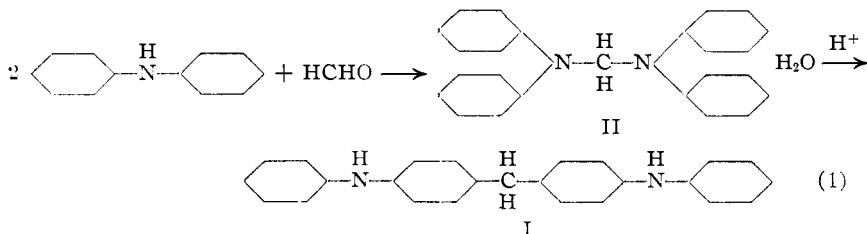


[CONTRIBUTION FROM THE CHEMICAL RESEARCH LABORATORY OF THE B. F. GOODRICH Co.]

## The Reaction of Formaldehyde with Diphenylamine

BY DAVID CRAIG

The formation of dianilindiphenylmethane as a product of the reaction of formaldehyde with diphenylamine<sup>1,2</sup> has long been claimed. However, the isolation of pure compounds from the products of the reaction has not been recorded up to this time. This is true notwithstanding the fact that Straus and Bormann<sup>3</sup> succeeded in preparing *p,p'*-dianilindiphenylmethane in a series of reactions starting with *p,p'*-diaminodiphenylmethane. A study of the reaction of formaldehyde with diphenylamine<sup>4</sup> under a variety of conditions was therefore undertaken, the results of which are described in this communication.



The course of the reaction of formaldehyde with diphenylamine in the presence of acids is dependent on the relative amounts of the reactants used. An excess of diphenylamine favors the formation of *p,p'*-dianilindiphenylmethane. On the other hand, if an excess of formaldehyde or even equimolecular amounts of the reactants are employed, resins are formed which hinder or prevent the isolation of a pure product. Possibly these resins result from subsequent condensation with formaldehyde to form long chain molecules of the Staudinger type. This condensation occurs readily in the absence or presence of acid catalysts. Resins may also be obtained directly from *p,p'*-dianilindiphenylmethane by heating with strong acids, diphenylamine being formed as one of the products.<sup>5</sup> Indeed, it appears that resins of this type are the ultimate condensation products of formaldehyde with amines rather than the simple diphenylmethanes as suggested by Wagner.<sup>6</sup>

(1) Meister, Lucius and Brüning, German Patent 58,072, June 24, 1891; *Friedländer*, **3**, 79 (1890-1894). See also Kostyschew, *Ber.*, **45**, 1291 (1912).

(2) Sen and Sen, *J. Indian Chem. Soc.*, **7**, 965 (1930).

(3) Straus and Bormann, *Ber.*, **43**, 729 (1910).

(4) Reaction products of formaldehyde with diphenylamine have recently been patented as antioxidants for rubber. (a) Clifford, U. S. Patent 1,849,822, March 15, 1932; (b) Clifford, U. S. Patent 1,763,579, June 10, 1930; (c) Semon, U. S. Patent 1,860,434, May 31, 1932; (d) Semon, U. S. Patent 1,890,916, Dec. 13, 1932.

(5) In this connection see von Braun, "The Thermal and Hydrolytic Decomposition of Amino and Hydroxy Diarylmethanes," *Ann.*, **472**, 1-89 (1929).

(6) Wagner, *THIS JOURNAL*, **55**, 724 (1933).

The structure of the *p,p'*-dianilinodiphenylmethane is established by reference to the properties reported by Straus and Bormann<sup>3</sup> and also by synthesizing the compound by the method of Ullmann<sup>7</sup> from *o*-chlorobenzoic acid and *p,p'*-diaminodiphenylmethane.

The formation of *p,p'*-dianilinodiphenylmethane from diphenylamine and formaldehyde probably takes place in more than one step. If no acid catalyst is used and the reaction is carried out in benzene solution, there may be isolated as the chief product a compound (Compound II) having the empirical formula and molecular weight of tetraphenylmethylenediamine.

Compound II is rapidly hydrolyzed by warm, dilute mineral acids to formaldehyde and diphenylamine. It rearranges in the presence of diphenylamine and hydrochloric acid to *p,p'*-dianilinodiphenylmethane in a manner characteristic of other arylmethylenediamines.<sup>8</sup> In the absence of added diphenylamine and in the presence of dry hydrogen chloride, resinification occurs with the splitting out of diphenylamine but without the formation of *p,p'*-dianilinodiphenylmethane. The hydrogenolysis of Compound II in the presence of the Adkins copper chromite catalyst occurs with the formation of diphenylamine and methyldiphenylamine. No phenyl-*p*-tolylamine is formed. However, a side reaction taking place during this reduction is the rearrangement to form *p,p'*-dianilinodiphenylmethane. This, together with the fact that greater amounts of diphenylamine are formed during the reduction than can be accounted for by simple hydrogenolysis, indicates that Compound II has a tendency to dissociate with the formation of free methylene  $\text{HCH}$ . It should be pointed out that methyldiphenylamine does not undergo reduction under the conditions found suitable for rapidly reducing Compound II.

The mode of formation and the reactions of Compound II indicate that it is tetraphenylmethylenediamine. It is interesting that Houben and Arnold<sup>9</sup> reported the formation of this substance as a product of the reaction of chloromethyl sulfate with diphenylamine. The product which they obtained readily hydrolyzed to formaldehyde and diphenylamine; however, it melted at 82–85°, while the tetraphenylmethylenediamine here reported melts at 104–105°. It is, therefore, believed that Houben and Arnold's compound was impure and probably contaminated with *p,p'*-dianilinodiphenylmethane. Houben and Arnold did not mention the previous crude preparation of tetraphenylmethylenediamine from the reaction of formaldehyde with diphenylamine.<sup>10</sup>

In searches for precursors of tetraphenylmethylenediamine it has not thus far been possible to isolate an amino alcohol;<sup>8,11</sup> an anhydroamino

(7) Ullmann, *Ann.*, **355**, 325 (1907).

(8) Morgan, *J. Soc. Chem. Ind.*, **49**, 245 (1930).

(9) Houben and Arnold, *Ber.*, **41**, 1577 (1908).

(10) German Patent 158,718, January 23, 1905; *Friedländer*, **8**, 402 (1905–1907).

(11) German Patent 97,710, November 21, 1898; *Friedländer*, **5**, 95 (1897–1900).

alcohol, or a polymer thereof from mixtures secured from the reactions of formaldehyde with diphenylamine.

### Experimental

**The Reaction of Formaldehyde with Diphenylamine to Form *p,p'*-Dianilinodiphenylmethane, I.**—This reaction was carried out by adding 1 cc. of concentrated hydrochloric acid to a mixture of 254 g. (1.5 moles) of diphenylamine and 16 g. (0.19 mole) of 36% formaldehyde dissolved in 250 cc. of alcohol at 40°. Reaction set in immediately and was complete after refluxing for thirty minutes on the steam-bath. Four grams of potassium carbonate was added and the product isolated by distillation in a 500-cc. Anders flask. The diphenylamine distilled off had a setting point of 53° and amounted to 192 g. The intermediate fraction amounting to 2.5 g. came over below 270° at 1.5 mm. of mercury and consisted mainly of *p,p'*-dianilinodiphenylmethane. The main fraction distilled with considerable superheating between 270 and 290° at the same pressure. The yield of this fraction amounted to 41.5 g. or to a yield of 63% of crude product calculated on the formaldehyde used. When recrystallized from 250 cc. of alcohol, 35 g. of *p,p'*-dianilinodiphenylmethane was obtained having a melting point of 114–115°. After melting, the compound resolidified and melted at 120°. On recrystallization the second melting point was raised to 122–123°, the initial melting point being at 118–120°. The residue from the distillation weighed 23 g.

*Anal.* Calcd. for  $C_{25}H_{22}N_2$ : C, 85.7; H, 6.32; N, 7.98. Found: C, 85.7; H, 6.13; N, 8.06.

Solvents such as benzene, acetone, gasoline, and acetic acid were used for this reaction and found suitable. If acetic acid was used as the solvent, hydrochloric acid was not necessary as the catalyst. The reaction may be carried out in the absence of a solvent if an efficient agitator is used.

Difficulties encountered by previous workers who may have tried to isolate this compound are partly due to the fact that they did not use sufficient diphenylamine in the reaction. Using the amounts of the reactants called for by Equation (1) drops the yield to about 40%.

Under the proper conditions formaldehyde may be replaced by other methylene compounds. Anhydroformaldehyde aniline, hexamethylenetetramine, and diaminodiphenylmethane reacted above 150° with an excess of diphenylamine to form *p,p'*-dianilinodiphenylmethane. Chloromethyl ether in benzene solution reacted as vigorously as formaldehyde with diphenylamine, *p,p'*-dianilinodiphenylmethane being the main product. In order to carry out the reaction with paraformaldehyde, water was added and the mixture refluxed for several hours.

A double melting point for *p,p'*-dianilinodiphenylmethane was also observed by Straus and Bormann.<sup>3</sup> It was frequently found, however, that only the high melting form was obtained.

**The Synthesis of *p,p'*-Dianilinodiphenylmethane by the Ullmann Method.**—Fifteen grams of *o*-chlorobenzoic acid, 15 g. of potassium carbonate, and 10 g. of *p,p'*-diaminodiphenylmethane were intimately mixed in a 500-cc. flask and heated to 150° with stirring in an oil-bath. A trace of cuprous iodide was added, whereupon a vigorous reaction set in. The mixture turned black and considerable foaming occurred. After a few minutes the product was cooled and dissolved in 500 cc. of water. The solution was acidified with acetic acid, which precipitated an oily solid. This oily solid, which was a mixture of *o*-chlorobenzoic acid with anthranilic acids, was separated and heated to 250° for a few minutes with stirring. Carbon dioxide was evolved. The resulting product was then extracted with 100 cc. of 10% sodium hydroxide and the insoluble part was distilled. Two grams of a fraction boiling at about 280° at 1.5 mm.

was obtained, which on being recrystallized from alcohol melted at 121° and did not depress the melting point of the material melting at 122–123° secured from formaldehyde and diphenylamine.

**The Preparation of Tetraphenylmethylenediamine, II.**—One hundred and sixty-eight grams (2 moles) of 36% formaldehyde was added during two hours to a refluxing solution of 338 g. (2 moles) of diphenylamine in 250 cc. of benzene. Refluxing was continued for forty-five minutes. When the product was distilled 87 g. of impure diphenylamine came over first. The next fraction boiling between 200 and 240° at 2.5 mm. pressure of mercury weighed 244 g. This represents a conversion of 70% based on the diphenylamine used. By redistillation and crystallization about two-thirds of this material was isolated as the pure compound melting at 104–105°. On dissolving the crude product in an equal volume of benzene and then stirring in two volumes of petroleum ether, thick transparent crystals were obtained. The compound was difficultly soluble in hot alcohol, from which it crystallized readily.

*Anal.* Calcd. for  $C_{25}H_{22}N_2$ : C, 85.7; H, 6.32; N, 7.98. Found: C, 85.1; H, 6.32; N, 7.98. *Mol. wt.* (in freezing benzene). Calcd. for  $C_{25}H_{22}N_2$ : 350. Found: 326, 329.

When warmed with very dilute hydrochloric acid or with 10% sulfuric acid, formaldehyde and diphenylamine were obtained. It also reacted with potassium bisulfite<sup>10</sup> and although the products of this reaction were not isolated.

**The Rearrangement of Tetraphenylmethylenediamine into *p,p'*-Dianilinodiphenylmethane.**—When 35 g. (0.1 mole) of the compound prepared by the above described method and melting at 103–105° was mixed with 33.8 g. (0.2 mole) of diphenylamine dissolved in 130 cc. of alcohol no reaction took place, but when 0.9 cc. of concentrated hydrochloric acid was added the temperature rose from 45 to 55° and an oil separated out which on standing overnight gave a small amount of crystals which was filtered off and washed with alcohol. After recrystallizing from alcohol the crystals melted at 148–152°. These crystals were not identified. The same material was secured from high boiling fractions of formaldehyde-diphenylamine reaction products. The alcoholic washings were united with the main solution and two volumes of water and 5 g. of sodium carbonate was added. The oil obtained was distilled in the usual way and gave as the main product *p,p'*-dianilinodiphenylmethane. After recrystallizing from alcohol the product melted at 122–123° when alone or when mixed with the *p,p'*-dianilinodiphenylmethane prepared directly from formaldehyde and diphenylamine.

**The Hydrogenolysis of Tetraphenylmethylenediamine.**—This reaction did not occur with sodium and alcohol but was successfully carried out by the method of Adkins. One hundred and seventeen grams (0.33 mole) of tetraphenylmethylenediamine, 250 cc. of benzene, and 4 g. of the copper chromite catalyst were placed in the reducer. Hydrogen at about 110 atmospheres pressure was admitted and the temperature raised to 225° gradually during four hours. The mixture was filtered and distilled at reduced pressure. Diphenylamine amounting to 63 g. or 0.37 mole, about 5 g. of methyldiphenylamine, and a trace of *p,p'*-dianilinodiphenylmethane were isolated from the product, besides about 30 g. of resinous material. The diphenylamine and methyldiphenylamine were separated from each other by the method described by Gibson and Vining.<sup>12</sup> The *p,p'*-dianilinodiphenylamine was isolated as described above. This compound and the diphenylamine were identified by melting points and mixed melting points with authentic specimens. The methyldiphenylamine was identified by the melting point and mixed melting point of its zinc-hydrochloride with an authentic specimen of this derivative, the preparation of which is described in the next section.

Under the conditions just described for the hydrogenolysis of tetraphenylmethylen-

(12) Gibson and Vining, *J. Chem. Soc.*, **123**, 834 (1923).

diamine no reaction with 38 g. of methyldiphenylamine, 2 g. of copper chromite and 100 cc. of benzene could be detected.

**The Zinc-hydrochloride of Methyldiphenylamine.**—Five grams (0.027 mole) of redistilled methyldiphenylamine obtained from the Eastman Kodak Company was dissolved in 40 cc. of glacial acetic acid. A solution of 5 g. of zinc chloride dissolved in a mixture of 5 cc. of concd. hydrochloric acid and 10 cc. of glacial acetic acid was added. A precipitate came down immediately. After cooling to 15° for fifteen minutes the precipitate was filtered off and washed consecutively with 20 and 10 cc. portions of glacial acetic acid. After standing in a vacuum desiccator to constant weight over potassium hydroxide a yield of 7.5 g. (95%) of a white powder was obtained, m. p. 186–188°, with evolution of hydrochloric acid. The compound can also be prepared in concentrated hydrochloric acid, in which it is difficultly soluble.

*Anal.* Calcd. for  $[(C_6H_5)_2NCH_2HCl]_2 \cdot ZnCl_2$ : Zn, 11.4. Found: Zn, 11.4, 11.8. Calcd. for  $[(C_6H_5)_2NCH_2HCl]_2 \cdot ZnCl_2$ , equiv. wt.: 143.5 according to the equation  $[(C_6H_5)_2NCH_2HCl]_2 \cdot ZnCl_2 + 4NaOH \rightarrow 2(C_6H_5)_2NCH_2 + Zn(OH)_2 + 4NaCl + 2H_2O$ . Found by titrating with 0.01 *N* NaOH using phenolphthalein as the indicator: 140, 141.

This compound is hydrolyzed to methyldiphenylamine, zinc chloride and hydrochloric acid when mixed with water but is not particularly hygroscopic. Mixtures with water were titrated with standard potassium ferrocyanide solution for the zinc analysis and with standard sodium hydroxide solution for the equivalent weight determination without removing the precipitated methyldiphenylamine. During the titration with sodium hydroxide a precipitate of zinc hydroxide came down.

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### Summary

The main reaction product of formaldehyde with an excess of diphenylamine in the presence of hydrochloric acid has been found to be *p,p'*-dianilinodiphenylmethane. A possible intermediate product has been identified as tetraphenylmethylenediamine.

AKRON, OHIO

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