Selective Reduction of 2,2′,4,4′-Tetranitrobiphenyl

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In connection with our research a series of diamines was desired. Since 2,2′,4,4′-tetranitrobiphenyl (I) could be easily prepared by the nitration of biphenyl,[2] the selective reduction of this tetranitro compound was studied. Of the possible selective reagents, alcoholic sodium sulfide appeared to be the most convenient to use with polyamines. Since sodium sulfide selectively reduced the 2-nitro group in 2,4-dinitrotoluene to produce 2-amino-4-nitrotoluene while stannous chloride selectively reduced the 4-nitro group,[3] it was of particular interest to determine which nitro groups in this tetranitro derivative would be reduced. A modification of the method of Hodgson and Birtwell,[4] in which the polynitro compound is reduced in a methanolic solution of sodium sulfide and sodium bicarbonate, was used. Under these conditions 2,2′,4,4′-tetranitrobiphenyl (I) was selectively reduced to 2,2′-dinitrobenzidine (II) in 62% yield. This reduction is particularly significant since the sodium sulfide reagent never had been successfully used to reduce selectively a tetranitro compound,[5] although Hodgson, Ward, and Whitehurst[6] selectively reduced 1,3,6,8-tetranitronaphthalene with stannous chloride.

The structure of the 2,2′-dinitrobenzidine (II) was proved by an independent synthesis. Nitration of benzidine by the method of Tauber[7] gave a 57% yield of II. Acetylation of both samples of II with acetic anhydride produced an 81% yield of identical samples of *N*,*N*′-diacetyl-2,2′-dinitrobenzidine (III).

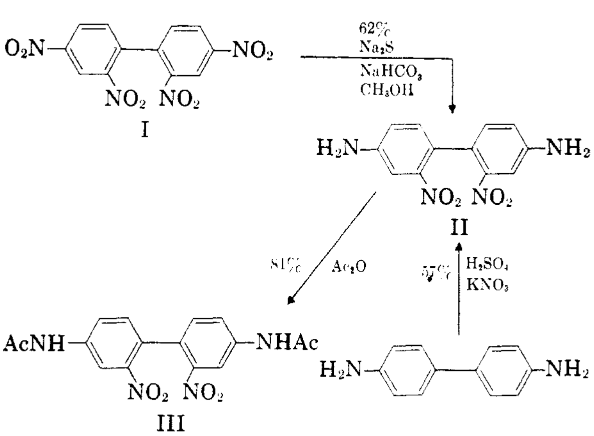
EXPERIMENTAL

2,2′-Dinitrobenzidine (II). *A. By selective reduction of 2,2′,4,4′-tetranitrobiphenyl* (I). The 2,2′,4,4′-tetranitrobiphenyl (I), m.p. 163–164° (reported[8] m.p. 163°), was prepared in 83% yield by the method of Huntress[2] in which biphenyl was nitrated with a mixture of concentrated nitric acid and sulfuric acid. To a solution of 67 g. (0.2 mole) of 2,2′,4,4′-tetranitrobiphenyl (I) in 2500 ml. of boiling methanol contained in a 5-liter, three-necked flask, equipped with a condenser, a stirrer, and a dropping-funnel, was added over a period of 1 hour a warm solution of 152 g. of sodium sulfide and 48 g. of sodium bicarbonate in 400 ml. of water. The presence of a large excess of sodium sulfide was avoided throughout the reaction by the periodic test of the solution with ferrous sulfate paper. The reaction mixture was cooled, and the resulting precipitate was removed by filtration. Concentration of the filtrate gave an additional crop of diamine. The combined crude material was recrystallized from ethanol to produce 34 g. (62%) of 2,2′-dinitrobenzidine (II), m.p. 212–214° (reported[7] m.p. 214°).

A mixture of 5 g. (0.018 mole) of II and 50 ml. of acetic anhydride was heated under reflux for 24 hours and the resulting product was recrystallized from acetic acid to yield 5.2 g. (81%) of *N*,*N*′-diacetyl-2,2′-dinitrobenzidine, m.p. 292–293° (dec.) [reported[9] m.p. 290° (dec.)].

B. From benzidine. In accordance with the procedure of Tauber,[7] benzidine was nitrated with potassium nitrate and sulfuric acid to yield 2,2′-dinitrobenzidine, m.p. 212–214°. A mixture melting point determination with the sample of II from the selective reduction showed no depression.

This sample of II was also acetylated with acetic anhydride to yield *N*,*N*′-diacetyl-2,2′-dinitrobenzidine (III), m.p. 292–293° (dec.), which did not depress the melting point of the sample of III prepared as described above.



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[2] Huntress, U. S. Patent 1,870,627 (1932) [*Chem. Abstr.*, **26**, 5579 (1932)].

[3] Anschutz and Heusler, *Ber.*, **19**, 2161 (1886).

[4] Hodgson and Birtwell, *J. Chem. Soc.*, 75 (1944).

[5] Wills, *Ber.*, **28**, 379 (1895).

[6] Hodgson, Ward, and Whitehurst, *J. Chem. Soc.*, 454 (1945)

[7] Tauber, *Ber.*, **23**, 795 (1890).

[8] Ullmann and Bielecki, *Ber.*, **34**, 2177 (1901).

[9] Cain and May, *J. Chem. Soc.*, **97**, 724 (1910).

Rauwolfia Alkaloids. XXIV.[1] Note on the Alkaloids of *Tonduzia Longifolia* (A.DC.) Mgf.

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During the course of our investigations on the reserpine content of various plants, we had occasion to examine the roots of *Tonduzia longifolia* (A.DC.) Mgf. obtained from Costa Rica. This small tree belonging to the Apocynacous family was of especial interest because of the close botanical

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[1] For previous paper, see Huebner, *Chemistry & Industry (London)*, 1186 (1955).

[2] Deceased October 24, 1955.