

been synthesized; it is entirely different from the substance obtained by nitrating chlorodurene. By analogy, the substance obtained by Willstätter and Kubli by nitrating bromodurene, and called by them dinitrodurylic acid bromide, can-

not have this structure.

3. A study of the reactions of the Willstätter and Kubli compound has been made, and a tentative formula suggested for it.

MINNEAPOLIS, MINNESOTA

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

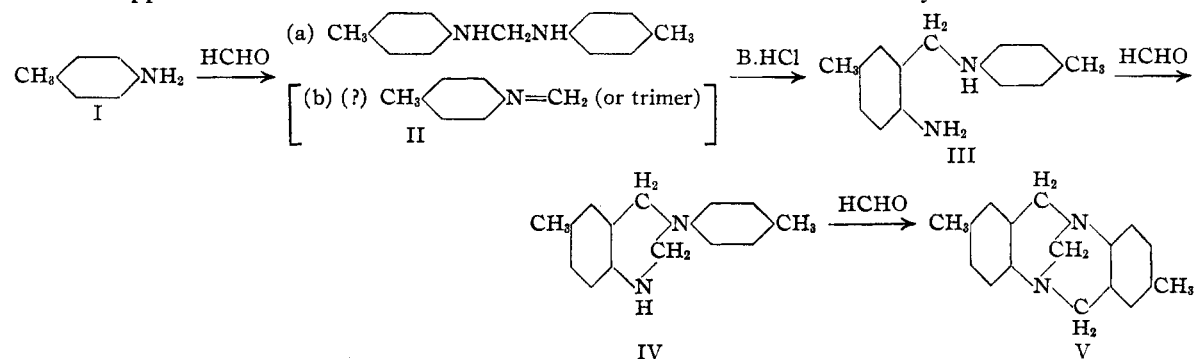
## Condensations of Aromatic Amines with Formaldehyde in Media Containing Acid.

### III. The Formation of Tröger's Base

By E. C. WAGNER

The structure of Tröger's base,  $C_{17}H_{18}N_2$ , was determined recently by Spielman.<sup>1</sup> Continuation of some preliminary work in this Laboratory<sup>2</sup> has yielded results which, in conjunction with Spielman's, indicate the probable course of the reactions by which Tröger's base is formed from *p*-toluidine and formaldehyde.

Preparation of the base by the methods of Tröger,<sup>3</sup> Löb,<sup>4</sup> or Goecke<sup>5</sup> gives no indication of the gross mechanism of its formation. This paper reports the preparation of Tröger's base (1) from methylene-bis-*p*-toluidine, (2) from *o*-amino-*m*-xylyl-*p*-toluidine, (3) from 3-*p*-tolyl-6-methyl-1,2,3,4-tetrahydroquinazoline by Spielman's method, and further (4) the conversion of methylene-bis-*p*-toluidine to *o*-amino-*m*-xylyl-*p*-toluidine, and (5) results which demonstrate the conversion of *o*-amino-*m*-xylyl-*p*-toluidine to tolyl-methyltetrahydroquinazoline as a step preliminary to formation of Tröger's base. These closely interrelated results reveal the steps in the elaboration of Tröger's base from *p*-toluidine and formaldehyde in acid solution. Their significance becomes apparent in the reaction scheme



(1) Spielman, *THIS JOURNAL*, **57**, 583 (1935).

(2) Eisner and Wagner, *ibid.*, **56**, 1938 (1934).

(3) Tröger, *J. prakt. Chem.*, [2] **36**, 227 (1887).

(4) Löb, *Z. Elektrochem.*, **4**, 428 (1897).

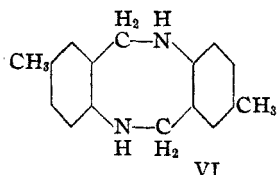
(5) Goecke, *ibid.*, **9**, 470 (1903).

that in the presence of alkali, formaldehyde converts III almost quantitatively to IV.<sup>6</sup> In this case absence of acid excludes the coupling

(6) Eisner and Wagner, *Ref. 2*, p. 1942.

reaction involved in the final step from IV to V.

Two other apparently possible reactions were not observed, *viz.*, direct conversion of II to IV by formaldehyde, and conversion of III to the dimeric anhydro-*p*-aminobenzyl alcohol (VI) related to *p*-toluidine:



This compound has not yet been obtained. Spielman's efforts to prepare it from the diacetyl compound or the dinitrosamine (from Tröger's base) were unsuccessful as were the writer's attempts to make it from III. The relationship of VI and Tröger's base (V) is interesting, as shown by Spielman, and presumably VI could yield Tröger's base by the action of formaldehyde. The possibility of forming VI and analogous compounds from other para substituted amines is being studied further as part of work under the general heading of this series of papers.

### Experimental

**General Procedure for Preparation of Tröger's Base from Precursors.**—The experimental conditions were essentially those given by Goecke, and later used by Spielman. To a mixture of 50 cc. of alcohol, 10 cc. of concd. hydrochloric acid and 10 cc. of 37% formalin, well chilled in an ice-bath, 5 g. of the selected starting compound was added in small portions during five to ten minutes, with agitation of the mixture until a clear solution was obtained. Except as noted below the liquid (flask stoppered) was allowed to stand in the ice-bath for some hours, and then at or below room temperature until the next day. The liquid, now deep red in color, was diluted with about 2 volumes of water, and made alkaline with ammonium hydroxide. The precipitated product was filtered off and dissolved in the least amount of warm 6 *N* hydrochloric acid. The solution was filtered, treated with about one-fifth its volume of concd. hydrochloric acid, and chilled. Separation of the hydrochloride of Tröger's base was sometimes delayed but reached a maximum after some hours. The hydrochloride was filtered off and dissolved in warm water containing some hydrochloric acid. The base was precipitated by ammonium hydroxide, filtered, washed with water, dried and weighed. Crystallization from hot dilute alcohol yielded the characteristic matted needles of Tröger's base, identified by m. p. alone or mixed with an authentic specimen of the compound.

**Preparation of Tröger's Base from *p*-Toluidine.**—The method of Goecke was used, except that the product was isolated through the hydrochloride as outlined above. The yield was about 30%.

**Preparation of Tröger's Base from Methylene-bis-*p*-toluidine.**—From 1 g. of the di-imine, made by the method of Eberhardt and Welter,<sup>7</sup> there was obtained 0.2 g. of Tröger's base, weighed after crystallization from dilute alcohol; m. p. 135°; mixed m. p. 136°.

**Preparation of Tröger's Base from *o*-Amino-*m*-xylyl-*p*-toluidine.**—*o*-Amino-*m*-xylyl-*p*-toluidine was prepared by an improved procedure based on the tedious method of German Patent 105,797.<sup>8</sup> When this compound was treated by the general procedure, with the reaction mixture kept in an ice-bath, a copious crystalline precipitate separated after fifteen minutes to an hour. On continued standing, especially at room temperature, this precipitate redissolved, giving finally the usual clear red liquid. When the reaction mixture was chilled only during addition of the *o*-amino-*m*-xylyl-*p*-toluidine and was then allowed to stand at room temperature, only a scanty precipitate appeared, and later redissolved. In both cases the final clear liquid, when treated by the isolation procedure given above, yielded Tröger's base in fairly good yield (71 and 56%).

In other experiments the liquid was kept in the ice-bath until the crystalline precipitate appeared to reach a maximum (about one hour), when it was filtered off and examined. The filtrate was allowed to stand further in ice, but in no case was there a weighable second crop deposited. The weight of precipitate was approximately that of the *o*-amino-*m*-xylyl-*p*-toluidine taken.

This material was not more than partially soluble in water, but dissolved readily in alcohol, hence was not predominantly a hydrochloride. The melting point was that of a mixture, and under the microscope the substance was seen to contain at least two compounds. The solution in alcohol was made alkaline with ammonium hydroxide, and by fractional crystallization, from the solution progressively diluted with water, there was isolated and identified 3-*p*-tolyl-6-methyl-1,2,3,4-tetrahydroquinazoline (m. p. 141°; yield 35%). The later fractions were mixtures containing some of the tolylmethyltetrahydroquinazoline and other material not identified.

In one experiment there was obtained, besides the tolylmethyltetrahydroquinazoline, a considerable quantity (2.5 g. from 5 g. of *o*-amino-*m*-xylyl-*p*-toluidine) of a product which separated as burr-like aggregates of short acicular crystals showing no color in polarized light, and mixed with some flat and characteristically colored plates of the tolylmethyltetrahydroquinazoline. The m. p. was poor (108–116°). On recrystallization from alcohol the crystal habit was unchanged and the m. p. 108–111°. It was believed that this compound might be the unknown anhydro-aminobenzyl alcohol (VI), but further study did not support this assumption, and was terminated when a number of later experiments failed to yield more of the same product, the only isolable compound being the tolylmethyltetrahydroquinazoline. The unidentified compound was found to yield Tröger's base (0.4 g. of hydrochloride from 0.5 g. of substance) by the general procedure. Reduction by 50% hydriodic acid and red phosphorus in a sealed tube gave a good yield of steam-volatile base. This was benzoyleated and crystallized fractionally from alcohol

(7) Eberhardt and Welter, *Ber.*, **27**, 1808 (1894).

(8) German Patent 105,797, *Friedl.*, **5**, 84; v. Walther and Bamberg, *J. prakt. Chem.*, [2] **71**, 153 (1905).

and dilute alcohol, yielding as a major component benzoyl-*unsym-m*-xylidine (m. p. 185° obs.; mixed m. p. 186°). There was present also a more soluble benzoyl derivative (m. p. 143° after three crystallizations) of another base, formation of which excludes a compound of formula VI whose cleavage by reduction should yield only *unsym-m*-xylidine.

The filtrate from the crystalline precipitate referred to first was steam-distilled to remove alcohol, made alkaline with sodium hydroxide, and steam-distilled further. No oily base passed over, but some fine needle crystals appeared in the distillate (about 0.1 g. in 500 cc.), and were identified as Tröger's base (m. p. 135.5°; mixed m. p. 136°), thus shown to be slightly volatile with steam. The residue in the distilling flask was removed, dissolved in 6 *N* hydrochloric acid and Tröger's base recovered as hydrochloride (about 27%).

The foregoing results show clearly that in the conversion of *o*-amino-*m*-xylyl-*p*-toluidine to Tröger's base, 3-*p*-tolyl-6-methyl-1,2,3,4-tetrahydroquinazoline is intermediate.

**Preparation of Tröger's Base from Tolylmethyltetrahydroquinazoline.**—The results reported by Spielman were duplicated.

**Conversion of Methylene-bis-*p*-toluidine to *o*-Amino-*m*-xylyl-*p*-toluidine.**<sup>9</sup>—A mixture of 2.3 g. of methylene-

bis-*p*-toluidine, 2.3 g. of *p*-toluidine hydrochloride, 5.5 g. of *p*-toluidine and 1 cc. of nitrobenzene was kept at 60° for two hours. The mixture was made alkaline and steam-distilled to remove nitrobenzene and excess *p*-toluidine. From the residue there was obtained *o*-amino-*m*-xylyl-*p*-toluidine, isolated as the benzal compound (m. p. 128°),<sup>8</sup> the conversion being 35%.

### Summary

The formation of Tröger's base (V) from *p*-toluidine (I) and formaldehyde in acid solution was shown to involve four steps yielding as successive intermediate compounds methylene-bis-*p*-toluidine (IIa) or methylene-*p*-toluidine (IIb), *o*-amino-*m*-xylyl-*p*-toluidine (III), and 3-*p*-tolyl-6-methyl-1,2,3,4-tetrahydroquinazoline (IV). This was demonstrated by the formation of Tröger's base from each of these compounds under the conditions which yield it from *p*-toluidine, and by effecting separately the conversion of II to III, of III to IV, and of IV to Tröger's base.

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(9) These results were obtained by Dr. J. K. Simons.

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF NEBRASKA]

## Catalytic Reduction of Nitroarylarsonic Acids

BY MELVIN R. STEVINSON<sup>1</sup> AND CLIFF S. HAMILTON

Several methods have been developed for the reduction of nitroarylarsonic acids to the corresponding amines. The alkaline ferrous hydroxide method<sup>2</sup> is generally applicable, but it involves tedious experimental manipulation. Sodium hydrosulfite may also be used, but, unless the temperature is controlled carefully, the arsono group may be converted into the arseno group. In this investigation a catalytic reduction method was developed.<sup>3</sup>

In view of the fact that nitroarylarsonic acids are sparingly soluble, at room temperature, in water, alcohols and acids, but readily soluble in alkalis, a catalyst which would effect reduction in alkaline solution seemed advisable. Raney nickel<sup>4</sup> prepared by the method of Covert and Adkins<sup>5</sup> was used. The apparatus utilized in the reduction work was essentially that of a standard "set-up" for effecting hydrogenation in the liquid phase with hydrogen gas under moderate pressures.

The method was used successfully on a number of nitroarylarsonic acids, and without exception the arsono group was unaffected. In every case the yields were as near the calculated amounts as individual properties, such as stability, would permit.

A search of the literature has failed to reveal the use of Raney nickel for the catalytic hydrogenation of nitro compounds, and for the hydrogenation of a compound containing a halogen as well.

### Experimental

Several experiments were made to determine which of the common contaminating impurities of nitroarylarsonic acids tended to inactivate the nickel catalyst. The data were obtained as follows.

A solution of 1.4 g. (0.01 mole) of pure *p*-nitrophenol (m. p. 114°) in 100 cc. of water and 5 cc. of 2 *N* sodium hydroxide was reduced by hydrogen under 30 lb. pressure in the presence of 2 g. of Raney nickel. The time of reduction was eleven minutes, which was used as a control. Similar experiments were run with all conditions held constant except that 10% by weight (based on *p*-nitrophenol) of various impurities were added.

(1) Parke, Davis and Company Fellow.

(2) Jacobs, Heidelberger und Rolf, *THIS JOURNAL*, **40**, 1580 (1918).

(3) Boehringer und Soehne, German Patent 288,547 (1914).

(4) Raney, U. S. Patent 1,628,190 (1927).

(5) Covert and Adkins, *THIS JOURNAL*, **54**, 4116 (1932).