the compound darkens and gradually decomposes, but does not melt below 250°. It is soluble in dilute alkalies. The solutions are colorless.

Anal. Calcd. for $C_{13}H_{15}O_6NHg_2$: Hg, 58.80; N, 2.05. Found: Hg, 58.69; N, 2.06.

Summary

1. A simple method of preparation of aminocresols from corresponding nitrocresols by reduction with sodium hydrosulfite is described.

2. 6-Amino-*o*-cresol, 6-acetylamino-*o*-cresol, 6-amino-*m*-cresol and 6-acetylamino-*m*-cresol were prepared and studied.

3. The following mercury derivatives of acetylaminocresols were synthesized and studied: 4-acetoxymercuri-6-acetylamino-*o*-cresol, 4,6-diacetoxymercuri-5-acetylamino-*o*-cresol, 2,4-diacetoxymercuri-6-acetylamino-*m*-cresol and 2,6-diacetoxymercuri-4-acetylamino-*m*-cresol.

PHILADELPHIA, PENNSYLVANIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

BENZOHYDRYLMAGNESIUM CHLORIDE AND THE APPARENT PRIOR FORMATION OF FREE BENZOHYDRYL RADICALS

BY HENRY GILMAN AND E. A. ZOELLNER

RECEIVED JUNE 6, 1930 PUBLISHED OCTOBER 6, 1930

Introduction

In the preparation of all Grignard reagents, there are side-reactions, and chief among these is the coupling reaction to give R·R compounds.[1] The extent of this coupling reaction varies between extreme limits,[2] and until recently it was essentially impossible, for example, to prepare allylmagnesium bromide because of the unusually high yield of diallyl.[3]

Perhaps the most unusual preparation of this type is that of benzohydrylmagnesium chloride, $(C_6H_5)_2CHMgCl$. Under ordinary conditions the yield of coupling product, *sym.*-tetraphenylethane, is astonishingly high and has reached 95.5%.[4] For this reason, the application of this RMgX compound in synthesis has followed the procedure of Barbier. This involves the preparation of the benzohydrylmagnesium halide in the presence of the reactant.[5] Ordinarily this procedure has two serious disadvantages:

---

[1] Gilman and Fothergill, THIS JOURNAL, 50, 3334 (1928).

[2] See Gilman, Zoellner and Dickey, *ibid.*, **51**, 1576 (1929), for the yields of some RMgX compounds. Some typical RMgX compounds like phenylmagnesium bromide and *n*-butylmagnesium bromide can be prepared in essentially quantitative yields when an excess of magnesium is used.

[3] It is now possible to prepare allylmagnesium bromide in yields greater than 93%. See Gilman and McGlumphy, *Bull. soc. chim.*, **43**, 1322 (1928).

[4] Gilman and Kirby, THIS JOURNAL, **48**, 1733 (1926).

[5] Gomberg and Cone, *Ber.*, **39**, 1461 (1906); Bert, *Compt. rend.*, **177**, 324 (1923); Grignard and Ono, *Bull. soc. chim.*, **39**, 830, 1589 (1926); Gilman and Kirby, THIS JOURNAL, **48**, 1733 (1926); Levy and Lagrave, *Bull. soc. chim.*, **43**, 437 (1928).

first, the yields are low; second, the formation of the Grignard reagent may be retarded and, in some cases, actually inhibited.[3,4]

We needed benzohydrylmagnesium chloride in connection with the extension of studies on the so-called abnormal reactions of Grignard reagents having α,β-unsaturation.[6] As a result of the present study, it is now possible to prepare this RMgX compound independently (and not in accordance with the Barbier procedure) and the yields are satisfactory (70%). Excellent yields of the corresponding carboxylic acid, diphenylacetic acid, have been realized by the customary procedure of carbonation.

Perhaps of greater significance than the development of a method for the preparation of this unusual Grignard reagent in satisfactory yields, is the direct observation of what appear to be transiently formed free radicals. During the addition of the benzohydryl chloride in ether to magnesium in ether, it was noted that a reddish color formed where the chloride came in contact with the ether containing magnesium and Grignard reagent. The same phenomenon was observed when the benzohydryl chloride was added to an ether solution of benzohydrylmagnesium chloride free of magnesium. With the rapid addition of halide to the Grignard solution, it was possible (in small containers) to have the color throughout the solution. The color disappears very shortly after its formation, and it is impossible to get the color when the Grignard reagent is used up.

It has already been suggested by Gomberg and Bachmann[7] that free radicals are formed initially in the *preparation* of Grignard reagents when iodine is used as a catalyst, as follows

$$\mathrm{Mg} + \mathrm{I_2} \longrightarrow \mathrm{MgI_2} \qquad (1)$$
$$\mathrm{MgI_2} + \mathrm{Mg} \longrightarrow 2\,\text{—MgI} \qquad (2)$$
$$\mathrm{RX} + \text{—MgI} \longrightarrow \text{R—} + \mathrm{XMgI} \qquad (3)$$
$$\mathrm{XMgI} + \mathrm{Mg} \longrightarrow \text{—MgI} + \text{—MgX} \qquad (4)$$
$$\text{R—} + \text{—MgX} \longrightarrow \mathrm{RMgX} \qquad (5)$$

In the absence of a catalyst, like iodine, it has been suggested[7] that the first step in the reaction is

$$2\mathrm{RX} + \mathrm{Mg} \longrightarrow \mathrm{R{\cdot}R} + \mathrm{MgX_2} \qquad (6)$$

and that the $\mathrm{MgX_2}$ so formed then reacts with magnesium in accordance with Reaction 1 to give —MgX which subsequently combines with the free radical to give the RMgX compound. However, we[1] are of the opinion that the formation of free radicals is the *first* step in the preparation of the Grignard reagent, even in the absence of any catalyst

$$2\mathrm{RX} + \mathrm{Mg} \longrightarrow 2\text{R—} + \mathrm{MgX_2} \qquad (7)$$

---

[6] Gilman and Kirby, THIS JOURNAL, **51**, 3475 (1929); Gilman and Jones, *ibid.*, **51**, 2840 (1929).

[7] Gomberg and Bachmann, *ibid.*, **49**, 236 (1927). This article contains leading references to explanations for the catalytic influence of some reagents for initiating the preparation of organomagnesium halides.

and that then the MgX_2 reacts with magnesium (Reaction 2) to give the —MgX, which subsequently combines with the free radical (Reaction 5). Possibly both reactions occur.

Whatever may be the correct explanation, and both mechanisms as well as others may be correct, there is experimental evidence by Gilman and Fothergill[1] and Gilman and Kirby[8] in support of the intermediate formation of free radicals incidental to the preparation of Grignard reagents.

The transitory color observed on the addition of benzohydryl chloride to benzohydrylmagnesium chloride indicates that free radicals are also formed *subsequent* to the preparation of RMgX compounds. The free radicals so formed might account in part at least for the side reactions of coupling and disproportionation described by Gilman and Fothergill.[1]

$$(C_6H_5)_2CHMgCl + (C_6H_5)_2CHCl \longrightarrow 2(C_6H_5)_2CH— + MgCl_2 \qquad (8)$$

$$2(C_6H_5)_2CH— \longrightarrow (C_6H_5)_2CHCH(C_6H_5)_2 \qquad (9)$$

and, where disproportionation can occur, the following general reaction[1] might be written

$$2R— \longrightarrow R(+H) + R(—H) \qquad (10)$$

It is interesting to note that apparently the same color phenomena are observed on the addition of benzohydryl chloride to some RMgX compounds other than benzohydrylmagnesium chloride. This is not entirely unexpected in view of the studies by Fuson,[9] who showed that the coupling reaction is best interpreted under certain conditions, as follows

$$2RX + 2R'MgX \longrightarrow R{\cdot}R + R'{\cdot}R' + 2MgX_2 \qquad (11)$$

In accordance with this reaction it is readily understandable that the formation of R·R compound from the RX compound might have taken place as indicated in Reaction 9, written above. Actually, Späth[10] has suggested such a general mechanism, but this is the first case where we have observed the apparent intermediate formation of free radicals other than those of *tri*-arylmethyls[11] and related compounds. It should be possible to capture[12] these radicals and extend our knowledge of free radicals to new types.

[8] Gilman and Kirby, THIS JOURNAL, 51, 1571 (1929). Another interpretation does not involve —MgX, and consists in the direct union of 2R— + Mg ⟶ R_2Mg. See Gilman and Brown, *ibid.*, 52, November, 1930.

[9] Fuson, *ibid.*, 48, 830, 2681, 2937 (1926). These papers have an excellent review of earlier studies on the coupling reaction.

[10] Späth, *Monatsh.*, 34, 1965 (1913).

[11] See, Gilman and Zoellner, THIS JOURNAL, 51, 3493 (1929), for the preparation of triphenylmethylmagnesium chloride.

[12] See, Gilman and Fothergill, *ibid.*, 51, 3149 (1929), for studies on the capture of free radicals formed in the preparation and reactions of Grignard reagents.

After the manuscript was submitted for publication, it was found that benzohydrylmagnesium chloride reacted with benzophenone to give benzopinacol and tetraphenylethylene. This is evidence for the dissociation of this RMgCl compound, and for the disproportionation of benzohydryl radicals.

Experimental Part

The benzohydryl chloride used in these studies may not have been as pure as that prepared previously by Gilman and Kirby.[4] Two fractions were used. One of them boiled at 147–148° (6 mm.) (m. p. 9–11°), and the other at 148–150° (6 mm.) (m. p. 13–15°). The apparatus and method of analysis were those described by Gilman, Zoellner and Dickey.[2] However, the procedure had the following slight variations: ten drops of halide were used to initiate the reaction; heat was applied by means of a microburner under a wire gauze; as soon as reaction set in (two to three minutes), stirring was commenced; then, refluxing and stirring were continued for ten minutes prior to addition of the remaining halide in ether. There was no difficulty in starting the reaction when the customary small quantity (0.03–0.05 g.) of iodine was used as a catalyst.

Without going into details of a series of experiments, it may be stated at once that the yield is markedly affected by the quantity of fine magnesium (30–80-mesh). In an experiment using 5.07 g. (0.025 mole) of benzohydryl chloride, 6.1 g. (0.25 atom) of magnesium and a total of 74 cc. (0.74 mole) of ether, the yield was 51%. The time of addition of the halide was one hour, and with a two-hour period of addition the yield was 53%. It was noted that the formation of precipitate was slightly progressive. In contrast with this, the precipitation is more pronounced at the beginning of the preparation of *tert.*-butyl- and *tert.*-amylmagnesium chlorides,[13] and in these cases the precipitate (under optimal conditions) disappears when the preparation is about one-half completed.

When the ratio of magnesium and ether to the chloride was doubled, so that for each mole equivalent of benzohydryl chloride 20 atom equivalents of magnesium and 60 mole equivalents of ether were used, the yield was 57%. Here there was less precipitate and its formation was not progressive.

When 30 atom equivalents (9.12 g.) of magnesium and 60 equivalents (74 cc.) of ether were used with one mole equivalent (2.53 g.) of benzohydryl chloride boiling at 148–150° (6 mm.), and when the time of addition was one and one-half hours, the yield was 71%. In a like experiment with the halide boiling at 147–148° (6 mm.), the yield was 68%. In these experiments the smallest quantity of precipitate formed. It appears altogether reasonable that with a still higher ratio of magnesium, pure halide and slow addition, the yield can be significantly increased.

A larger-sized run was made in order to prepare the corresponding carboxylic acid. In this experiment the conditions were those described for the 51% yield preparation: 10.14 g. (0.05 mole) of the chloride was used and the time of addition was two hours. The yield by titration was 50%. After cooling the RMgCl solution to −15°, carbon dioxide was added[14] rapidly and was taken up almost instantly. The yield of diphenylacetic acid, $(C_6H_5)_2CHCOOH$, was 84% (based on the quantity of available RMgCl compound).[15] The identity of the acid was confirmed by a mixed melting point determination with an authentic specimen. In addition to the acid, there was isolated 2.5 g. or 30% of *sym.*-tetraphenylethane.

Summary

Under ordinary conditions it is practically impossible to prepare benzohydrylmagnesium chloride, $(C_6H_5)_2CHMgCl$, because of an extreme tend-

---

[13] Gilman and Zoellner, *Rec. trav. chim.*, **47**, 1058 (1928).

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

[15] This high yield is remindful of the very high yield of triphenylacetic acid obtained by the carbonation of triphenylmethylmagnesium chloride.[11]

ency for coupling which results in a 95% yield of R·R compound. Directions are now available for the preparation of this unusual Grignard reagent in yields upwards of 70%. The coupling reaction is apparently due to the prior formation of free benzohydryl radicals, which are of red color and of short life.

AMES, IOWA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF MIDDLEBURY COLLEGE]

ALIPHATIC ACYLOINS. I. PREPARATION[1]

BY B. B. CORSON, W. L. BENSON AND T. T. GOODWIN

RECEIVED JUNE 9, 1930 PUBLISHED OCTOBER 6, 1930

The most promising method which has been described for the preparation of aliphatic acyloins involves the action of sodium on ethereal or benzene solutions of aliphatic esters. This reaction was first described by Bouveault and Locquin[2] and the following mechanism was assumed

$$\begin{gathered}2RCOOR' + 4Na \longrightarrow 2NaOR' + RC(ONa){=}C(ONa)R \\ RC(ONa){=}C(ONa)R + 2H_2O \longrightarrow RC(OH){=}C(OH)R + 2NaOH \\ RC(OH){=}C(OH)R \longrightarrow RCHOHCOR\end{gathered}$$

Other mechanisms have been suggested.[3]

According to the original directions the reaction was run at 0° except in one case, pivaloin (2,2,5,5-tetramethylhexanol-3-one-4), where the reaction temperature was that of the room. The implication was that the acetoacetic ester condensation would result at higher temperatures and it was suggested that acyloins represented an intermediate step in the acetoacetic ester condensation.[4] Other investigators, however, have used higher temperatures, with equally good results.[5]

When the original directions are followed the reaction proceeds very slowly. In preparing pivaloin at room temperature Bouveault found it necessary to allow the reaction mixture to stand for eight to ten days. The use of a higher reaction temperature cuts down the time from days to hours. It has been suggested that the slowness of reaction in this particular case was due to the highly branched chain and the absence of enolizable hydrogen in the starting material, ethyl trimethylacetate.[5a] However, following the original directions the reaction also goes very slowly

---

[1] Preliminary work was done by N. E. Sanborn and P. B. Smith in 1928–1929.

[2] Bouveault and Locquin, *Bull. soc. chim.*, [3] **35**, 629–643 (1906); *cf.* Bacon, *Am. Chem. J.*, **33**, 68 (1905), and Higley, *ibid.*, **37**, 293 (1907).

[3] (a) Scheibler and Voss, *Ber.*, **53**, 388 (1920); (b) Scheibler and Emden, *Ann.*, **434**, 265 (1923); (c) Egorova, *J. Russ. Phys.-Chem. Soc.*, **60**, 1199 (1928); *C. A.*, **23**, 2935 (1929); (d) *cf.* Gomberg and Bachmann, THIS JOURNAL, **50**, 2762 (1928).

[4] Bouveault and Locquin, *Ann. chim. phys.*, [8] **19**, 186 (1910).

[5] (a) Scheibler and Emden, *Ann.*, **434**, 265 (1923); (b) Feigl, *Ber.*, **58**, 2299 (1925); (c) *cf.* McElvain, THIS JOURNAL, **51**, 3124 (1929).