

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]
**THE REDUCTION OF BENZALANILINE, BENZOPHENONE-ANIL
 AND BENZIL-ANIL BY THE SYSTEM MAGNESIUM +
 MAGNESIUM IODIDE**

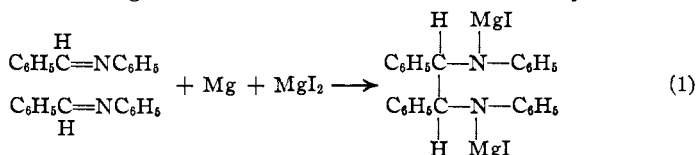
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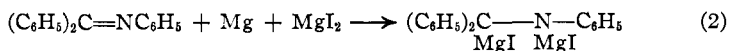
The successful addition of the MgI group to the N=N group¹ as well as to the C=O group² encouraged the belief that the C=N group would take up MgI in a similar fashion. Experiment showed that benzalaniline, benzophenone-anil and benzil-anil react readily with a mixture of magnesium and magnesium iodide and in each case addition of MgI to the C=N group takes place.

Benzalaniline is reduced by the binary system in the manner of benzaldehyde; unlike the reduction of the aldehyde, however, the reaction stops when the iodomagnesium derivative of dianilino-dibenzyl is formed.



Exactly one gram atom of metallic magnesium reacts for two gram molecules of benzalaniline. This addition of the MgI group is analogous to the addition of sodium to benzalaniline,³ which results in the disodium derivative of dianilino-dibenzyl. Hydrolysis of the reduction product gives dianilino-dibenzyl.

Benzophenone-anil, unlike benzophenone⁴ which gives a pinacol derivative, takes up two MgI groups and is reduced to the iodomagnesium derivative of N-benzohydril-aniline.



The amount of metallic magnesium that reacts corresponds exactly to that required by the equation. Hydrolysis of the reduction product gives N-benzohydril-aniline. Fluorenone-anil is reduced by the binary system in the same manner. These reactions are similar to the action of sodium on benzophenone-anil³ and on fluorenone-anil, in which cases the disodium derivatives are formed.

Benzil-anil reacts with the binary system in the manner of benzil.⁵

¹ Bachmann, *THIS JOURNAL*, **53**, 1524 (1931).

² See Gomberg and Bachmann, *ibid.*, **52**, 4967 (1930), for principal references.

³ Schlenk and Appenrodt, *Ber.*, **47**, 473 (1914).

⁴ Gomberg and Bachmann, *THIS JOURNAL*, **49**, 236 (1927).

⁵ Gomberg and Bachmann, *ibid.*, **49**, 2584 (1927); Gomberg and Van Natta, *ibid.*, **51**, 2238 (1929).

By repeated recrystallizations colorless needles of m. p. 165–166° were obtained which were identical with those isolated from the amalgam reduction product.

Reduction of Benzophenone-anil.—Benzophenone-anil was prepared according to the directions of Reddelien⁷ from benzophenone and aniline with aniline hydrochloride as a catalyst. In agreement with Reddelien we obtained 80% yields of benzophenone-anil although Gilman and Dickey⁸ reported recently that they obtained yields of only 20% by this method.

A mixture of 12.85 g. of benzophenone-anil, 15 g. of magnesium iodide and a rod of magnesium in 105 cc. of ether–benzene (1:2) was shaken for several days. The reaction began immediately as was evidenced by the violet-colored streamers which came off from the surface of the rod. The solution became opaque red and finally dark reddish-brown in color: loss in magnesium, 1.21 g.; calcd., 1.21 g. The same loss of magnesium occurred when only one-quarter of the above amount of magnesium iodide was employed, indicating that the iodomagnesium derivative is able to split off magnesium iodide and thus make the latter available for further reaction as in other similar reductions.⁹

Hydrolysis of the reduction product gave a solid melting at 54–58°. When this solid was recrystallized from alcohol, a small amount of the addition complex¹⁰ composed of a molecule each of benzophenone-anil and of benzohydryl-aniline crystallized out; from the filtrate there was obtained pure benzohydryl-aniline. Repeated crystallizations raised the melting point of the complex to 84°; the compound so obtained was found to be identical with the complex obtained by recrystallizing a mixture of equal parts of benzophenone-anil and benzohydryl-aniline from alcohol. The crude reduction product as obtained by hydrolysis was shown in the following manner to contain 90% of benzohydryl-aniline. The product was heated with concentrated hydrochloric acid until the mixture became colorless; this treatment hydrolyzed the benzophenone-anil to benzophenone and aniline and at the same time formed the hydrochloride of benzohydryl-aniline. This hydrochloride was filtered off, dried and extracted with warm petroleum ether in order to remove the benzophenone. The hydrochloride was converted to the free base by treatment with ammonium hydroxide and extracting with ether in a separatory funnel. After recrystallization from alcohol the benzohydryl-aniline melted at 57–58°; its identity was established by comparison with authentic benzohydryl-aniline.

It was found that benzohydryl-aniline can be prepared in practically quantitative yields by reduction of benzophenone-anil by means of magnesium and methyl alcohol, a method employed successfully by Zechmeister and Rom¹¹ for reducing nitro compounds. A mixture of 5 g. of benzophenone-anil and 1.8 g. of magnesium ribbon in 80 cc. of methyl alcohol was warmed until all of the metal had dissolved and the solution was colorless. Addition of dilute acetic acid caused precipitation of the benzohydryl-aniline.

The benzohydryl-aniline was further identified by rearranging it to *p*-aminotriphenylmethane.¹² We found that a few minutes of heating with aniline hydrochloride sufficed for complete rearrangement. One gram of benzohydryl-aniline was heated with a gram of aniline hydrochloride in 2 cc. of aniline at 180° for five minutes. The cooled mixture was shaken with 30% acetic acid in order to remove aniline and its salt, and the *p*-aminotriphenylmethane was filtered off; yield 72%, m. p. 84°. The product was

⁷ Reddelien, *Ber.*, **46**, 2720 (1913); **48**, 1462 (1915).

⁸ Gilman and Dickey, *THIS JOURNAL*, **52**, 4573 (1930).

⁹ Gomberg and Bachmann, *ibid.*, **49**, 247, 2588 (1927).

¹⁰ Alessandri, *Gazz. chim. ital.*, **51**, 75 (1921).

¹¹ Zechmeister and Rom, *Ann.*, **468**, 1117 (1928).

¹² Baeyer and Villiger, *Ber.*, **37**, 599 (1904).

identical with *p*-aminotriphenylmethane prepared by reduction of *p*-nitrotriphenylmethane.¹²

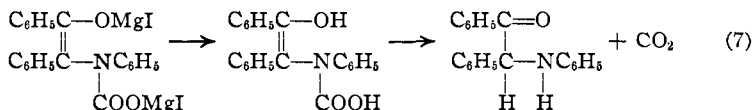
Reduction of Fluorenone-anil.—A mixture of 5.10 g. of fluorenone-anil, 6.6 g. of magnesium iodide and a magnesium rod in 60 cc. of ether-benzene (1:2) was shaken for several days. As the reaction proceeded, the orange-red solution became dark green in color and a precipitate appeared. This green product is probably a complex formed from unchanged fluorenone-anil and the fully reduced product. Further shaking changed the mixture color to a bright scarlet; loss in magnesium, 0.485 g., or 100% of the theoretical value. Hydrolysis gave 9-fluorenyl-aniline. By recrystallization from a mixture of acetone and methyl alcohol, it was obtained in the form of needle-like prisms melting at 121–123°; yield, 83%. Staudinger and Gaule¹³ report the value 121° and Schlenk¹⁴ gives 124° for the melting point of 9-fluorenyl-aniline.

Reduction of Benzil-anil.—Addition of 10 g. of benzil-anil to a solution of magnesium iodide gave a dark red solution which quickly deposited a large amount of a complex in the form of orange-red crystals. After one and one-half hours of shaking with a rod of magnesium, the crystalline complex had completely disappeared and the solution was opaque reddish-brown in color. After six hours of shaking the solution was transparent yellow in color: loss in magnesium, 0.86 g.; calcd., 0.85 g. Hydrolysis was carried out in an atmosphere of carbon dioxide in order to avoid oxidation of the reduction product, and there was obtained 8.0 g. (80% yield) of anilbenzoin¹⁵ (desylaniline), C₆H₅CH(NHC₆H₅)CO(C₆H₅); after recrystallization from alcohol, the anilbenzoin melted at 97–98° and was identical with the product prepared from benzoin and aniline. Prior to hydrolysis, the reduction product did not react with phenylmagnesium bromide, indicating the absence of a free C=O group (see I, equation 4); after hydrolysis the anilbenzoin reacted readily with the Grignard reagent.

Reaction of the Reduction Product with Iodine and with Oxygen (Equation 5).—The calculated amount of iodine (2.54 g.) was added to the reduction mixture which had been prepared from 2.85 g. of benzil-anil. A considerable amount of heat was developed in the reaction that took place, and the solution became opaque reddish-brown in color. A large amount of the complex of benzil-anil and magnesium iodide precipitated. Hydrolysis gave 2.50 g. (88%) of benzil-anil.

In another experiment, dry air was passed into the transparent yellow reduction mixture obtained from 2.85 g. of benzil-anil. The solution became opaque reddish-brown and finally transparent red in color. Hydrolysis, after passing in air for four hours, gave 2.45 g. (86%) of benzil-anil.

Reaction with Carbon Dioxide.—Carbon dioxide was passed into the reduction mixture which had been prepared from 5.0 g. of benzil-anil. Within ten minutes glistening, granular crystals of the salt of the *N*-carboxylic acid (equation 6) appeared. After three hours the crystals were filtered off, washed with ether and dried. When this salt was treated with dilute acetic acid, carbon dioxide was evolved (collected in barium hydroxide solution) and the solid that remained was found to be pure anilbenzoin; weight, 3.6 g. (71%). The reactions that take place are undoubtedly the following



¹³ Staudinger and Gaule, *Ber.*, **49**, 1956 (1906).

¹⁴ Schlenk, *Ann.*, **463**, 318 (1928).

¹⁵ See Cameron, *Trans. Roy. Soc. Can.*, [3] **23**, Sect. 3, 53 (1929), *Chem. Abstracts*, **24**, 610 (1930), for the structure of anilbenzoin.

Summary

Benzalaniline is reduced by a mixture of magnesium and magnesium iodide to the iodomagnesium derivative of dianilino-dibenzyl.

Benzophenone-anil is reduced by the binary system to the iodomagnesium derivative of N-benzohydrylaniline.

Benzil-anil takes up two MgI groups to give a stilbene derivative which is very reactive to iodine, oxygen and carbon dioxide. Hydrolysis of the reduction product yields anilbenzoin.

The results of this investigation substantiate the hypothesis that the active reducing agent is MgI.¹⁶

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PURDUE UNIVERSITY AND THE ELI LILLY LABORATORIES]

THE ACTIVATION OF ERGOSTEROL WITH RADIUM EMANATION

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Introduction

The existence of an antirachitic vitamin (D) has been recognized for some time. Recently, however, it has become possible to prepare an antirachitic substance by "irradiative" or "activating" ergosterol with ultraviolet radiation. Such a product is called viosterol and is considered by some to be vitamin D.

To Huldchinsky² perhaps should go the credit for first using ultraviolet light on children afflicted with rickets. Two years later in 1924, Steenbock reported on his work³ with rats cured by the use of activated cholesterol. He took out patents that same year. The high-speed electrons from a Coolidge tube have been used by Knudsen.⁴ He and C. N. Moore activated cholesterol in a few minutes with 200,000 volt electrons, such that 0.0050 g. per day was the minimum dosage required to cure rachitic rats, whereas 0.00002 was the minimum dosage using ultraviolet activated cholesterol.

The activation of cholesterol or ergosterol with radium has not been

¹⁶ In a recent article [*Z. physik. Chem.*, **153**, 83 (1931)], Sven Bodfors reports results obtained from a study of magnesium potentials in aqueous salt solutions, which are best explained by considering that magnesium metal can send into solution univalent ions, Mg⁺.

¹ Deceased Jan. 20, 1931.

² Hess, "Rickets, Osteomalacia and Tetany," p. 107.

³ Steenbock, *J. Biol. Chem.*, **61**, 405 (1924); **64**, 263 (1925).

⁴ Knudsen, *Proc. Soc. Exptl. Biol. Med.*, **24**, 366 (1927); *J. Biol. Chem.*, **81**, 49 (1929).