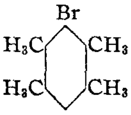
[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Studies on the Polymethylbenzenes. XII. The Nitration of Bromodurene, and the Structure of the "Dinitrodurylic Acid Bromide" of Willstätter and Kubli[1,2]

BY LEE IRVIN SMITH AND DAVID TENENBAUM

Some time ago, Willstätter and Kubli[3] reported that the nitration of bromodurene (I) at 0° in the absence of sulfuric acid or any other solvent gave dinitrodurylic acid bromide (II). Their evidence for this consisted in the analysis and the fact that on hydrolysis with alcoholic alkali, a very small yield of dinitrodurylic acid was obtained. In connection with some other work, we needed considerable amounts of dinitrodurylic acid, which is usually prepared directly from durylic acid by nitration.[3,4] But the preparation of large amounts of durylic acid is very tedious, and in the hope of simplifying the preparation of the dinitro acid, we decided to study the hydrolysis of the dinitro acid bromide of Willstätter and Kubli.

It soon became apparent that the compound obtained by Willstätter and Kubli could not possibly be an acid bromide. Prolonged action of alcoholic silver nitrate gave no silver bromide; the action of alkali on the colorless substance under the most varied conditions gave rise to a series of color changes, starting with yellow, and progressing through green, blue, purple to brown, but yielded *no* dinitrodurylic acid.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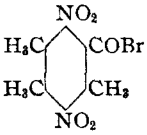
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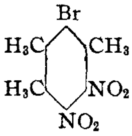
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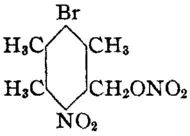
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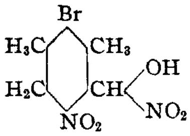
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To settle definitely whether or not the compound of Willstätter and Kubli was an acid bromide, we decided to synthesize II from dinitrodurylic acid. The synthesis, however, was unsuccessful, for neither phosphorus tribromide nor thionyl bromide converted the dinitro acid to the acid bromide, although both reagents could be made to react—sometimes vigorously. The corresponding chloro compounds, however, proved more tractable. When chlorodurene is nitrated by the same procedure used in the case of the bromo compound, the chlorine analog (m. p. 93–94°) of the Willstätter and Kubli compound results. Like the latter, this chlorine compound has an unreactive halogen atom and cannot be hydrolyzed to dinitrodurylic acid. When dinitrodurylic acid is treated with thionyl chloride there is produced the true dinitrodurylic acid chloride, m. p. 90–91°. This substance reacts at once with methyl or ethyl alcohol, giving the corresponding esters of dinitrodurylic acid; it is hydrolyzed to the acid quickly and quantitatively by alcoholic alkali; and with alcoholic silver nitrate it gives an immediate, quantitative precipitation of silver chloride. Finally the two substances melting at 93–94 and 90–91°, respectively, show a depression of 15° when melted together. It follows, therefore, that the substance obtained by nitrating chlorodurene cannot be dinitrodurylic acid chloride, and, by analogy, the compound obtained by Willstätter and Kubli by nitrating bromodurene cannot be dinitrodurylic acid bromide.

When bromodurene is treated with fuming nitric acid, *d* 1.52, at room temperature, or with acid of density 1.6 at 0°, or when bromonitrodurene (m. p. 179–181°) is treated with acid of density 1.52 at 0°, there results a light yellow, crystalline product $C_9H_9O_4N_2Br$, m. p. 181–182°. When bromodurene is nitrated at 0° with acid of density 1.52, the product is the Willstätter and Kubli compound, which is colorless and melts at 122°. If the latter compound is allowed to stand at room temperature in contact with nitric acid of density 1.52, or is stirred with concentrated sulfuric acid for half an hour, it is transformed into the yellow compound melting at 181–182°. This yellow compound is related in composition to bromodurene in the same way that pentamethylbenzene is related to its nitration product: thus

$$A - CH_4 + 2NO_2 = B$$

(A = bromodurene or pentamethylbenzene; B =

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[1] Paper XI, THIS JOURNAL, **57**, 1289 (1935).

[2] Abstracted from a thesis by David Tenenbaum, presented to the Graduate Faculty of the University of Minnesota, in partial fulfilment of the requirements for the degree of Master of Science, October, 1934.

[3] Willstätter and Kubli, *Ber.*, **42**, 4151 (1909).

[4] Gissmann, *Ann.*, **216**, 207 (1883); Nef, *Ber.*, **18**, 2801 (1885); *Ann.*, **237**, 1 (1887).

$C_9H_9O_4N_2Br$ or dinitroprehnitene). Since the nitration product of pentamethylbenzene is dinitroprehnitene, we suspected that the yellow compound obtained from bromodurene was 3-bromo-5,6-dinitropseudocumene, III. Accordingly we synthesized III by nitrating 3-bromopseudocumene; it was identical with the 181–182° compound in every respect.

Willstätter and Kubli state that bromonitrodurene with nitric acid of density 1.52 at 0° gives their "acid bromide." This indicates that bromonitrodurene is a probable intermediate in the conversion of bromodurene to the "acid bromide." We were able to transform the "acid bromide" into III in two ways, and, although we have not as yet been able to duplicate the results of Willstätter and Kubli on transformation of bromonitrodurene into the "acid bromide," we believe both compounds to be intermediates between I and III.

Our work on the structure of the Willstätter and Kubli compound is still incomplete. Our analyses, and also those of Willstätter and Kubli, agree better with the formula $C_{10}H_{11}O_5N_2Br$, than with the formula $C_{10}H_9O_5N_2Br$, which is the composition of II. On reduction, the compound gives aminodurene as the only isolable product. Assuming that the skeleton of bromonitrodurene is still intact in this compound, there remains the residue H_2NO_3 to be attached to one of the side chain carbon atoms if the composition is $C_{10}H_{11}O_5N_2Br$. Since the substance can be converted into an ortho dinitro compound, it is likely that the carbon atom involved is ortho to the nitro group in the bromonitrodurene. This then leads to IV or V as possible structures. IV is the nitrate of an ortho nitrobenzoyl alcohol; V is a nitrous acid addition product of an ortho nitrobenzaldehyde. At present we prefer IV, but our conclusions regarding the structure of this compound are but tentative and further work is necessary in order to decide among these and other formulas. Similarly, we represent the course of the nitration as I $\longrightarrow$ bromonitrodurene $\longrightarrow$ IV $\longrightarrow$ III, although further work will be necessary in order to establish this definitely.

Experimental

The Willstätter and Kubli Compound.—Bromodurene (10 g.) was dropped slowly into fuming nitric acid (d. 1.52) with cooling (0 to −5°) and stirring. After the addition was complete, the mixture was stirred for thirty minutes at 0°, then poured onto ice. The product was crystallized twice from ethyl alcohol as white needles, m. p. 122–123°, yield 9 g.

Anal. Calcd. for $C_{10}H_9O_5N_2Br$: C, 37.86; H, 2.86; N, 8.84; Br, 25.21; mol. wt., 317. Calcd. for $C_{10}H_{11}O_5N_2Br$: C, 37.6; H, 3.44; N, 8.79; Br, 25.1; mol. wt., 319. Found: C, 37.72, 37.95; H, 3.38, 3.44; N, 9.35; Br, 25.3; mol. wt. (Rast), 314.

The substance was recovered quantitatively after forty-eight hours of refluxing with alcoholic silver nitrate, not a trace of silver bromide precipitating. When 5 g. of it was dissolved in alcohol and treated with concentrated aqueous potassium hydroxide, there resulted a series of color changes ending with brown, which persisted after several hours of refluxing. Acidification at the brown stage gave a brown amorphous solid, insoluble in all the usual organic solvents, and which could not be purified. Acidification at the blue stage gave an orange precipitate which could not be separated into pure constituents. When dilute alkali was used, the color changes stopped at the purple stage, but on acidifying the product was again the intractable orange-brown precipitate.

Reduction.—The substance (3 g.) in glacial acetic acid (10 cc.) was treated with granulated tin (15 g.) and hydrochloric acid (20 cc.) under reflux for one hour, and then allowed to stand for several hours at room temperature. The solid which separated was removed and steam distilled with alkali, giving 0.7 g. of aminodurene, m. p. 70–72° and after sublimation m. p. 72.5–73.5°; mixed m. p. with an authentic specimen prepared by the reduction of nitrosodurene, 72–73°.

Anal. Calcd. for $C_{10}H_{15}N$: C, 80.5; H, 10.07; N, 9.4. Found: C, 80.1, 80.1; H, 10.2, 10.2; N, 9.6.

The acetyl derivative resulted when the amine was treated with acetic anhydride for five minutes; m. p. 201–203°; mixed m. p. with an authentic specimen, 201–203°.

Anal. Calcd. for $C_{12}H_{17}ON$: C, 75.4; H, 8.9. Found: C, 75.0; H, 9.3.

The only other products of the reduction were resinous materials which could not be purified.

Bromonitrodurene.—Bromodurene (20 g.) in 100 g. of chloroform was added to 40 g. of concd. sulfuric acid. The mixture was stirred vigorously, with cooling, while a solution of nitric acid (8 g., *d* 1.6 for 98% HNO_3) in 20 g. of chloroform was slowly added. The reaction mixture was carefully diluted with ether, the layers separated and the ether–chloroform layer washed with dilute carbonate and then with water. The solvent was partially evaporated, alcohol was added and the solution cooled. The product was recrystallized from alcohol; yield 80%, m. p. 179–181°. As this m. p. was only slightly different from that of bromodinitropseudocumene and there is no depression in the mixed melting point, we analyzed the substance.

Anal. Calcd. for $C_{10}H_{12}O_2NBr$: C, 46.5; H, 4.65. Found: C, 46.1; H, 5.0.

Reduction with tin and hydrochloric acid in acetic acid solution gave aminodurene, m. p. 71–73° (after sublimation).

3-Bromo-5,6-dinitropseudocumene. III

(A) 3-Bromopseudocumene (3 g.) was nitrated directly by dissolving it in a mixture of equal parts of fuming nitric acid (*d* 1.52) and sulfuric acid, with stirring and cooling. The product was recrystallized from alcohol; yield 4.1 g., m. p. 181–182°.

Anal. Calcd. for $C_9H_9O_4N_2Br$: C, 37.38; H, 3.15; Br, 27.7; N, 9.69; mol. wt., 289. Found: C, 37.3, 37.3; H, 3.38, 3.26; Br, 27.8, 27.8; N, 9.42, 9.7; mol. wt. (Rast), 297, 288.

No depression in melting point is shown when this compound is mixed with bromonitrodurene.

(B) Bromonitrodurene (5 g.) was slowly stirred into fuming nitric acid (*d* 1.52) at 0°. After half an hour, the mixture was poured onto ice. The purified product weighed 3 g., m. p. 181–182°.

(C) Bromodurene (5 g.) similarly nitrated with acid of *d* 1.52 at 25°, gave 3.1 g. of product, m. p. 181–182°; with fuming nitric acid, *d* 1.6 at 0°, 10 g. of bromodurene gave 7.8 g. of product, m. p. 181–182°.

(D) The Willstätter and Kubli compound (3 g.) was allowed to stand in contact with fuming nitric acid (*d* 1.52) at 25° for two hours. The purified product weighed 2 g., m. p. 181–182°.

(E) The Willstätter and Kubli compound (4 g.) was stirred into concentrated sulfuric acid, giving an orange solution with suspended solid in it. After half an hour the solid was filtered off, washed with cold concentrated sulfuric acid, dissolved in benzene and the benzene partially evaporated. Low boiling petroleum ether was added until incipient cloudiness resulted, and the solution then cooled. The yield of purified product was 2.2 g., m. p. 181–182°. The orange sulfuric acid filtrate, on dilution with water, gave an uncrystallizable precipitate.

5,6-Diaminopseudocumene.—The bromodinitro compound (III) made by method (A) and samples made by the other methods were reduced in parallel experiments. The nitro compound III (2 g.) was dissolved in alcohol, and a solution of stannous chloride (10 g.) in hydrochloric acid was added. After refluxing for half an hour, the mixture was made alkaline and steam distilled. The product was isolated by extracting the distillate with ether, evaporating, and crystallizing the residue from water. The average yield of product was 0.7 g., m. p. and mixed m. p. of all preparations, 90–92°.[5]

2,4,6,7-Tetramethylbenzimidazole.—The diaminopseudocumene (0.5 g.) was refluxed with 5 cc. of glacial acetic acid for half an hour, the solution made alkaline and extracted with ether. The ether was evaporated and the product crystallized from aqueous alcohol. Several of these experiments were run in parallel on the diamine prepared from various specimens of bromodinitropseudocumene, according to methods A to E. The average yield of benzimidazole was 0.5 g., m. p. and mixed m. p. of all samples, 229–230°.[6]

Attempted Syntheses of Dinitrodurylic Acid Bromide (II). With Phosphorus Tribromide.—Dinitrodurylic acid (3 g.) was added to 10 cc. of freshly distilled phosphorus tribromide, and the mixture warmed on the steam-bath for half an hour. It was then cooled and poured onto ice. The resulting solid was extremely insoluble in all solvents except alcohol, from which it could be recovered with no apparent change in purity or m. p. (150–175°).

With Thionyl Bromide.—Dinitrodurylic acid was unchanged when warmed for half an hour on the steam-bath with thionyl bromide; if refluxed, complete decomposition ensued. When the acid (3 g.) was dissolved in benzene and refluxed with a benzene solution of thionyl bromide, a mixture of white and orange crystals separated on cooling. The solid was filtered off and the white crystals removed by extracting with ether. The white solid was dinitrodurylic acid; the insoluble orange solid was a mixture which could not be separated into its constituents.

The Chlorine Analog of the Willstätter and Kubli Compound.—This was made from chlorodurene in the same way the corresponding bromo compound was made as long white needles (from alcohol), m. p. 93–94°.

Anal. Calcd. for $C_{10}H_9O_5N_2Cl$ (272.5): C, 44.03; H, 3.33. Calcd. for $C_{10}H_{11}O_5N_2Cl$ (274.5): C, 43.72; H, 4.07. Found: C, 43.83, 43.77; H, 3.87, 3.92.

The substance shows the same properties as its bromine analog. With alcoholic silver nitrate there is no precipitation of silver chloride on refluxing for forty-eight hours; with alcoholic alkali it gives the same series of color changes as the bromine compound and no pure material could be obtained from the reaction; dropped into concentrated sulfuric acid, 3 g. of it gives 1.1 g. of 3-chloro-5,6-dinitropseudocumene, m. p. 174°.[7]

Dinitrodurylic Acid Chloride.—The dinitro acid (3 g.) was refluxed with thionyl chloride for thirty minutes, the solution cooled and poured onto ice. The solid was filtered off and crystallized from petroleum ether; yield 2.5 g., m. p. 90–91°.

Anal. Calcd. for $C_{10}H_9O_5N_2Cl$: C, 44.03; H, 3.33; Cl, 13.01. Found: C, 44.13; H, 3.31; Cl, 12.5.

That this is the true acid chloride is shown by its complete, quantitative hydrolysis on treatment with warm alcoholic potassium hydroxide for five minutes (yield of dinitrodurylic acid, m. p. 211–212°, 2.5 g. from 3 g. of the chloride), and by the quantitative precipitation of silver chloride when it was warmed for five minutes with alcoholic silver nitrate. (The chlorine determination in the above analysis was made in this way.)

Methyl Ester of Dinitrodurylic Acid.—Solution of the acid chloride in methyl alcohol gave the methyl ester, m. p. and mixed m. p. with a sample prepared by way of the silver salt, 103–106°.

Ethyl Ester of Dinitrodurylic Acid.—In a similar manner the ethyl ester, m. p. 99–101°, was obtained.

Anal. Calcd. for $C_{12}H_{14}O_6N_2$: C, 51.1; H, 4.97. Found: C, 51.2; H, 5.12.

Finally, this acid chloride, m. p. 90–91°, when mixed with the chlorine analog of the Willstätter and Kubli compound, m. p. 93–94°, shows a mixed m. p. of 73–77°. The two substances are thus entirely different, and the substance obtained by nitrating chlorodurene is not an acid chloride.

Summary

1. The nitration of bromodurene under varying conditions has been described.

2. The acid chloride of dinitrodurylic acid has

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[5] Edler, *Ber.*, **18**, 630 (1885); Nölting and Baumann, *ibid.*, **18**, 1148 (1885).

[6] Bogert and Bender, THIS JOURNAL, **36**, 568 (1914).

[7] Tohl, *Ber.*, **25**, 1529 (1892).

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, cannot 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.

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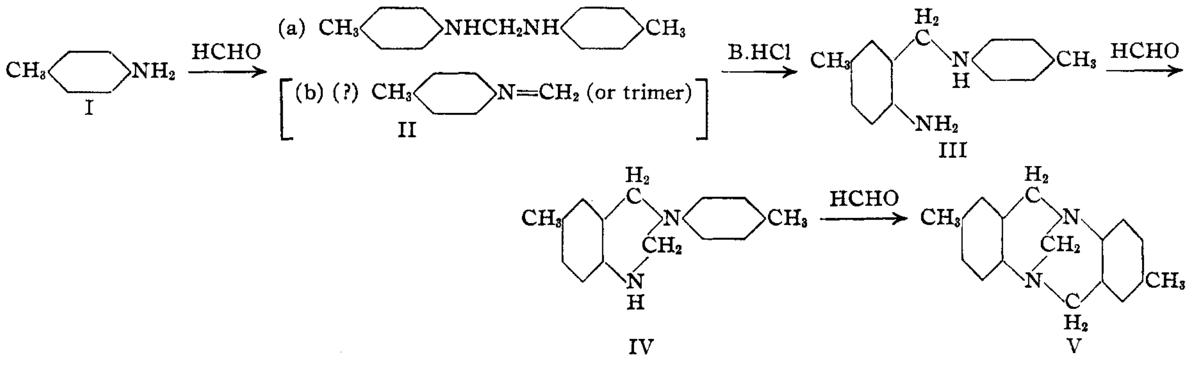
[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

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.[1] Continuation of some preliminary work in this Laboratory[2] 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,[3] Löb,[4] or Goecke[5] 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 tolylmethyltetrahydroquinazoline 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



Steps I to V inclusive represent the methods of Tröger and Goecke. Step IV to V is Spielman's synthesis. Steps II to V and III to V are described in the experimental part, as are the individual intermediate steps II to III and III to IV. With one exception all these reactions occurred under conditions practically identical with those of Goecke's procedure (action of excess formaldehyde in aqueous alcoholic hydrochloric acid solution). Conversion of the di-imine (IIa) to the aminobenzylarylamine (III) was effected under the regulated conditions necessary for preparation of such compounds. This step involves a "rearrangement" under the influence of acid, and if carried out in presence of formaldehyde the aminobenzylarylamine would react to form IV and then V. Formation of IIa from I in acid solution was not demonstrated. It is possible that the first reaction may yield methylene-*p*-toluidine (IIb) or its trimer, which also is convertible to III and hence would fit into the scheme. Efforts to obtain IV from II or III by action of only one equivalent of formaldehyde were not successful. Attention may be called to the fact that in the presence of alkali, formaldehyde converts III almost quantitatively to IV.[6] In this case absence of acid excludes the coupling

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[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).

[6] Eisner and Wagner, Ref. 2, p. 1942.