

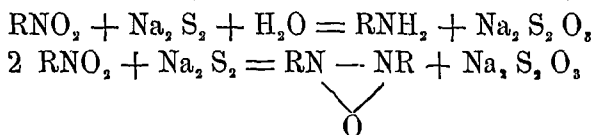
**Chemistry.** — “Reduction of aromatic nitro-compounds by sodium disulphide.” By Dr. J. J. BLANKSMA, (Communicated by Prof. A. F. HOLLEMAN).

(Communicated in the meeting of May 30, 1908).

I have pointed out previously <sup>1)</sup> that sodium disulphide may act on aromatic nitro-compounds in two different ways, namely by substitution or by reduction.

1. Substitution occurs when halogen atoms or nitro-groups are present which under the influence of *ortho*- or *para*-placed nitro-groups have become moveable. These on being treated with sodium disulphide are readily replaced by S<sub>2</sub>, and the disulphides thus formed may be converted by oxidation into sulphonic acids. A fairly large number of these cases have been communicated previously <sup>1)</sup>.

2. Reduction takes place when the nitro-compounds do not contain any moveable halogen atoms or nitro-groups; a nitro-group is then reduced to an amido-group, whilst generally a small quantity of azo-oxycompound is also produced according to the equations:



A preliminary investigation had shown me previously that alcoholic solutions of nitrobenzene and *o*-nitrotoluene are readily converted by Na<sub>2</sub>S<sub>2</sub> into aniline and *o*-toluidine, the Na<sub>2</sub>S<sub>2</sub> being oxidised to Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub>. *m*-Dinitrobenzene and *p*-dinitrobenzene when treated with Na<sub>2</sub>S<sub>2</sub> yielded, respectively, *m*-dinitroazo-oxybenzene and *p*-dinitroazo-benzene. It was then <sup>2)</sup> our intention to further investigate the reducing action of Na<sub>2</sub>S<sub>2</sub>.

Meanwhile, however, a patent has been granted to KUNZ <sup>3)</sup> for the reduction of aromatic nitro-derivatives to amido-derivatives by means of sodium disulphide in aqueous solution and afterwards sodium disulphide has been used by BRAND <sup>4)</sup> as a partial reducing agent.

I have now studied the reduction of aromatic nitro-compounds by Na<sub>2</sub>S<sub>2</sub> in alcoholic solution in a number of cases. The reduction is carried out as follows:

Six grams of nitrobenzene are added to a boiling solution of 12 grams of crystallised sodium sulphide and 1.6 gram of sulphur in

<sup>1)</sup> Dissertation. Amsterdam 1900; Rec. 21, 121, 141.

<sup>2)</sup> These Proc. 1900, (Oct.)

<sup>3)</sup> Chem. Centr. 1903 II 813.

<sup>4)</sup> Journ. f. pract Chem. 1906. (2) 74, 499.

300 cc. of 96 % alcohol. After boiling for 6 hours, the alcohol is recovered by distillation and the aniline which still contains a little nitrobenzene is distilled in a current of steam. It is then converted into the hydrochloride to separate it from the admixed nitrobenzene; about 5 grams of aniline hydrochloride are obtained. In the same manner were treated *o*-*m*- and *p*-nitroanisol, *m*-chloro- and bromo-nitrobenzene and dichloro- and dibromonitrobenzene 1. 3. 5. from which were readily obtained the corresponding amido-derivatives to the extent of about 70 % of the theoretical quantity.

In the case of *ortho*- and *para*-chloronitrobenzene where the halogen atom is replaced by S, a simultaneous reduction takes place to a slight extent with formation of *o*- and *p*-chloroaniline.

*Ortho*- and *m*-nitrotoluene readily yield *ortho*- and *meta*-toluidine; with *para*-nitrotoluene a secondary reaction occurs, *p*-amidobenzaldehyde being formed as well as *p*-toluidine<sup>1</sup>).

Besides the above mentioned mononitro-compounds a few dinitro-compounds were subjected to a partial reduction. From sym-dinitrotoluene we readily obtain by means of alcoholic Na<sub>2</sub>S<sub>2</sub> 3-nitro-5-amidotoluene; sym-dinitroanisol yields 3-nitro-5-amidoanisol; from 2-4-dinitroanisol (or phenetol) is obtained 2-amido-4-nitroanisol (or phenetol) whilst sym. trinitrobenzene yields 3-5-dinitraniline. A small quantity of the azo-oxycompounds is generally formed in addition to the amido-derivatives. I will also point out that in the reduction with Na<sub>2</sub>S<sub>2</sub> the formation of chlorinated byproducts, which are often generated in the reduction of aromatic nitro-compound with Sn and HCl, is avoided. The fact that sodium disulphide may be weighed also gives it an advantage over ammonium sulphide as a reducing agent.

From the above facts it is obvious that an alcoholic solution of Na<sub>2</sub>S<sub>2</sub> may be used as a convenient reducing agent.

**Physiology.** — “*About the determination of hardness in muscles.*”

By A. K. M. NOYONS, Assistant in the Physiological Laboratory at Utrecht. (Communicated by Prof. H. ZWAARDEMAKER.)

(Communicated in the meeting of May 30, 1908).

At an inquiry into the causes and qualities of the autotonus it struck me how a muscle seemed to become harder, as its autotonus increased. Hitherto the hardness of a muscle was always estimatively determined by digital touching. The above mentioned fact caused

<sup>1</sup>) Chem. Centr. 1900. I. 1084. I hope to communicate more analogous cases of intramolecular oxidation later on.