

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE STATE COLLEGE OF WASHINGTON]

## The Reduction of Aromatic Nitro Compounds with Activated Iron

BY STEWART E. HAZLET AND CLINTON A. DORNFELD

In this investigation, a number of aromatic nitro compounds were reduced by the use of activated iron. The method employed was essentially that of Jenkins, McCullough, and Booth,<sup>1</sup> which had been used successfully for the reduction of 2- and 4-nitrobiphenyl. The method was found to be desirable because the materials are cheap and undesired chlorinated products, which are obtained by certain other methods, are not formed by side reactions.

## Experimental Part

**Preparation of Activated Iron.**—Ten milliliters of concentrated hydrochloric acid was added slowly with stirring to 50 g. of granulated iron (40 mesh); care was taken to prevent the generation of excessive heat during the course of the ensuing reaction. The activated iron was stirred frequently to prevent the formation of lumps and was allowed to dry thoroughly.

**General Procedure.**—Five grams of the nitro compound was dissolved in 200 ml. of benzene in a three-necked flask which was provided with a reflux condenser and an efficient stirrer. The benzene solution was heated almost

TABLE I  
REDUCTION OF AROMATIC NITRO COMPOUNDS

Nitro compound	Product	Yield, %	Identified as	Identification product, m. p., °C.	
				Observed	Reported
Nitrobenzene	Aniline hydrochloride <sup>a</sup>	82 86	Hydrochloride	195	198 <sup>i</sup>
<i>o</i> -Nitrotoluene	<i>o</i> -Toluidine hydrochloride <sup>a</sup>	61 73	Acetyl deriv.	108–111	110 <sup>j</sup>
<i>p</i> -Nitrotoluene	<i>p</i> -Toluidine hydrochloride <sup>a</sup>	91 72	Acetyl deriv.	147–149	153 <sup>k</sup>
4-Nitrobiphenyl	4-Aminobiphenyl hydrochloride <sup>a</sup>	93 78	Acetyl deriv.	168–171	171 <sup>l</sup>
$\alpha$ -Nitronaphthalene	$\alpha$ -Naphthylamine hydrochloride <sup>a</sup>	96 95	Amine	50	50 <sup>m</sup>
<i>o</i> -Chloronitrobenzene	<i>o</i> -Chloroaniline hydrochloride <sup>a</sup>	92 71	Acetyl deriv.	83–86	87–88 <sup>n</sup>
<i>p</i> -Bromonitrobenzene	<i>p</i> -Bromoaniline hydrochloride <sup>a</sup>	97 95	Acetyl deriv.	165–168	167–168 <sup>n</sup>
2-Chloro-4-nitrotoluene	3-Chloro-4-methylaniline hydrochloride <sup>a</sup>	89 87	Acetyl deriv.	102–103	105 <sup>p</sup>
<i>o</i> -Nitroaniline	<i>o</i> -Phenylenediamine <sup>b</sup>	33 28	Amine	100–101.5	102–103 <sup>q</sup>
<i>m</i> -Nitroaniline	<i>m</i> -Phenylenediamine hydrochloride <sup>a</sup>	32 33	Acetyl deriv.	70	70 <sup>r</sup>
<i>p</i> -Nitroaniline	<i>p</i> -Phenylenediamine hydrochloride <sup>a</sup>	14 14	Acetyl deriv.	ca. 300	303 <sup>s</sup>
	<i>p</i> -Phenylenediamine <sup>c</sup>	41	Amine	135	140 <sup>t</sup>
6-Nitro-2-amino-naphthalene	2,6-Diaminonaphthalene <sup>b,d</sup>	28	Amine	215–218	220 <sup>u</sup>
	2,6-Diaminonaphthalene hydrochloride <sup>a,d</sup>	74			
<i>o</i> -Nitrophenol	<i>o</i> -Aminophenol <sup>e,f</sup>	28 26	Amine	173–175	172–173 <sup>v</sup>
<i>p</i> -Nitrophenol	<i>p</i> -Aminophenol <sup>b</sup>	Low	Amine	184	186 <sup>w</sup>
<i>p</i> -Nitrophenyl acetate	<i>p</i> -Aminophenyl acetate <sup>b,g</sup>	9 13	Amine	73–74	75 <sup>x</sup>
<i>p</i> -Nitrophenyl benzenesulfonate	<i>p</i> -Aminophenyl benzenesulfonate <sup>b</sup>	90	Amine	100–101	<sup>y</sup>
<i>n</i> -Butyl <i>p</i> -nitrobenzoate	<i>n</i> -Butyl <i>p</i> -aminobenzoate <sup>b,h</sup>	72	Amine	56–58	57–59 <sup>z</sup>

<sup>a</sup> The product was isolated according to method (a). <sup>b</sup> The product was isolated according to method (b). <sup>c</sup> The product was isolated according to method (c). <sup>d</sup> Prepared by Chas. F. Martin. <sup>e</sup> In the first preparation, the benzene was removed from the reaction vessel by distillation, and the residue was extracted with ether in a Soxhlet apparatus. The ether was evaporated in an atmosphere of carbon dioxide, the amine was taken up with dilute hydrochloric acid, and the solution was filtered and made alkaline; the free aminophenol was precipitated with carbon dioxide. <sup>f</sup> In the second preparation, the benzene was removed from the reaction vessel by distillation, and the residue was extracted with dilute alkali. This solution was just neutralized with dilute acid, and the aminophenol was extracted with ether. <sup>g</sup> Prepared by Karl Koyama. <sup>h</sup> Prepared by T. H. Schlosser. <sup>i</sup> Ullmann, *Ber.*, 31, 1699 (1898). <sup>j</sup> Alt, *Ann.*, 252, 319 (1889). <sup>k</sup> Feitler, *Z. physik. Chem.*, 4, 76 (1889). <sup>l</sup> Heusler, *Ann.*, 260, 234 (1890). <sup>m</sup> Zinin, *J. prakt. Chem.*, [1] 27, 143 ("Beilstein's Handbuch der organischen Chemie," 4th ed., Julius Springer, Berlin, 1929, Vol. 12, p. 1213). <sup>n</sup> Beilstein and Kurbatow, *Ann.*, 182, 100 (1876). <sup>o</sup> Hübner, *ibid.*, 209, 355 (1881). <sup>p</sup> Wallach, *ibid.*, 235, 254 (1886). <sup>q</sup> Hübner, *ibid.*, 209, 361 (1881). <sup>r</sup> The derivative softens at 70° and decomposes at about 100°; cf. Schiff and Ostrogovich, *ibid.*, 293, 382 (1896). <sup>s</sup> Troeger and Westercamp, *Arch. Pharm.*, 247, 663 ("Beilstein's Handbuch der organischen Chemie," 4th ed., Julius Springer, Berlin, 1930, Vol. 13, p. 97). <sup>t</sup> Hübner, *Ann.*, 208, 296 (1881). <sup>u</sup> Sweet and Hamilton, *THIS JOURNAL*, 56, 2408 (1934). <sup>v</sup> Barr, *Ber.*, 20, 1498 (1887). <sup>w</sup> Gattermann, *ibid.*, 26, 1847 (1893). <sup>x</sup> Galatis, *ibid.*, 59, 850 (1926). <sup>y</sup> Recrystallized from dilute methanol. *Anal.* Calcd. for C<sub>12</sub>H<sub>11</sub>O<sub>2</sub>NS: N, 5.64. Found: N, 5.62. <sup>z</sup> "Pharmacopœia of the United States of America," 12th revision, Mack Printing Co., Easton, Pa., 1942, p. 90.

The purpose of this study was to investigate further the applicability of this method to the reduction of nitro compounds of various representative types.

(1) Jenkins, McCullough and Booth, *Ind. Eng. Chem.*, 22, 31 (1930).

to boiling on a steam-bath before the iron was added. Then the activated iron was introduced, and vigorous stirring and refluxing were maintained throughout the course of the subsequent steps. After one-half hour of refluxing, 1 ml. of water was added to the reaction mixture; thereafter, small quantities of water were introduced from time to time at such a rate that, at the end of seven hours,

20 ml. of water had been used. Finally, refluxing was continued for an additional hour.

**Recovery of Products.**<sup>2</sup>—For the isolation of the reduction products, different procedures were found to be necessary: (a) In those preparations in which the product was soluble in benzene and was isolated as the hydrochloride, the reaction mixture was freed of iron by filtration, and dry hydrogen chloride was passed through the benzene solution; the insoluble hydrochloride precipitated and was collected by filtration. (b) In other instances where the amine which was formed in the course of the reduction was soluble in benzene, the reaction mixture was filtered while still hot, and the iron residue was extracted three times with hot benzene. The extracts were combined with the original filtrate. The crude free amine was obtained by removal of the benzene by distillation, and purification was effected by recrystallization from a suitable solvent. (c) With one amine which was insoluble in benzene, the solvent was removed from the reaction mixture by distillation from a steam-bath, the desired product was extracted from the residue with hot methanol, and the iron compounds which were dissolved by the hot solvent were removed by precipitation with hydrogen sulfide. Purification was accomplished by recrystallization.

(2) Any deviations from these general procedures are indicated as notes to Table I.

**Identifications of Products.**—Identifications of the reaction products were made by means of melting points of: (a) the free amines, (b) the acetyl derivatives, or (c) the hydrochlorides.

**Results.**—The results which were obtained when various nitro compounds—a number of them bifunctional in character—were reduced by the method outlined above are summarized in Table I.

### Summary

Seventeen nitro compounds were reduced by the use of activated iron, and products were obtained, for the most part, in good yields. In contrast to methods involving more severe conditions, there was no evidence of undesired introduction into or removal from the amines of halogen. Preliminary results suggested the possible use of this method for the reduction of esters of nitro substituted acids and similar compounds which would be subject to hydrolysis if reduced in acidic or basic aqueous media; this end was realized in several cases.

PULLMAN, WASHINGTON

RECEIVED JUNE 26, 1944

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

## A New Method for the Polarographic Determination of Nitrate

BY I. M. KOLTHOFF, W. E. HARRIS AND G. MATSUYAMA

The reduction of nitrate at the dropping mercury electrode in the presence of various cations has been studied by Tokuoka and Ruzicka.<sup>1,2</sup> They observed that in the presence of a large excess of lanthanum, the diffusion current of nitrate was proportional to the nitrate concentration. Scott and Bambach<sup>3</sup> applied these results to the determination of nitrate in blood and urine. It is found, in this Laboratory, that the proportionality holds only over a narrow range of nitrate concentrations.

One of the authors, in his work on the polarography of uranium, observed the reduction of nitrate at the dropping mercury electrode in the presence of small amounts of uranyl ion. The nitrate wave appears at a more positive potential and is more normal in appearance than that observed in the presence of lanthanum. Furthermore, this wave is subject to less interference by other anions.

A method for determining small amounts of nitrate, based on its reduction in the presence of uranyl ion, with some observations on the nitrate wave obtained in the presence of lanthanum are described in this paper.

### Experimental

Qualitative observations were made with a Heyrovsky Type VIII Polarograph, and quanti-

(1) M. Tokuoka, *Coll. Czechoslov. Chem. Commun.*, **4**, 444 (1932).

(2) M. Tokuoka and J. Ruzicka, *ibid.*, **6**, 339 (1934).

(3) E. W. Scott and K. Bambach, *Ind. Eng. Chem., Anal. Ed.*, **14**, 136 (1942).

tative measurements, with a manual apparatus<sup>4</sup> at 25°. All chemicals used were of "reagent quality," and conductivity water was used in the preparation of all solutions.

**Comparison of the Nitrate Waves in the Presence of Lanthanum and of Uranyl Ions.**—The nitrate wave in the presence of lanthanum is peculiar in the abruptness at which the current increases at the start of the wave, and in the irregularities and large oscillations in the current at the rising and limiting portions of the wave. These irregularities are largely eliminated by adding a trace of the sodium salt of methyl red to the solution. The half-wave potential varies between  $-1.3$  and  $-1.5$  volt against the saturated calomel electrode (hereafter abbreviated to S.C.E.) with variations in the concentrations of lanthanum and nitrate. When the wave is determined backward, *i. e.*, by gradually decreasing a large negative applied potential, the wave does not coincide with that found by gradually increasing the potential (see Fig. 1).

In moderate concentrations of hydrochloric acid (0.001 to 0.1 *N*), uranyl chloride gives two reduction waves at the dropping mercury electrode (see curve 2, Fig. 2). The first wave of uranium corresponds to a reduction to pentavalent uranium while the second corresponds to the two consecutive reductions of pentavalent uranium to tetravalent and trivalent uranium.

When the solution contains some nitrate in

(4) I. M. Kolthoff and J. J. Lingane, *Chem. Rev.*, **24**, 1 (1939).