

Citation:

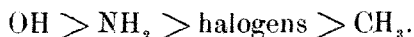
A.F. Holleman, The nitration of the mixed dihalogen benzenes, in:
KNAW, Proceedings, 17 II, 1914, pp. 846-849

Chemistry. - "The nitration of the mixed dihalogen benzenes".

By Prof. A. F. HOLLEMAN.

(Communicated in the meeting of Oct. 31, 1914).

When in benzene are present two substituents and a third is introduced, the substitution velocity caused by the two groups already present is unequal. From the *data* given in the literature it may be deduced that those velocities for the substituents pointing to the p-o-positions decrease in the subjoined order:



The question now arose how to express those velocities also in figures.

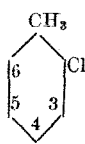
Dr. WIBAUT has done this for chlorine and methyl by determining in what proportion the isomerides are formed in the nitration of o-chlorotoluene. In this compound the positions 4 and 6 are occupied, under the influence of methyl, by a nitro-group, the positions 3 and

5 under the influence of chlorine. If now we determine the proportion in which the mononitro-chlorotoluenes 4 + 6 are present in regard to the isomerides 3 + 5 in the nitration product, this is then also the proportion of the substitution velocities caused by methyl and chlorine, because they can exert their action in this o-chlorotoluene independently of each other; for the positions which are substituted under the influence of methyl are different from those that are substituted under the influence of chlorine. For this proportion was found $\text{CH}_3 : \text{Cl} = 1 : 1.475$.

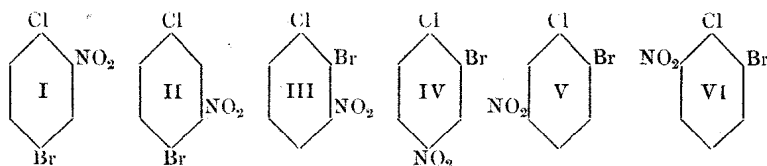
Dr. VAN DEN AREND had previously determined the proportion in which the nitro-p-chlorotoluenes are formed in the nitration of p-chlorotoluene. If now, with the above mentioned ratio, we calculate the relative quantities, those calculated figures appear to agree approximately with the observed ones.

These researches, carried out in my laboratory, have now been continued, partly by Dr. HEINEKEN, so as to determine also the ratios of the halogens. The method followed previously for the quantitative determination of the isomerides, namely by means of the solidification curves, could, however, not be applied here as the two nitro-p-chlorobromobenzenes give a continuous series of mixed crystals and because it was to be expected, on account of the fact that the properties of the nitrodihalogen benzenes present a strong mutual resemblance, that this would occur in other cases also.

Hence, for the quantitative determination of the isomerides present in the nitration mixtures, we made use of the property that a halogen in nitrohalogen benzenes is taken from the nucleus by Na-methoxide



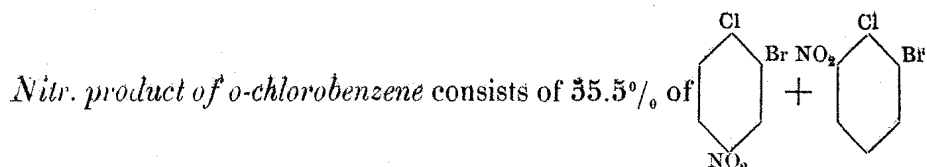
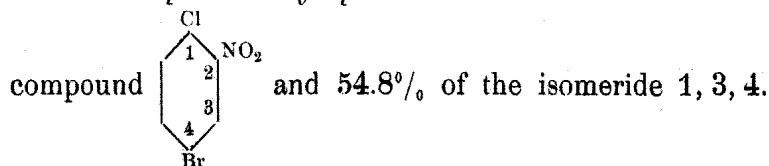
only then when it is placed in the ortho- or the paraposition in regard to a nitro-group. Of the isomerides



I, IV and VI only chlorine, of II, III and V only bromine will be replaced by OCH_3 . Hence, if we determine the proportion in which chlorine and bromine are split off from the nitration product of *p*-chlorobromobenzene and from that of *o*-chlorobromobenzene, we get at once the proportion wherein in the first nitration product I and II are present in the second one IV + VI on one side, III + V on the other side. This method has also the considerable advantage that all the isomerides for the construction of the fusion lines now need not be prepared individually and that in the nitration products the various isomerides need not be separated; this latter attempt in particular would, presumably, have failed owing to insuperable obstacles.

The results obtained are as follows:

Nitration product of *p*-chlorobromobenzene contains 45.2% of the



The substitution velocity caused by chlorine and bromine when present together in the benzene nucleus is therefore as 1:0.80. When calculating this proportion from the composition of the nitration product of *p*-chlorobromobenzene it must be remembered that in the nitration of chlorobenzene there is formed 30.1% of the *o*-compound, but in that of the bromobenzene 38.3% of the same. If we call x the ratio of the velocities caused by chlorine and bromine we have

$$30.1 : 38.3x = 45.2 : 54.8,$$

from which $x = 0.96$. Hence, the result is here $\text{Cl} : \text{Br} = 1 : 0.96$. The mean result of these two experimental series is therefore: $\text{Cl} : \text{Br} = 1 : 0.88$.

The nitration of *p*-chloriodobenzene caused the separation of large quantities of iodine with formation of *p*-chloronitrobenzene. Hence, for my purpose it was unsuitable.

In the nitration of *o*-chloriodobenzene, there was also some separation of iodine, but the formation of *o*-chloronitrobenzene did not amount to more than about 3%. When determining the proportion in which Cl and I were separated from the nitration product by NaOCH_3 , a correction for this must therefore, be applied. For the velocity ratio $\text{Cl} : \text{I}$ was thus found the mean value of $1 : 1.84$.

It now became interesting to also investigate the nitration product of *o*-bromiodo benzene quantitatively as to its components. For, as $\text{Cl} : \text{Br}$ was found $= 1 : 0.80$ and $\text{Cl} : \text{I} = 1 : 1.84$, $\text{Br} : \text{I}$ should be $= 1 : 2.30$, if indeed the two halogens present, act quite independently of each other.

Also in this nitration a little separation of iodine took place; the content of *o*-bromonitrobenzene in the nitration product was in this case 4.4%. Applying a correction for this the mean ratio $\text{Br} : \text{I} = 1 : 1.75$ was found, which rather differs from the calculated figure. If, however, we calculate the percentages of the isomerides with the ratios 1.75 and 2.30 the theoretical value gives 69.7% of the isomerides $\text{Br}, \text{I}, \text{NO}_2 = 1, 2, 3 + 1, 2, 5$, and the experimental value 63.6% which may be considered as a sufficient approximation if we bear in mind the difficulties of these quantitative determinations.

The conclusions from the above are obvious. Since it has appeared that two substituents simultaneously present in ortho- and in parapositions do not sensibly interfere with their respective actions in regard to a third entering group, we shall be able to *calculate* from the figures now found with sufficient probability in what proportion are formed the isomerides of other compounds, for instance in the nitration of *o*- and of *p*-bromotoluene.

The above mentioned order of the substituents towards the decreasing substitution velocity caused by the same now becomes:



Hence, the ratio $\text{OH} : \text{NH}_2$ and $\text{NH}_2 : \text{I}$ still remains to be determined. As, however, in the nitration of the iodoanilines great difficulties may be expected, A. F. H. LOBRY DE BRUYN has taken in hand a quantitative research of the nitration of *o*- and *p*-chloroaniline in the above direction. As a preliminary result of his experi-

ments it may be mentioned that the ratio $\text{Cl} : \text{NH}_2$ is very large. The above velocity series must, therefore, be resolved into two parts: OH and NH_2 which cause a great substitution velocity and which are presumably of the same order of magnitude; on the other side the halogens and CH_3 with a lesser velocity, also of the same order of magnitude. A more detailed description of the above experiments will be published in the *Recueil*.

Oct. '14.

Org. Chem. Lab. University Amsterdam.

Physics. — “*The reduction of aromatic ketones. III. Contribution to the knowledge of the photochemical phenomena.*” By Prof. J. BÖESEKEN and Mr. W. D. COHEN. (Communicated by Prof. A. F. HOLLEMAN).

(Communicated in the meeting of October 31, 1914).

I. *The reduction of the aromatic ketones in a perfectly neutral medium.*

In our former communications ¹⁾ we have shown that the reduction of the aromatic ketones does not proceed any further than to pinacone, which is presumably formed from the primary generated half pinacone molecule by rapid polymerisation. The fact that in an alkaline medium hydrol is always obtained, must be attributed to the rapid transformation of the pinacone, under the influence of the hydroxylions, into an equimolecular mixture of hydrol and ketone, the latter of which can be again reduced to pinacone.

This explanation was confirmed by the study of the reduction of ketones by means of aluminium amalgam.

Here is formed a mixture of pinacone and hydrol; the proportion in which these two substances are formed differs from ketone to ketone and now it appeared that the quantities of hydrol ran strictly parallel to the velocities with which the diverse pinacones are converted into a mixture of ketone and hydrol under the influence of sodium ethoxide.

Hence, aluminium amalgam in 80% alcohol may by no means be considered as a neutral reducing agent.

The only *modus operandi* that gives the necessary guarantee that complete neutrality would prevail during and after the reduction is the action of the aromatic ketone on an alcohol under the cooperation of sunlight. The original intention of this part of the research,

¹⁾ Proc. XVI p. 91 and 962 (1913).