

*Citation:*

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At Mesch, at a depth of thirty three ells and at Bannet, near Mheer, at a depth of one hundred and nine ells, sand-stone and coal-slate are found.

This considerable difference in level would be explained by fault VIII.

From the information we have gained from STARING, two conclusions may be drawn: In the first place, it will be advisable not to limit further researches in Limburg, to the tongue of Kohlscheid and its immediate surroundings, but to extend them to the other two tongues, especially to the one of Sippenaken. It is true there does not seem to be much chance of finding coal at the latitude on which Bommerig is situated but the very absence of productive carbon increases the chance of finding ore, whereas the seamlike construction and also the comparison with other spots add to the chance of there being more north, perhaps on a latitude with Valkenburg, a fresh synclinal fold, containing productive carbon.

The tongue of Aubel, on the other hand is probably of less importance to us, since, on that latitude we are on Belgian territory.

The second conclusion relates to a border-line, mentioned in the Report of the Royal-mining-Commission, instituted on April 17<sup>th</sup> 1899.

In this Report mention is made of "a probable border-line of the productive coal-beds", a line which from Bocholtz bends to Valkenburg and from there runs north. As will be seen, that line touches the tongue of Sippenaken, and it is very well possible and according to my opinion even probable, that west of that line coal-beds will be found.

*The Hague*, March 29<sup>th</sup> 1902.

**Chemistry.** — „*Bromination and nitration in the aromatic series*”.

By Dr. J. J. BLANKSMA. (Communicated by Prof. LOBRY DE BRUYN).

(Communicated in the meeting of March 29, 1902).

In a previous article<sup>1)</sup> a few particulars were communicated on the bromination and nitration of some derivatives of phenol and aniline. Attention was then called to the fact that the nitration of aniline derivatives containing the group NH<sub>2</sub> presents difficulties

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<sup>1)</sup> Rep. Meeting 25 Jan. 1902.

but that this readily takes place with derivatives of methylaniline; for instance *m.*-nitro-methylaniline was readily converted into VAN ROMBURGH'S tetranitro-phenylmethylnitramine. Several observations have already been made as to the bromination and nitration of methylamine derivatives and it seemed of importance to further extend the same.

VAUBEL <sup>1)</sup> has shown that methylaniline readily yields a tribromo-derivative, while VAN ROMBURGH <sup>2)</sup> has obtained trinitro-phenylmethylnitramine by nitration of methylaniline. VAN ROMBURGH <sup>3)</sup> has also proved that if the *o.*- and *p.*-positions are occupied by a CH<sub>3</sub>-group only two NO<sub>2</sub>-groups are introduced. The same has been demonstrated by GRIMAUX en LEFÈVRE <sup>4)</sup> for the group OCH<sub>3</sub>.

The object of my research was to ascertain the influence exercised on the further substitution by the occupation of ortho- and para-positions and also of the meta-positions of methyl and ethyl derivatives. The first substance examined was *p.*-nitro-methylaniline obtained by heating *p.*-chloronitrobenzene with methylamine in alcoholic solution for 4 hours at 160°. By treatment with nitric acid of sp. gr. 1.52 it was directly converted into trinitro-phenylmethylnitramine. A treatment with 1 mol. of bromine in glacial acetic acid gave 2-bromo-4-nitro-methylaniline, m. p. 118°; with 2 mols. of bromine 2,6-dibromo-4-nitro-methylamine, m. p. 113° is obtained.

By the action of nitric acid the first compound gave 2-bromo-4,6-dinitro-phenylmethylnitramine, m. p. 125°, the last one gave 2,6-dibromo-4-nitro-phenylmethylnitramine, m. p. 84°.

*o.*-Nitro-methylaniline, obtained like the para-compound from *o.*-chloronitrobenzene is converted by the action of nitric acid into trinitro-phenylmethylnitramine. Bromine converts this substance first into 4-bromo-2-nitro-methylaniline, m. p. 101° and then into 4,6-dibromo-2-nitro-methylaniline, m. p. 100°. Treatment with HNO<sub>3</sub> gives 4-bromo-2,6-nitro-phenylmethylnitramine, m. p. 109° and 2,4-dibromo-6-nitro-phenylmethylnitramine, m. p. 90°.

On treating oxyethyl-dinitrobenzotrile (1.2.4.6) in alcoholic solution with methylamine or ethylamine the OC<sub>2</sub>H<sub>5</sub>-group is replaced by NHCH<sub>3</sub> or NHC<sub>2</sub>H<sub>5</sub>. By the action of nitric acid of sp. gr. 1.52 on these substances, the hydrogen combined with the nitrogen is replaced by NO<sub>2</sub> and consequently the corresponding nitramines are formed. In the same way it was shown that when a Cl-atom

<sup>1)</sup> Journ. pract. Chem. (2) 48. 315.

<sup>2)</sup> Rec. 2. 108. <sup>3)</sup> Rec. 3. 392. <sup>4)</sup> C. R. 112. 727.

occupies the para-position, the as yet free ortho-positions get occupied by  $\text{NO}_2$  and the hydrogen in combination with the N is replaced by  $\text{NO}_2$ . If, however, a  $\text{COOH}$ -group occupies an ortho- or para-position in regard to  $\text{NHCH}_3$  this will then be replaced by Br or  $\text{NO}_2$ . If a chlorine or bromine atom occupies the meta-position in regard to the  $\text{NHCH}_3$  (obtained by treating chloro- or bromodinitrobenzene with methylamine) these groups will have no influence on the further introduction of bromine atoms or nitrogroups.

We therefore, see:

1<sup>o</sup>. That on bromination of methyl-(ethyl) aniline derivatives, the free ortho- and para-positions are always occupied by bromine, while the hydrogen atom linked at the nitrogen is not attacked. The same happens during the nitration but there the hydrogen-atom of the  $\text{NHCH}_3$ -group gets replaced by  $\text{NO}_2$ .

2<sup>o</sup>. that a carboxyl group in an *o*- or *p*-position is replaced by Br or  $\text{NO}_2$  with evolution of  $\text{CO}_2$ .

3<sup>o</sup>. that the occupation of the meta-position by other groups ( $\text{NO}_2$ , Cl, Br,  $\text{CH}_3$ ) has no influence on the introduction of bromine atoms and nitrogroups in ortho- and para-positions.

In the previous communication it has already been observed that during the bromination and nitration of phenol and aniline derivatives, the  $\text{NO}_2$ -groups and halogen atoms probably first enter into the side chain to shift later on towards the nucleus.<sup>1)</sup> One might call this substitution of the hydrogen atoms of the nucleus an indirect substitution in contrast to the direct substitution which takes place with benzene and substituted benzenes containing the groups  $\text{COOH}$ , Cl, Br,  $\text{NO}_2$ ,  $\text{SO}_3\text{H}$ , etc.

We then see that:

1<sup>o</sup>. indirect substitution as is well known, takes place very readily. Phenol and aniline, for instance, are readily nitrated, or brominated by dilute nitric acid or bromine water; the direct substitution is much more difficult (nitration of benzene, nitrobenzene, chlorobenzene etc.)

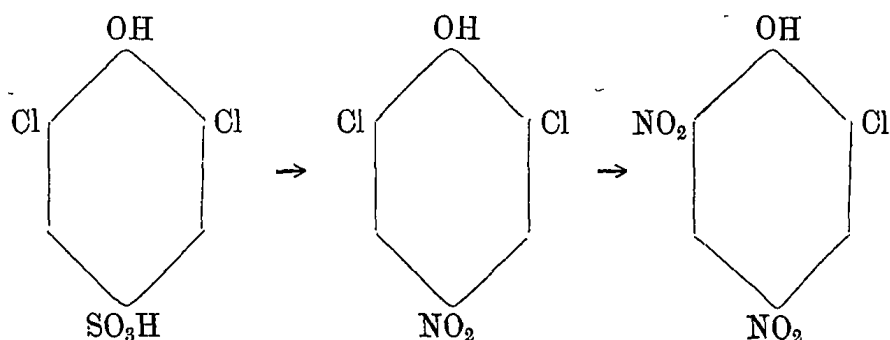
2<sup>o</sup>. during the indirect substitution, the substituents always occupy the ortho- and para-positions in regard to the side chain; during the direct substitution meta-substitution products are also formed, sometimes by preference.

3<sup>o</sup>. during the indirect substitution it is possible to replace some

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<sup>1)</sup> Bunge, Ann. Supp. 7. 117. (1869). ARMSTRONG, Soc, 77. 1047. CHATTAWAY and ORTON, Soc. 79. 274.

groups by others. COOH,<sup>1)</sup> CH<sub>3</sub><sup>2)</sup> CH<sub>2</sub>OH<sup>3)</sup> and SO<sub>3</sub>H<sup>4)</sup> when in ortho- or para-position in regard to OH may be replaced by bromine with formation of tribromophenol. A chlorine atom may, by indirect substitution enter in the place of bromine (HANTSCH,<sup>5)</sup> CHATTAWAY and ORTON<sup>6)</sup>) while chlorine may again in turn be replaced by NO<sub>2</sub> (ARMSTRONG<sup>7)</sup>)



A group COOH may further be replaced by C<sub>6</sub>H<sub>5</sub>NN and also by NO.

We, therefore, see that during the indirect substitution the following groups may successively replace each other: COOH, SO<sub>3</sub>H, Br, Cl, NO<sub>2</sub>; the nitro-derivatives are, therefore, the most stable so that the phenol derivatives finally produce picric acid and the methyl-aniline derivatives trinitro-phenylmethylnitramine. In the direct nitration a similar substitution is not noticed; benzoic acid and benzenesulphonic acid are nitrated and halogenated without elimination of the COOH or SO<sub>3</sub>H-group.

In the same manner, tribromobenzene (1.3.5) yields on nitration successively mono- di- and trinitro-tribromobenzene without any substitution of bromine atoms taking place; a behaviour totally different from that of tribromophenol.

The group CH<sub>3</sub> behaves in many cases analogous to OH, NH<sub>2</sub> and NHX. It is not impossible that we meet also here with indirect substitution, witness the researches of AUWERS, ZINCKE and

1) BENEDIKT, Ann. 199. 128.

2) BAUMANN and BRIEGER, Ber. 12. 804.

3) AUWERS and BÜTTNER, Ann. 302. 133.

4) *p*-Potassium phenolsulphonate readily assimilates three mols. of bromine, the liquid remains clear and slowly deposits tribromophenol (more rapidly on heating).

5) Ber. 30. 2334, 33. 505.

6) Journ. Chem. Soc. 1901. 823.

7) Zeitschrift 1871, 516.

BAMBERGER where the investigated substances generally contained one or more CH<sub>3</sub> groups next to OH.

It should also be pointed out that in tribromo-mesitylene the Br atoms may be replaced by NO<sub>2</sub>, while dimethylmesitylene yields dinitro-mesitylenenitramine with NO<sub>2</sub> groups in the meta-positions. (KLOBBIE<sup>1)</sup>).

The particulars of this research will be published in the „Recueil”.

**Physiology.** — “*On the effect as a time-function.*” By Dr. J. K. A. WERTHEIM SALOMONSON. (Communicated by Prof. C. WINKLER).

(Communicated in the meeting of March 29, 1902).

In the course of three former communications we have considered the relation between the magnitude of effect and stimuli of different intensity. In its strictest sense the law there formulated by us, is valid only in cases of momentaneous stimuli, where the effect appears after the stimulus has ceased to act.

The following essay will consider the manner in which an effect proceeds — the way it changes perpetually from one moment to another, whether under the influence of momentaneous stimuli or of lasting constant stimuli.

Considering the effect as being due to the transformation of chemical substance, we may admit with GULDBERG and WAAGE that the rapidity of this transformation will be proportional to the available quantity of transformable substance. If the amount of the latter may be represented by  $W$ , then:

$$-\frac{dW}{dt} = \alpha W \quad . . . . . (1)$$

Now let us examine what will be the amount of this quantity  $W$  in general. Firstly we may admit that at the moment  $t$  there is in store a certain quantity of transformable substance  $P$ .

But we are dealing with living protoplasma.

After activity of the protoplasma we know that products of fatigue will have been formed. These will gradually disappear and be replaced by fresh substance. In general it is a most plausible supposition that the quantity of new transformable substance sup-

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<sup>1)</sup> Rec. 6. 31.