

Citation:

Blanksma, J.J., The introduction of halogen atoms into the benzene core in the reduction of aromatic nitro-compounds., in:

KNAW, Proceedings, 8 II, 1905-1906, Amsterdam, 1906, pp. 680-683

	Quantity of by-product in %	Quantity of by-prod. in 100 parts of main prod.
<i>o</i> -C ₆ H ₄ Cl ₂	7.2	7.8
<i>m</i> -C ₆ H ₄ Cl ₂	4.0	4.1
<i>o</i> -C ₆ H ₄ Br ₂	18.3	22.4
<i>m</i> -C ₆ H ₄ Br ₂	4.6	4.8
C ₆ H ₅ Cl	29.8	42.0
C ₆ H ₅ Br	37.6	60.5

compounds. One would feel inclined to attribute this to "steric disturbances" introduced into Organic Chemistry by V. MEIJER, were it not that the specific volume of chlorine and of bromine in the dichloro- and dibromobenzenes differs but little.

Perhaps it is rather the atomic weight of chlorine and bromine which has some connection with the above. For further particulars concerning this research the "Recueil" should be consulted.

Amsterdam, Org. chem. Lab. of the University, January 1906.

Chemistry. — "*The introduction of halogen atoms into the benzene core in the reduction of aromatic nitro-compounds*". By Dr. J. J. BLANKSMA. (Communicated by Prof. A. F. HOLLEMAN).

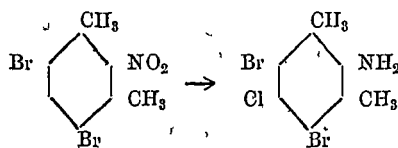
(Communicated in the meeting of January 27, 1906).

Some time ago I cited and communicated some experiments¹⁾ which showed that, in some cases, in the reduction of aromatic nitrocompounds, halogen atoms may be removed from the benzene core. In 1901 an article by PINNOW²⁾ appeared in which a fairly large number of cases are mentioned, where halogen atoms are introduced into the benzene core in the reduction of aromatic nitrocompounds. PINNOW endeavours to find the conditions under which this secondary reaction is as much as possible prevented in order to prevent formation of halogenised amidocompounds as by-products, alongside the amidocompounds.

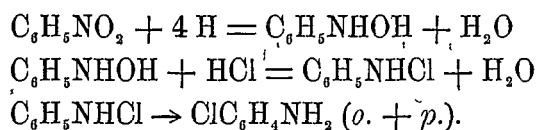
¹⁾ Proc. 30 March 1904, Recueil 24, 320.

²⁾ Journ. für Prakt. Chem. (2) 63, 352.

So when I obtained 5-chloro-4-6-dibromo-2-amido-*m*-xylene as by-product in the reduction of 4-6-dibromo-2-nitro-*m*-xylene, I tried to



introduce halogen atoms into the core, taking the simplest case, namely, the reduction of nitrobenzene with tin and hydrochloric acid. As is well-known, various intermediate products are formed in the reduction of nitrobenzene to aniline. The formation of chloroaniline from nitrobenzene may be explained in the following manner:¹⁾



The fact that, in the reduction of nitrobenzene, phenylhydroxylamine occurs as an intermediate compound, has been demonstrated by BAMBERGER, who has also proved that, on boiling phenylhydroxylamine with hydrochloric acid, *o*- and *p*-chloroaniline are formed²⁾. It has also been proved by LÖB that *o*- and *p*-chloroanilines are formed in the electrolytic reduction of nitrobenzene in alcoholic hydrochloric acid solution³⁾. The object of the experiments to be described was to try and conduct the reduction of nitrobenzene with tin and hydrochloric acid in such a manner that instead of aniline, as much as possible chloroaniline was formed.

The experiment had, therefore, to be carried out in such a way, that the phenylhydroxylamine formed was not at once further reduced to aniline, but to give this substance an opportunity to be converted into chloroaniline, under the influence of hydrochloric acid. The conditions were also to be such that the phenylchloroamine $\text{C}_6\text{H}_5\text{NHCl}$, which is formed intermediary, could be readily converted into chloroaniline.

The intramolecular conversion of phenylchloroamine into *o*- and *p*-chloroaniline is, however, but little known, as the first substance is very unstable but the conditions under which acetylchloroanilide is converted into *p*-chloroacetanilide have been closely investigated. It has been shown that this reaction is very much accelerated by increase of the temperature and also by addition of hydrochloric acid⁴⁾.

¹⁾ LÖB, Die Electrochemie der Organischen Verbindungen p. 166, 3e Auflage (1905).

²⁾ Ber. 28, 451. BAMBERGER and LAGUTT, Ber. 31, 1503.

³⁾ Ber. 29, 1896.

⁴⁾ BENDER, Ber. 19, 2273 BLANKSMA, Recueil 21, 366, 22, 290.

If, on account of the analogy between phenyl-chloroamine and acetylchlorophenylamine, we assume that in the case of the first substance the velocity of the conversion into *o*- and *p*-chloroaniline is also strongly accelerated by elevation of temperature and addition of hydrochloric acid, the conditions for obtaining chloroaniline instead of aniline, in the reduction of nitrobenzene with tin and hydrochloric acid, are as follows:

1. Slow reduction, or addition of tin in small quantities at the time, in order not to at once reduce the phenylhydroxylamine to aniline.
2. Excess of hydrochloric acid so as to rapidly convert the phenyl-chloroamine formed into chloroaniline.
3. The reaction should take place at the boiling temperature, as elevation of temperature also promotes this conversion.

The experiment was now conducted as follows:

10 cc. of nitrobenzene were dissolved in 100 cc. of alcohol and 200 cc. of 25 % hydrochloric acid were added. This solution was boiled over the naked flame, whilst 15 grams of tin were added through the reflux condenser in small portions. Each time, after adding a small amount of tin, the boiling was continued until everything had dissolved before adding a fresh portion. The experiment lasted six hours. The unaltered nitrobenzene was now removed by steam, the residue was rendered alkaline and the aniline and chloroaniline recovered by distillation in steam.

In this way, 6.5 gram of oil were obtained. The greater portion of this oil was distilled between 182° and 225°, the residue solidified in the distilling flask, and proved to be *p*-chloroaniline (m. p. 70°). The oil consisted of aniline and *o*- and *p*-chloroaniline.

From a chlorine determination according to CARIUS, it appeared that the mixture consisted of 55% of chloroaniline and 45% of aniline.

If the reduction experiment was made with SnCl_2 and HCl (*o*+*p*) chloroaniline (53%) were formed together with aniline. In this case, the stannous chloride was also added in small portions, so as to give the intermediary formed phenylhydroxylamine an opportunity of being converted into *o*- and *p*-chloroaniline. Nitroso-benzene gives the same result ¹⁾.

In the same manner, the reduction of nitrobenzene with tin and hydrobromic gave a mixture of aniline and (*o*- and *p*)-bromoaniline.

At present it is still difficult to predict which aromatic nitro-

¹⁾ Cf. GOLDSCHMIDT, Zeitschrift für Phys. Chem. 48, 435.

compounds will yield a large quantity of halogenised by-products on reduction with tin and hydrochloric acid. It would be necessary to know something more about the reduction velocity of the nitrocompounds ¹⁾ (and of the intermediary formed hydroxylamine derivatives), and about the intramolecular conversion velocities of the halogenphenylamines.

It is known, for instance, that *o*-nitrotoluene gives a large amount of chlorinated by-product on reduction with tin and hydrochloric acid ²⁾. The *o*-tolylhydroxylamine formed as intermediate product is, therefore converted here into 5-chlorotoluidine, and the reduction experiments of GOLDSCHMIDT ³⁾ on *o*-nitrotoluene are in agreement with this. GOLDSCHMIDT has shown that, with increase of the temperature the reduction velocity also increases, whilst an elevation of temperature also increases the conversion velocity of the halogenphenylamines. It now appears that this last reaction is the most strongly accelerated, for the amount of halogenised by-products increases with elevation of the temperature ⁴⁾.

Resumé. It has been shown that the reduction of nitrobenzene with tin (or Sn Cl₂) and hydrochloric acid may be carried out in such a manner that *p*-chloroaniline occurs as the main product. The cause of this must be explained by the fact that, in the reduction of nitrobenzene, phenylhydroxylamine occurs as an intermediate product. As on reduction of all aromatic nitrocompounds, hydroxylamine derivatives are formed as intermediate compounds, we shall generally notice on reduction of such nitrocompounds with tin and hydrochloric acid, besides amidocompounds, also halogenised amidocompounds (with halogen atoms *o*- or *p*- in regard to the NH₂ group), whilst the quantity of these two last substances will be dependent on the conditions under which the reduction is carried out. In some cases no halogen atoms are introduced, but they are even eliminated from the benzene core ⁵⁾.

I hope to record more fully further experiments in the *Recueil* later on.

Amsterdam, January 1906.

¹⁾ See the note on the preceeding page.

²⁾ BEILSTEIN and KÜHLBERG, *Ann.* **156**, 81. HOLLEMAN and JUNGUIS, *Chemisch Weekblad* II. 553.

³⁾ *l. c.*

⁴⁾ PINNOW, *l. c.*

⁵⁾ *Recueil* **24**, 320.