

XCII.—*Studies in Orientation. Nitration Products of 3-Chloro-5-bromotoluene.*

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3-CHLORO-5-BROMOTOLUENE contains three dissimilar substituents, symmetrically arranged in the nucleus. It forms with great ease a mono-, di-, and tri-nitro-derivative, all of which are apparently homogeneous. The positions taken up by the entrant nitro-groups would therefore determine the relative orienting effect of the electropositive methyl group and that of the two halogens. The main object of the present inquiry has been to elucidate this point. Incidentally, we have examined the products obtained by introducing the two halogens into toluene in a different order; for, according to the Kekulé formula for benzene with three alternate double linkings, the two substances should be dissimilar,



but no difference could be detected. This agrees with the experimental evidence of Wohl (*Ber.*, 1910, **43**, 3474).

3-Chloro-5-bromotoluene on nitration gives a mononitro-derivative melting at 70° (Cohen and Smithells, *T.*, 1914, **105**, 1907), which, on reduction, yields a base. The position of the amino-group, and consequently of the original nitro-group, was determined by comparing the melting points of the base and its mono- and di-acetyl derivatives with those of the three isomeric 3-chloro-5-bromotoluidines.

The results are recorded in the following table:

Melting points of the Isomeric 3-Chloro-5-bromotoluidines.

Substance.	Amino-compound.	Monoacetyl derivative.	Diacetyl derivative.
3-Chloro-5-bromo-4-toluidine	62.5°	199°	82°
3-Chloro-5-bromo-2-toluidine.	60	171	90.5
3-Chloro-5-bromo-6-toluidine.	43	186.5	86
Reduction product of 3-chloro-5-bromo-nitro-toluene	42	187	85

The above results leave no doubt that the first entrant nitro-group replaces the hydrogen between the methyl group and the bromine atom. This agrees with the observation of Cohen and Dakin (*T.*, 1902, **81**, 1344) on the nitration of 3:5-dichlorotoluene

in so far as the first nitro-group was shown to enter the ortho-position with respect to the methyl group.

A careful redetermination of the melting point of the dinitro-derivative has shown that the substance prepared by Cohen and Smithells was probably a mixture of mono- and dinitro-compounds. The correct constant is 144° , which, with the exception of the 2-chloro-6-bromo-derivative of the same melting point, is the highest of the isomeric chlorobromotoluenes. As we have failed to discover any satisfactory way of directly establishing the position of the second entrant nitro-group, we have to rely on the evidence of the high melting point as indicating, as it almost invariably does, symmetrical structure. If this is so, the second nitro-group will occupy the second ortho-position with respect to the methyl group. This view is in agreement with observations made by Cohen and Dakin (*loc. cit.*) on the nitration of the dichlorotoluenes, namely, that where the nitro-group cannot avoid entering the nucleus between two other groups (as in the present case), it selects the position between the methyl group and a halogen in preference to that between two halogen atoms. It would seem a priori natural that a strong electronegative nitro-group should place itself beside an electropositive methyl group.

The third nitro-group, in the substance melting at 211° , therefore, enters the nucleus between the two halogens and in the para-position with respect to the methyl group.

EXPERIMENTAL.

Preparation of 3-Chloro-5-bromotoluene in Two Ways.

Method I.—Fifty grams of aceto-*p*-toluidide were dissolved in 100 c.c. of glacial acetic acid, and 20 c.c. of concentrated hydrochloric acid and 18 c.c. of bromine were added, with constant shaking. The mixture was left overnight, and then precipitated with water. After crystallising from spirit, the bromoaceto-toluidide melted at 117° . The yield was 70 grams. Twenty grams were dissolved in a mixture of 50 c.c. of glacial acetic acid and 50 c.c. of concentrated hydrochloric acid. The mixture was cooled in ice and salt, and 4 grams of sodium chlorate, dissolved in 20 c.c. of water, were slowly added, with vigorous shaking during and after the addition of the chlorate.

The mixture, after being kept overnight, was poured into water and filtered. After crystallisation from spirit, 23 grams of the chloro-derivative were obtained, melting at 195 – 200° . The pure substance, which was subsequently obtained by hydrolysis of the diacetyl derivative, melts at 199° , but recrystallisation of the above product did not improve the result.

The substance was hydrolysed by boiling with three times the weight of a mixture of equal volumes of concentrated sulphuric acid and water for two hours. The liquid was neutralised, and distilled in a current of steam. The product melted sharply at 63.5° . Fifteen grams of the 3-chloro-5-bromo-4-toluidine were dissolved in 50 c.c. of absolute alcohol and 12 c.c. of concentrated hydrochloric acid added. To the mixture 5 grams of finely powdered sodium nitrite were slowly added. The solution was then warmed on the water-bath until effervescence ceased, and the product distilled in a current of steam. The 3-chloro-5-bromotoluene which distils solidifies on cooling. It was shaken with a little sodium hydroxide solution to remove any phenol. About 8 grams of 3-chloro-5-bromotoluene were obtained, melting at 25° .

Method II.—Fifty grams of aceto-*p*-toluidide were dissolved in a mixture of 100 c.c. of glacial acetic acid and 150 c.c. of concentrated hydrochloric acid. To the mixture, which was cooled in ice and salt, 15 grams of sodium chlorate dissolved in 40 c.c. of water were slowly added, with vigorous shaking. It was left overnight, and a further 100 c.c. of concentrated hydrochloric acid were added, and the whole boiled for two hours. The product was distilled in a current of steam to remove a small quantity of volatile impurity; sodium carbonate was then added to liberate 3-chloro-4-toluidine, and the latter driven over with steam. The base, which distilled at $110^{\circ}/10$ mm., amounted to 33 grams. It was dissolved in 200 c.c. of glacial acetic acid, and 12.6 c.c. of bromine were slowly added, the temperature being maintained below 25° . The mixture was left overnight, and then poured into water. After crystallisation from alcohol, the substance was found to have nearly the same melting point as that obtained by the previous method, and to yield a 3-chloro-5-bromotoluene, melting at 25° . When the two specimens of 3-chloro-5-bromotoluidine were mixed, no change in melting point was observed. It may be assumed, therefore, that they are identical.

Nitration of 3-Chloro-5-bromotoluene.

Ten grams of finely powdered chlorobromotoluene were very slowly added to 30 c.c. of fuming nitric acid, the temperature being kept below 5° by cooling in ice and salt. As soon as complete solution was obtained, the liquid was poured on crushed ice. The solid which separated was collected and washed, and crystallised from a mixture of 9 parts of alcohol and 1 part of benzene. The mononitro-derivative crystallises in colourless needles, melting at 71° .

Reduction of 3-Chloro-5-bromonitrotoluene.

Fifteen grams of the nitro-compound were dissolved in 225 c.c. of concentrated hydrochloric acid, and 30 grams of tin added. The mixture was heated until the reaction set in, and was then left until the tin had dissolved. A further 3 grams of tin were added, and the mixture was boiled for a few minutes until complete solution was obtained. On cooling, the crystalline double salt of the hydrochloride of the base and stannic chloride separated. It was poured on to a filter, then decomposed with sodium carbonate, and distilled in a current of steam. About 10 grams of 3-chloro-5-bromotoluidine were obtained, melting at 42°. (Found, $\text{AgBr} + \text{AgCl} = 0.1605$. $\text{C}_7\text{H}_7\text{NClBr}$ requires $\text{AgCl} + \text{AgBr} = 0.1635$.)

A portion of the amino-compound was dissolved in four times its weight of acetic anhydride, and boiled under reflux for two hours. The hot solution was poured into water, and the precipitate was crystallised from glacial acetic acid. It formed colourless needles, melting at 85°:

0.5219 gave 21.3 c.c. N_2 at 12.9° and 750.6 mm. $\text{N} = 4.7$.

$\text{C}_{11}\text{H}_{11}\text{O}_2\text{NClBr}$ requires $\text{N} = 4.6$.

Some of the diacetyl derivative was suspended in water, a drop of phenolphthalein added, and then sodium hydroxide, until a pink colour was obtained. The liquid was heated for two hours on a water-bath, and then boiled over gauze for a few minutes. On cooling, chlorobromoacetotoluidide separated, and was collected. After crystallisation it was obtained in colourless needles, melting at 187°.

3-Chloro-5-bromo-2-toluidine.

The compound was obtained from aceto-*o*-toluidide by a method similar to that used in the preparation of 3-chloro-5-bromotoluene. The acetotoluidide was brominated in acetic acid solution, and the bromine derivative treated with sodium chlorate in the presence of concentrated hydrochloric acid. After distilling the product in a current of steam and crystallising from spirit, it formed colourless needles, melting at 60°. The mono- and di-acetyl derivatives were obtained by the method already described. On removing the amino-group by diazotisation, 3-chloro-5-bromotoluene was obtained, melting at 23°, thus showing that the halogens had entered positions 3 and 5.

3-Chloro-5-bromo-6-toluidine.

This compound was prepared by a method identical with the second method used in the preparation of 3-chloro-5-bromotoluene,

that is, the chlorine was first introduced by the use of sodium chlorate and hydrochloric acid, and was followed by bromination of the base in chloroform. In this way, the positions of the chlorine and bromine atoms were reversed. A yield of 90 per cent. of the theoretical quantity of chlorobromotoluidine was obtained from the chlorotoluidine. The mono- and di-acetyl derivatives were prepared, and the base was converted into 3-chloro-5-bromotoluene, melting at 23.5° .

3-Chloro-5-bromodinitrotoluene.

Five grams of 3-chloro-5-bromo-6-nitrotoluene were dissolved in 15 c.c. of fuming nitric acid, and the solution was kept for several hours. The product was poured on powdered ice, and the solid collected and washed. After crystallisation from alcohol and benzene, the dinitro-compound formed fine, colourless prisms with a brilliant lustre, and melted at 144° :

0.1603 gave 12.61 c.c. N_2 at 6° and 746.7 mm. $N=9.36$.

$C_6H_2O_4N_2ClBr$ requires $N=9.44$ per cent.

Alcoholic potassium hydroxide readily removes the halogens, but no crystalline hydroxy-compound was isolated.

3-Chloro-5-bromotrinitrotoluene.

Four grams of the mononitro-derivative were dissolved in a mixture of 20 c.c. of fuming nitric acid and 20 c.c. of concentrated sulphuric acid. The solution was heated on the water-bath for two to three hours, and the product poured into water, washed, dried, and crystallised from glacial acetic acid. It melts at 211° . It has been shown (T., 1902, **81**, 26; 1904, **85**, 527) that in the case of trinitrobenzene and trinitrotoluene reduction by hydrogen sulphide takes place vigorously in the presence of a trace of ammonia. It is a remarkable fact that in the present case there is scarcely any action in the cold, and a very slow change on heating. The alkali hydroxides readily remove both the halogens completely from the trinitro-compound. The nature of these products has not been investigated.

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