mixture with occasional shaking. The product which crystallized was sucked as dry as possible on a funnel and washed with 25 cc. of 95% ethyl alcohol which had been cooled on an ice and salt bath; 25 g. of a product melting from 90 to 105° was obtained. Recrystallization from alcohol yielded 18 g. of nitro ketone, melting at 153 to 153.5°.

Anal. Calcd. for $C_{20}H_{17}O_4N$: C, 71.7; H, 5.07. Found: C, 71.7, 71.8; H, 5.11, 5.20.

γ-Phenyl-γ-nitro-β-furyl-*p*-bromobutyrophenone.—This ketone was prepared as described for γ-phenyl-γ-nitro-β-furylbutyrophenone. A 29% yield of product melting at 87 to 88.5° was obtained.

Anal. Calcd. for $C_{20}H_{16}O_4NBr$: C, 58.0; H, 3.86. Found: C, 57.8, 57.8; H, 3.81, 3.75.

Summary

The addition products of nitromethane and phenylnitromethane to furfuralacetophenone and furfural-*p*-bromo-acetophenone are described.

College Park, Maryland

[Contribution from the Chemistry Laboratory of the University of Michigan]

THE REACTION BETWEEN THE BINARY SYSTEM MAGNESIUM + MAGNESIUM IODIDE AND AROMATIC ALDEHYDES

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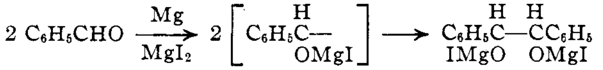
From the behavior of ketones, benzils and acids toward a mixture of magnesium and magnesium halide[1] it was inferred that the carbonyl group in aldehydes as well would be affected in a similar manner. Thus, benzaldehyde, the aldehyde which we have studied most in detail, should react as follows



$$2\,C_6H_5CHO \xrightarrow[MgI_2]{Mg} 2\left[C_6H_5\overset{H}{C}\text{—}\underset{}{OMgI}\right] \longrightarrow \underset{IMgO}{\overset{H}{C_6H_5C}}\text{—}\underset{OMgI}{\overset{H}{CC_6H_5}} \qquad (1)$$

I

It was found that the binary system reacts with benzaldehyde. Although, in reality, no hydrobenzoin to correspond to compound (I) is obtainable on the hydrolysis of the reaction mixture, there is nonetheless every reason to assume that the reaction indicated actually represents the first stage of the process. The disappearance of this intermediate product (I) is brought about by reactions subsequent to that given as the first step (Equation 1). We found, namely, that this hydrobenzoinate salt, which readily can be prepared directly from hydrobenzoin itself by treatment with methylmagnesium iodide, rapidly and completely reduces benzaldehyde to iodomagnesium benzylate (III), and thus becomes oxidized to iodomagnesium benzoinate (II).

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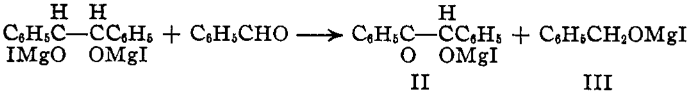
[1] Gomberg and Bachmann, This Journal, **49**, 236 (1927); **49**, 2584 (1927); **50**, 2762 (1928); Gomberg and Bailar, *ibid.*, **51**, 2229 (1929); Gomberg and Van Natta, *ibid.*, **51**, 2238 (1929); Bachmann and Shankland, *ibid.*, **51**, 306 (1929).

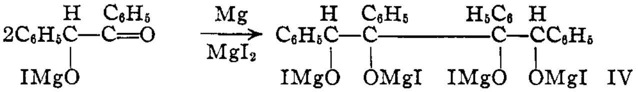


$$\underset{\mathrm{IMgO}}{\overset{\mathrm{H}}{C_6H_5C}}-\underset{\mathrm{OMgI}}{\overset{\mathrm{H}}{CC_6H_5}} + C_6H_5CHO \longrightarrow \underset{\mathrm{O}}{C_6H_5C}-\underset{\underset{\mathrm{II}}{\mathrm{OMgI}}}{\overset{\mathrm{H}}{CC_6H_5}} + \underset{\mathrm{III}}{C_6H_5CH_2OMgI} \qquad (2)$$

The speed of Reaction 2 is ever so much greater than that of 1, so that in the reaction between benzaldehyde and the binary system no appreciable amount of hydrobenzoinate can remain present as such. As soon as formed it becomes oxidized by the portion of the aldehyde which is still unchanged.

However, when the reactants are taken in the proportion indicated jointly by Equations 1 and 2 (*i. e.*, 3 moles of aldehyde + 1 atom of magnesium), then the final reaction mixture, hydrolyzed, still contains invariably some unchanged aldehyde; the amount of benzoin is only about half of that calculated, and there is present, in addition, nearly an equal amount of a resinous substance of approximately the same composition as benzoin but of a much higher molecular weight than the latter. On the other hand, when, instead of one atom, an excess of metallic magnesium is taken, the total consumption becomes finally 1.5 atoms of the metal for 3 molecules of the aldehyde, and no more than that even when the reaction period is allowed to extend for two years. The reaction mixture yields now the calculated amount (1 mole) of benzyl alcohol, but no benzoin, while the polymerized resin is proportionately larger in amount. Obviously the resinous substance must be continually being formed at the expense of the benzoinate salt (II) through a third step in the process, which step is brought about, like the first step, again by the binary system.

Indeed, the benzoinate salt, as a ketone, should be susceptible to reduction



$$2\underset{\mathrm{IMgO}}{\overset{\mathrm{H}}{C_6H_5C}}-\overset{C_6H_5}{C}{=}O \xrightarrow[\mathrm{MgI_2}]{\mathrm{Mg}} \underset{\mathrm{IMgO}}{\overset{\mathrm{H}}{C_6H_5C}}-\underset{\mathrm{OMgI}}{\overset{C_6H_5}{C}}-\!\!-\!\!-\underset{\mathrm{IMgO}}{\overset{H_5C_6}{C}}-\underset{\mathrm{OMgI}}{\overset{\mathrm{H}}{CC_6H_5}} \quad \mathrm{IV} \qquad (3)$$

That salt, prepared directly from benzoin itself by the use of just enough methylmagnesium iodide to affect only the hydroxyl group, was found to react, although somewhat slowly, with the binary system. While the amount of metallic magnesium consumed corresponds near enough to that required by Equation 3, the quantity of tetraphenylerythritol produced is only 5 to 12% of the calculated, the rest consisting of polymerized resin which, however, appears to be identical with that obtainable when one starts with benzaldehyde itself.

The conclusion, therefore, seems justified that the mechanism of the reaction between the binary system and benzaldehyde consists in three consecutive steps, and these commence to overlap each other soon after the reaction ensues: (1) reduction by the binary system, in moderate speed, of the aldehyde to hydrobenzoin salt; (2) very rapid oxidation of the salt produced by still unchanged aldehyde to the salt of benzoin;

(3) slow reduction of the latter again by the binary system, with simultaneous, or subsequent, polymerization or condensation. The relative proportions of benzoin and polymer will depend in each case upon the comparative speeds of Reactions 1 and 3, respectively, and upon how nearly the amount of magnesium consumed approaches the ratio of 1.5 atoms for 3 moles of aldehyde.

It still remains to determine the constitution of the polymer and the factors which induce its formation from the tetraphenylerythritol salt (IV). Nor can we offer at this time any explanation why, when starting with pure iodomagnesium benzoinate, one gets on reduction with MgI, in addition to the resin, at least 5–10% of tetraphenylerythritol, while when starting with benzaldehyde, the final reduction product consists wholly of the polymerized resin. Other aromatic aldehydes that have been investigated in this Laboratory by Mr. R. V. Shankland were found to react with the binary system essentially in the same manner as benzaldehyde.

The fact that the binary system—with the surmised MgI as the real active reducing agent—is generally very analogous in its effects to that of metallic sodium, suggests that the mechanism of the much discussed reaction between sodium and aldehydes is fundamentally similar to that between our binary system and aldehydes.

Experimental

Numerous experiments were carried out, varying the relative amounts of the principal reactants, using small amounts and large amounts of magnesium iodide, and allowing the reaction to run for periods from a few hours to two years. Only a few experiments, typical of the others, are here described.

It was established that benzaldehyde and magnesium iodide, in the absence of metallic magnesium, form merely a molecular complex, which, in the form of an etherate, separates as a heavy oil insoluble in the ether–benzene mixture employed as a solvent. On hydrolysis the complex is resolved completely into its components. With magnesium bromide, a crystalline complex is formed which, by coating the metallic magnesium, greatly slows down the reaction although in the end the same reduction product is formed. For this reason, magnesium iodide is to be preferred.

Benzaldehyde (3 Moles) + Mg (1 Atom) + MgI_2.—To a filtered solution of magnesium iodide, prepared from 70 g. of iodine and excess magnesium powder, in a mixture of 125 cc. of absolute ether and 150 cc. of dry benzene, were added 53 g. of benzaldehyde and 4.1 g. of magnesium ribbon. The jar was tightly closed with a stopper and placed on a shaking machine. After several days the insoluble oil, the complex of benzaldehyde and magnesium iodide, nearly all disappeared, and by the end of two weeks all the magnesium had dissolved. The solution, hydrolyzed with dilute acid and addition of more benzene, was extracted with a solution of sodium carbonate (yield of benzoic acid, 1.2 g.) and the solvents, ether and benzene, were removed by distillation under reduced pressure. The residue was digested with ether, the precipitated benzoin, only slightly soluble in ether, was removed by filtration; to the filtrate was added some petroleum ether, which induced separation of more benzoin. In all, 15.1 g. of benzoin was obtained. Distillation of the filtrate under a pressure of 1 mm. on a steam-bath gave 15 g. of an oil, from which, by use of sodium bisulfite, there were obtained 3 g. of benzaldehyde and 11 g. of benzyl alcohol. The non-volatile portion of the reaction mixture, the polymerized resin, weighed 15 g.

In another experiment, with only 3.6 g. of metallic magnesium, the reaction was finished after the mixture was heated on a steam-bath for twelve hours. The result was 17.5 g. of benzoin, 4 g. of unchanged aldehyde, 10 g. of benzyl alcohol and 15 g. of resin.

In experiments in which only small amounts of magnesium and magnesium iodide were employed, considerable quantities of benzyl benzoate were formed. The condensation of the aldehyde to the ester is here brought about in virtue of the catalytic influence of iodomagnesium benzylate, an effect similar to that of sodium benzylate.

Benzaldehyde (3 Moles) + Mg (1.5 Atom) + MgI_2.—Benzaldehyde, 106 g., was added to a solution of 150 g. of magnesium iodide in a mixture of 200 cc. of ether and 300 cc. of benzene. Magnesium turnings, 12.2 g., were introduced and the mixture, protected from access of air by a mercury trap, was boiled under a reflux condenser. After twenty hours of heating, the magnesium was nearly all gone. The mixture was hyrolyzed, the mixed solvents removed by distillation and replaced by ether alone, but no precipitation of benzoin occurred. The ether was then evaporated, the benzyl alcohol distilled under 1 mm. pressure and the non-volatile material extracted repeatedly with petroleum ether. There were isolated: benzaldehyde, none; benzoin, 2.5 g.; benzil, 1 g.; benzyl alcohol, 30 g.; resin, 65 g.

In another experiment, with the reactants in the same amounts as above and the magnesium in long ribbon strips, the mixture was placed in a one-liter graduated cylinder and the reaction allowed to proceed at room temperature. The magnesium was all dissolved in ten weeks. No benzaldehyde was left and no benzoin obtained, the reaction products consisting solely of benzyl alcohol and the resin.

Benzaldehyde + Mg (Excess) + MgI_2.—A mixture, in ether-benzene, of 53 g. of benzaldehyde, 75 g. of magnesium iodide and 8 g. of metallic magnesium was boiled for thirty hours. However, the amount of magnesium that reacted was only 6.35 g., *i. e.*, 1.5 atoms for 3 moles of the aldehyde, and the reaction products were benzyl alcohol, 15.2 g., and polymerized resin.

In a series of experiments, with 53 g. of aldehyde in each and with large excess of magnesium in form of strips, the reaction was allowed to proceed at room temperature from a year to eighteen months, but the loss in weight of magnesium was again about the same, namely, 6.36, 6.7, 6.36, 6.77 g., respectively. In still another experiment, the mixture was allowed to stand for two years—the loss in weight of the metal was 6.42 g., and the magnesium hydroxide produced on hydrolysis of the reaction mixture required 135 cc. of 4 *N* acid instead of the calcd. 132 cc. The products were benzyl alcohol and resin.

Oxidation of Iodomagnesium Hydrobenzoinate by Benzaldehyde to Iodomagnesium Benzoinate (Equation 2).—While hydrobenzoin itself is without effect upon benzaldehyde, the salt readily reduces it to benzyl alcohol. The salt was prepared by adding solid hydrobenzoin to a solution of methylmagnesium iodide until evolution of methane no longer took place.

$$C_6H_5CH(OH)CH(OH)C_6H_5 + 2CH_3MgI = C_6H_5CH(OMgI)(IMgO)CHC_6H_5 + 2CH_4$$

To such a solution, prepared from 10.6 g. of hydrobenzoin, 5.3 g. of benzaldehyde was added. The reaction was complete after the mixture had been warmed for five to ten minutes. From the mixture, hydrolyzed, there was isolated 9.5 g. of benzoin and 3 g.

of benzyl alcohol. In many experiments on a larger scale the yields also of alcohol obtained were much nearer to those calculated.

The reduction of benzaldehyde by the hydrobenzoinate salt consists in the transfer of an H and MgI from the salt to the aldehyde. That only one of the two groups (HCOMgI) is involved in this transfer has been proved in several ways. (a) Were the second group also involved, the reaction would then become as follows

$$C_6H_5COCH(OMgI)C_6H_5 + C_6H_5CHO = C_6H_5COCOC_6H_5 + C_6H_5CH_2OMgI \quad (4)$$

In reality, however, the reverse of this occurs—iodomagnesium benzylate reduced benzil to the benzoinate salt, itself becoming oxidized to aldehyde. In an experiment with iodomagnesium benzylate from 8 g. of alcohol with 8 g. of benzil, there was isolated 4.6 g. of benzoin and 1.9 g. of benzaldehyde. (b) Whether we start with benzaldehyde and the binary system, or with the aldehyde and the hydrobenzoinate salt, the actual presence of iodomagnesium benzoinate as one of the main resulting products has been confirmed by subjecting the mixture of the reaction products, prior to hydrolysis, to the action of phenylmagnesium iodide. In each case, then, after hydrolysis, triphenylethylene glycol resulted.

$$C_6H_5COCH(OMgI)C_6H_5 + C_6H_5MgI = (C_6H_5)_2C(OMgI)CH(OMgI)C_6H_5 \quad (5)$$

In one experiment, using 21 g. of benzaldehyde, 5.2 g. of pure triphenylethylene glycol was obtained, m. p. 168°. In another experiment, starting with 2.4 g. of hydrobenzoin, 2.5 g. of the same glycol was isolated from the mixture of the reaction products.

Reduction of Iodomagnesium Benzoinate by Mg + MgI_2.—To a solution of 20 g. of benzoin and 16.5 g. of magnesium iodide in a mixture of 30 cc. of ether and 80 cc. of benzene, a concentrated ether solution of ethylmagnesium iodide was gradually added until no more ethane was being evolved. Magnesium powder, 2.5 g., was now added and the mixture refluxed on a steam-bath for fifteen hours. The solution was filtered and decomposed with dilute acid. Fine threads of tetraphenylerythritol crystallized from the solution, and some more from the filtrate, 2.8 g. in all, which is 14% of that possible. The remaining 17 g. of product consisted of the polymerized resin. Other similar experiments varied in yield of tetraphenylerythritol from 3 to 20% of the calculated. The erythritol compound melted at 236°, and is identical with that which Kaufmann[2] obtained by electrolytic reduction of benzoin. By oxidation with copper sulfate in pyridine it gives benzil, almost weight for weight.

The Resinous Component of the Reaction Mixture.—This material, whether obtained in the process of reduction by means of the binary system either of benzaldehyde or of iodomagnesium benzoinate, has the consistency of a thick sirup if the removal of the benzyl alcohol has been done merely by distillation under reduced pressure. The last traces of alcohol are best removed by steam distillation. If the resinous mass is now dissolved in ether and, after thorough drying of the solution, is completely freed from the solvent, it is obtained as a yellow, transparent, solid, brittle mass of the appearance of rosin. It softens at about 50° and is all molten at about 60–65°. It is insoluble in petroleum ether. It remains entirely dissolved in ethyl ether when the solution is fairly concentrated—about 1 to 5—but on further dilution there separates, about 10% by weight, an amorphous white powder which is only very slightly soluble in ether and which melts at 160 to 180°. The original resinous mass is probably a mixture of several individual substances. It has an average molecular weight of 600 to 800 and a percentage composition of carbon and hydrogen not far from that of tetraphenylerythritol itself. Treatment with acids or alkalies, or acetylation, gave unsatisfactory results. While the erythritol (m. p. 236°) gives on oxidation with copper sulfate in pyridine benzil almost quantitatively, the resin is unaffected by that reagent, which makes it appear hardly probable that the resin contains stereoisomers of this crystalline erythritol.

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[2] Kaufmann, *Z. Elektrochem.*, **4**, 461 (1898).

Various Aromatic Aldehydes and the System MgI_2 + Mg.[3]—Other aromatic aldehydes were found to react with the binary system essentially in the same manner as benzaldehyde. When excess of magnesium was employed and the reaction was allowed to go to completion, just slightly more than 0.5 gram atom of magnesium dissolved for each mole of aldehyde reduced. Under those circumstances no corresponding benzoin was obtained, the only products being the primary alcohol and viscous oil analogous to the resin resulting from benzaldehyde. If, however, the reduction was only allowed to proceed until the complex of the aldehyde with magnesium iodide had disappeared, during which time approximately two-thirds of the maximum amount of metallic magnesium had dissolved, or when only that limited amount of magnesium was used for the reaction, then a fair yield of the corresponding benzoin resulted. These substituted benzoins, unfortunately, proved, in general, so soluble that they could not be separated readily from the viscous condensation products which always accompanied the other products. It was found advantageous to treat the mixture of the benzoin and the viscous oil with a solution of cupric sulfate in pyridine, thus obtaining the corresponding benzils. These proved usually only sparingly soluble in benzene or acetic acid and could, therefore, be more readily separated. The results are summarized in Table I. Excess of magnesium iodide was used in each case, while the amount of magnesium was one-third of an atom to a molecule of the aldehyde. The solvents used for each experiment comprised 75 cc. of ether and 150 cc. of benzene.

TABLE I

REDUCTION OF ALDEHYDES BY BINARY SYSTEM

Aldehyde reduced	Moles	G.	Alcohol obtained	G.	Benzoin isolated as	G.
α-Naphth-	0.1	15.6	α-Naphthenyl	4.1	α-Naphthil	5.3
p-Tolu-	.25	30.0	*p*-Methylbenzyl	7.5	*p*-Tolil	7.0
p-Anis-	.25	34.0	*p*-Anisalcohol	10.0	*p*-Anisil	8.2
p-Bromobenz-	.25	45.3	*p*-Bromobenzyl	11.3	4,4'-Dibromobenzil	13.0
p-Chlorobenz-	.25	35.1	*p*-Chlorobenzyl	8.5	4,4'-Dichlorobenzil	8.4

Summary

Benzaldehyde is reduced by a mixture of magnesium and magnesium iodide to the iodomagnesium derivative of hydrobenzoin, $C_6H_5CH(OMgI)$-$(IMgO)HCC_6H_5$, thus using up two molecules of the aldehyde.

The iodomagnesium hydrobenzoinate so produced reacts immediately with a third molecule of the aldehyde, with formation of the salts of benzoin and benzyl alcohol, $C_6H_5COCH(OMgI)C_6H_5$ and $C_6H_5CH_2OMgI$.

The benzoinate salt suffers further, partial or complete, reduction by the binary system to tetraphenylerythritol and a polymer, or condensation product, of the latter.

Other aromatic aldehydes are affected by the binary system, *i. e.*, by MgI, in a manner essentially similar to that in which benzaldehyde is affected.

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[3] From a dissertation by R. V. Shankland, du Pont Fellowship holder, presented to the Faculty of the University of Michigan in partial fulfilment of the requirements for the degree of Doctor of Science, 1930.