are free of any hereditary and acquired taint of halogen.

Benzylmagnesium Chloride and Cupric Chloride.—From the reaction carried out in the customary manner[14] between 0.3 mole of benzylmagnesium chloride and 0.3 mole of cupric chloride there was obtained a 70% yield of pure dibenzyl and a trace of di-*p*-tolyl. The 4.6 g. of non-steam distillable tar gave only benzoic acid on oxidation.

Benzylmagnesium Chloride and Azobenzene.—From one mole of benzylmagnesium chloride and 0.44 mole of azobenzene there was obtained 52.3% of benzidine and 37% of dibenzyl.

Benzylmagnesium Chloride and Formaldehyde.—Formaldehyde was led over the surface of 0.4 mole of benzylmagnesium chloride until a negative color test[21] was obtained showing that all of the Grignard reagent had been used up. In addition to a 26.9% yield of *o*-tolylcarbinol there was obtained about 0.3 g. of di-*p*-tolyl.

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Summary

Di-*p*-tolyl is formed in very small quantities incidental to the preparation of benzylmagnesium chloride. The presence of this coupling product is advanced as additional evidence for the preliminary formation of free radicals in the preparation of Grignard reagents.

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THE YIELDS OF SOME GRIGNARD REAGENTS. ALTERNATING PROPERTIES OF NORMAL ALKYL BROMIDES

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Introduction

In connection with studies on the relative reactivities of alkyl and aryl halides toward magnesium in ether,[1] it was necessary to determine the yields of some Grignard reagents. These yields were determined under optimal conditions. They differ in several instances from the yields previously determined in this Laboratory.[2] In general, because of an improved mode of preparation and refinements in analytical procedure, the yields are

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[21] Gilman and Schulze, THIS JOURNAL, 47, 2002 (1925), and *Bull. soc. chim.*, 41, 1479 (1927).

[1] A preliminary account of these studies has been reported by Gilman and Zoellner, THIS JOURNAL, 50, 2520 (1928).

[2] (a) Gilman and Meyers, *ibid.*, 45, 159 (1923); (b) Gilman and McCracken, *ibid.*, 45, 2462 (1923); (c) Gilman and McCracken, *Rec. trav. chim.*, 46, 463 (1927). Marvel, Blomquist and Vaughn, THIS JOURNAL, 50, 2810 (1928), have determined the yields of some Grignard reagents prepared in di-*n*-butyl ether.