product was dried overnight at 90° and then *in vacuo* over concd. sulfuric acid. Yield varied from 30–50%.

Condensation of 3-Nitro-4-chlorophenylarsonic Acid with 2-Amino-2-methyl-1-propanol.—Five grams of 3-nitro-4-chlorophenylarsonic acid and 10 cc. of 2-amino-2-methyl-1-propanol were heated, under reflux, on an oil-bath at 160–170° for six hours. During this time the mixture became almost black and was very viscous. The tarry residue was *dissolved* out in 50 ml. of hot water, the solution charcoaled, filtered and then made neutral to congo red with concd. hydrochloric acid. The yellow solid that separated was purified by reprecipitation from alkaline solution with concd. hydrochloric acid, dried at 90° in an oven overnight and then *in vacuo* over concd. sulfuric acid.

General Procedure for the Preparation of the 3-Amino Derivatives.—The nitro groups in the compounds described above were reduced to amino groups using the method of Jacobs, Heidelberger and Rolf.[5] The products obtained were light-red solids, which turned dark rapidly on exposure to air; yields, 10–30%.

Summary

The preparation of a number of 3-nitro-4-substituted aminophenylarsonic acids and the corresponding 3-amino compounds has been reported.

[5] Jacobs, Heidelberger and Rolf, THIS JOURNAL, **40**, 1581 (1918).

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[CONTRIBUTION FROM THE DEPARTMENT OF PHYSIOLOGY AND VITAL ECONOMICS, UNIVERSITY OF ROCHESTER SCHOOL OF MEDICINE AND DENTISTRY]

The Synthesis of 4,5-Diethyl-*o*-phenylenediamine through the Nitration of *o*-Diethylbenzene

BY JOHN P. LAMBOOY

Until relatively recently *o*-diethylbenzene has been available in such limited quantities that it has been used for synthetic purposes by no one but its discoverer. A. Voswinkel[1] first synthesized *o*-diethylbenzene in 1888 and along with it he reported the syntheses of barium *o*-diethylbenzenesulfonate, *o*-diethylbenzenesulfonamide and 1,2-diethyl-3,4,5,6-tetrabromobenzene. He was discouraged from more than preliminary efforts at nitration because of lack of starting material and the explosive nature of the product he obtained. The nature of this product as well as the position of the sulfonic acid group remain unknown.

Karabinos, Serijan and Gibbons[2] have introduced a method by which relatively large amounts of pure *o*-diethylbenzene are made available. Our need for compounds related to 4,5-diethyl-*o*-phenylenediamine made the prospect of obtaining it through successive nitrations of *o*-diethylbenzene attractive.

o-Diethylbenzene was nitrated and while it is probable that other products were produced, repeated vacuum fractional distillations yielded only one readily available product. This was shown by oxidation to the nitrophthalic acid to be exclusively 1,2-diethyl-4-nitrobenzene. The nitro compound was reduced catalytically to 3,4-diethylaniline. After carbethoxylation of the amino group the material was again subjected to nitration with the formation, for the most part, of 4,5-diethyl-2-nitrocarbethoxyaniline. Removal of the carbethoxy group to produce 4,5-diethyl-2-nitroaniline followed by deamination located the second nitro group by producing 1,2-diethyl-4-nitrobenzene. The 4,5-diethyl-2-nitroaniline was reduced catalytically to produce 4,5-diethyl-*o*-phenylenediamine.

Experimental

1,2-Diethyl-4-nitrobenzene.—A mixture of 175 ml. of fuming nitric acid (sp. gr. 1.59–1.60) and 87.5 ml. of glacial acetic acid was cooled to 10°. While this solution was stirred vigorously, 50 g. of *o*-diethylbenzene[3] was added at a rate to maintain the temperature between 10–20°. After the last of the *o*-diethylbenzene had been added the stirring was continued for forty-five minutes at the same temperature. The reaction mixture was then poured into one liter of ice-water. The crude nitro compounds were extracted with four 125-ml. portions of ether and the ether extract washed with three 50-ml. portions of water, with six 50-ml. portions (until the reaction has become alkaline) of 10% sodium hydroxide solution and again with three 50-ml. portions of water. The ether extract was dried over anhydrous sodium sulfate and the solvent removed. After preliminary studies the following procedure was used for the separation of the desired product. The combined nitration products obtained from the nitration of 422 g. of *o*-diethylbenzene were distilled from a Claisen flask at 10 mm. pressure. Only that material collected over the temperature range 130–150°, which amounted to 380 g. or 74% yield, was fractionated. The column used was 60 cm. long, 1.5 cm. i. d., and filled with small, single-turn glass helices. The fractionating head was designed so that any desired portion of the condensate could be returned to the column. The material was fractionated three consecutive times into three degree ranges between 120–141°. The material collected in the boiling point range 139–141° at 10 mm. weighed 230.5 g., which is 41% of the theoretical amount, and was identified as 1,2-diethyl-4-nitrobenzene; yellow oil, b. p. 139–141° at 10 mm. mercury pressure, d^{22} 1.0852, $n^{25}\text{D}$ 1.5440.

Anal. Calcd. for $C_{10}H_{13}NO_2$: C, 67.02; H, 7.31; N, 7.82. Found: C, 67.22; H, 7.24; N, 8.10.

The 1,2-diethyl-4-nitrobenzene was characterized by permanganate and also nitric acid oxidation to the 4-nitrophthalic acid which was identified by the melting points of the acid, anhydride, the acid aniline salt and the anil. No evidence could be found for the presence of any of the 3-nitrophthalic acid.

3,4-Diethylaniline.—The 1,2-diethyl-4-nitrobenzene was reduced catalytically in a Parr hydrogenator at initial pressures of 60 p.s.i., using platinum oxide, platinum on zirconium or palladium on zirconium oxide. Seventeen and nine-tenths grams (0.1 mole) of 1,2-diethyl-4-nitrobenzene was dissolved in 150 ml. of absolute alcohol and

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[1] Voswinkel, *Ber.*, **21**, 3499 (1888).

[2] Karabinos, Serijan and Gibbons, THIS JOURNAL, **68**, 2107 (1946).

[3] The *o*-diethylbenzene used in this study was generously furnished by the National Advisory Committee for Aeronautics.

0.2 g. of platinum oxide added. At 24° the reduction was 97% complete in twenty minutes and 100% in one hour. The catalyst and solvent were removed and the 3,4-diethylaniline distilled at 10 mm. pressure to obtain 13.9–14.7 g. (93–99% yield) of product; colorless or very pale yellow oil, b. p. 116–117° at 10 mm., d^{28} 0.952, $n^{29}\text{D}$ 1.5458.

Anal. Calcd. for $C_{10}H_{15}N$: C, 80.48; H, 10.13; N, 9.39. Found: C, 80.17; H, 10.10; N, 9.4.

The material becomes discolored rapidly on exposure to air.

The **acetanilide** recrystallized from 50% alcohol as white platelets, m. p. 119°.[4]

Anal. Calcd. for $C_{12}H_{17}NO$: N, 7.33. Found: N, 7.1.

The **benzanilide** recrystallized from 70–80% alcohol as white needles, m. p. 116–117°.

Anal. Calcd. for $C_{17}H_{19}NO$: N, 5.53. Found: N, 5.5.

The **aniline hydrochloride** was prepared by passing dry hydrogen chloride into an anhydrous ether solution of the aniline. When recrystallized from a mixture of chloroform and ligroin it was obtained as white needles, m. p. 196–197°.

Anal. Calcd. for $C_{10}H_{16}NCl$: Cl, 19.10. Found: Cl, 19.17.

4,5-Diethyl-2-nitrocarbethoxyanilide.—The procedure outlined by Karrer and Becker[5] was used for the synthesis of this compound. Twenty-eight and seven-tenths grams (0.193 mole) of 3,4-diethylaniline, 73 ml. of acetone, 43 ml. of water and 34 ml. of sodium hydroxide solution (24%) and 29 g. of ethylchlorocarbonate were used to prepare the urethan. The urethan was used directly in the nitration which was accomplished in a mixture of 118 ml. of concentrated nitric acid and 43 ml. of concentrated sulfuric acid. After the product was poured onto ice and had solidified, it was dissolved in ether. The ether solution was washed with water until neutral, dried over anhydrous sodium sulfate and the solvent removed on the steam-bath. The product was recrystallized from alcohol to produce 29.8 g. (57% yield) of fine yellow needles, m. p. 60°.

Anal. Calcd. for $C_{13}H_{18}N_2O_4$: C, 58.63; H, 6.81; N, 10.52. Found: C, 58.74; H, 6.64; N, 10.2.

4,5-Diethyl-2-nitroaniline.—To a solution of 20 g. of sodium hydroxide, 50 ml. of water and 150 ml. of alcohol, 12.0 g. (0.062 mole) of 4,5-diethyl-2-nitrocarbethoxyanilide was added. While the solution was stirred the temperature was raised to 70° and held there for one hour. The alcohol was removed under diminished pressure and 100 ml. of water added. The suspension was extracted repeatedly with benzene. The benzene solution was dried over anhydrous sodium sulfate and the benzene removed under diminished pressure. The residue was recrystallized from dilute alcohol to produce 7.1 g. (81% yield) of orange prisms, m. p. 64–65°.

Anal. Calcd. for $C_{10}H_{14}N_2O_2$: C, 61.83; H, 7.26; N, 14.43. Found: C, 62.10; H, 7.33; N, 14.2.

The nitroaniline is steam distillable. The position of the nitro group was determined by deamination of 2.6 g. of the nitroaniline by the procedure outlined by Hodgson and Turner.[6] The nitro compound produced was isolated by steam distillation and the distillate extracted with ether. After the solution was dried and the ether removed the residue was distilled at reduced pressure to produce 1.4 g. (58% yield) of product. The boiling point could not be determined with certainty on this amount so it was reduced to the aniline and converted to the benzanilide, m. p. 114–115°. A mixture of this material and the benzanilide prepared from known 3,4-diethylaniline melted at 116°. This proves the nitro group to be in the 2-position.

4,5-Diethyl-*o*-phenylenediamine.—One and nine-tenths grams (0.01 mole) of 4,5-diethyl-2-nitroaniline was reduced in 75 ml. of absolute alcohol with 1.1 g. of platinum on zirconium with an initial pressure of 60 p.s.i. After removal of the catalyst and removal of the solvent the residue was recrystallized from benzene to produce 1.3 g. (81% yield) of white platelets, m. p. 114–115°.

Anal. Calcd. for $C_{10}H_{16}N_2$: C, 73.12; H, 9.82; N, 17.07. Found: C, 73.16; H, 9.66; N, 17.6, 17.7.

o-Phenylenediamine sublimes.[7] 4,5-Diethyl-*o*-phenylenediamine was found to sublime slowly at 78° at 2 mm. mercury pressure and very slowly at 100° at atmospheric pressure. 4-Methyl-*o*-phenylenediamine was prepared in 90% yield by catalytic (platinum oxide at 60 p.s.i.) reduction of a tenth mole lot of 3-nitro-4-aminotoluene to produce material of m. p. 90–92°. This material was found to sublime under the same conditions as those described above.

Summary

1. The synthesis of 4,5-diethyl-*o*-phenylenediamine through the successive nitrations of *o*-diethylbenzene has been described.

2. Several new compounds involved as intermediates in the above synthesis have been reported including 1,2-diethyl-4-nitrobenzene, 3,4-diethylaniline, 4,5-diethyl-2-nitrocarbethoxyanilide and 4,5-diethyl-2-nitroaniline.

3. The nitration of *o*-diethylbenzene has been shown to result in approximately a 40% yield of 1,2-diethyl-4-nitrobenzene.

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[4] All melting points given were observed on thermometers calibrated against U. S. P. Melting Point Reference Standards and Anschütz thermometers.

[5] Karrer and Becker, *Helv. Chim. Acta*, **18**, 1435 (1935).

[6] Hodgson and Turner, *J. Chem. Soc.*, 748 (1942).

[7] Zincke and Sintenis, *Ber.*, **6**, 123 (1873).