

[CONTRIBUTION FROM THE KENT CHEMICAL LABORATORY OF THE UNIVERSITY OF CHICAGO.]

THE THREE AMINO-TRIPHENYLAMINES.

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The three mononitro-triphenylamines are known. The *para* compound has been prepared by Richard Herz,² while the *o*- and the *m*-nitro-triphenyl amines were obtained by Piccard and Larsen.³ Up to the present only the *para* compound has been reduced to the corresponding amino derivative.⁴ Believing that the description of a nitro compound was not complete without the description of the corresponding amine and its acetyl derivative, the reduction of the nitro-triphenylamines newly prepared by Piccard and Larsen was undertaken. The reduction was carried out by Gambarjan's method with zinc dust in a solution of acetic acid and alcohol but the nitro compound was added very gradually to the reducing agent. In this way one avoids having simultaneously the nitro compound and an amino compound in the same solution. These two compounds are often able to react with the formation of disagreeable by-products.

Experimental Part.

***m*-Amino-triphenylamine Hydrochloride.**—A solution of 1.9 g. of *m*-nitro-triphenylamine in 20 cc. of glacial acetic acid was added during the course of 10 to 15 minutes to a mixture of 8 g. of zinc dust, 6 cc. of absolute alcohol and 6 cc. of glacial acetic acid. Heat was evolved at each addition and the red color of the nitro compound faded rapidly. The liquid was filtered from the excess of zinc at the pump and washed with hot glacial acetic acid. Care was taken to draw as little air as possible through the zinc. The filtrate was made alkaline with a dilute solution of sodium hydroxide, and the precipitated base was removed by filtration, dissolved in ether and dried. Saturation of the ether solution with dry hydrogen chloride precipitated the hydrochloride of the *m*-amino-triphenylamine; yield, 1.9 g. This was dissolved in 400 cc. of hot water to which 15 cc. of conc. hydrochloric acid had been added. The solution was then decolorized with charcoal and cooled in a freezing mixture. About 1 g. of the hydrochloride crystallized in glistening colorless plates. An additional quantity (0.5 g.) could be precipitated out of the mother liquor by hydrogen chloride.

Analyses. Subs., 0.1374: 4.70 cc. of 0.1 *N* NaOH (methyl orange). Subs. 0.2287: AgCl, 0.1081.

¹ The material presented here is used by Ray Q. Brewster in his dissertation presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Chicago (1919).

² Herz, *Ber.*, **23**, 2537 (1890).

³ Piccard and Larsen, *THIS JOURNAL*, **39**, 2006 (1917).

⁴ Herz, Ref. 2, was the first to prepare *p*-amino-triphenylamine although he published only a rough analysis of the hydrochloride and the acetyl derivative. Haeussermann, *Ber.*, **39**, 2763 (1906), isolated the base itself in a pure and stable form and published a good nitrogen determination. This work must have been overlooked by Gambarjan, *ibid.*, **41**, 3507 (1908), who published a new description and analysis.

Calc. for $C_{18}H_{17}N_2Cl$: Cl, 11.96. Found: 12.12, 11.69.

The hydrochloride is very slightly soluble in water.

***m*-Amino-triphenylamine.**—The *m*-amino-triphenylamine was precipitated from the aqueous solution of its hydrochloride by the addition of ammonium hydroxide. The base was dissolved in 95% ethyl alcohol, boiled with charcoal, filtered and allowed to crystallize. The substance was thus obtained in nearly colorless form, m. p. 116°. It is readily soluble in alcohol, ether and benzene.

Analyses. Subs., 0.1800, 0.1837: dry N_2 , 17.0 cc. (15° and 739 mm.), 17.6 cc. (19° and 743 mm.). Calc. for $C_{18}H_{16}N_2$: N, 10.77. Found: 10.88, 10.94.

***m*-Acetylamino-triphenylamine.**—One g. of the *m*-amino-triphenylamine was boiled for 15 minutes with 10 cc. of acetyl chloride. Water was added and the precipitated acetyl derivative recrystallized from alcohol, m. p. 167°.

Analyses. Subs., 0.1323: CO_2 , 0.3865; H_2O , 0.0698. Calc. for $C_{20}H_{18}ON_2$: C, 79.49; H, 5.96. Found: C, 79.68, H, 5.94.

***o*-Amino-triphenylamine.**—The *o*-nitro-triphenylamine was reduced in the manner just described for the *meta* compound. The crude yield was practically the calculated quantity. After recrystallization from alcohol the base was obtained in thin plates which had only a slight pink tint, and melted at 145°. It is readily soluble in alcohol and benzene but only fairly soluble in ether or ligroin.

Analysis. Subs., 0.1878: dry N_2 , 17.7 cc. (16° and 740 mm.). Calc. for $C_{18}H_{16}N_2$: N, 10.77. Found: 10.84.

***o*-Acetylamino-triphenylamine.**—This compound was prepared in the same manner as the corresponding *meta* derivative. It is quite readily soluble in ether, alcohol and benzene, but only fairly soluble in ligroin; m. p. 130°.

Analyses. Subs., 0.1340: CO_2 , 0.3905; H_2O , 0.0725. Calc. for $C_{20}H_{18}ON_2$: C, 79.49; H, 5.96. Found: C, 79.37; H, 6.10.

Reduction of Nitro-triphenylamines in Concentrated Sulfuric Acid Solution.

L. Gattermann⁵ has obtained *p*-aminophenol by the electrolytic reduction of nitrobenzene in conc. sulfuric acid solution. The same author has applied this method for the reduction of many other nitro compounds. Piccard and Larsen used it for the reduction of *m*-nitro-diphenylamine. It is surprising, that *m*-nitro-triphenylamine and *o*-nitro-triphenylamine cannot be reduced by this method to the corresponding *p*-oxy derivatives. We obtained in both cases only high molecular compounds with a lower nitrogen content than the one calculated for the diphenylamino-*p*-aminophenols.

Summary.

1. The *o*- and *m*-amino triphenylamines have been prepared and characterized. Since the *para* derivative is already known the series is now complete.
2. Attempts to reduce the nitro-triphenylamines to their corresponding amino phenols met with no success.

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⁵ Gattermann, *Ber.*, 26, 1846 (1893).