XLI.—*The Action of Sodium Hypochlorite on the Aromatic Sulphonamides.*

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ALTHOUGH the general nature of the chemical change * resulting from the interaction of sodium hypochlorite and the aromatic sulphonamides resembles that described by Chattaway and Orton in the case of the aromatic acylamines (Trans., 1899, '75, 1046 ; 1900, '77, 134, 789 ; Ber., 1899, 32, 3573), yet there are certain well-marked differences in the character of the products which we venture to think are not without interest.

These authors have shown that by the action of sodium hypochlorite on the acyl-anilides and -toluidides, the halogen in the first

* A preliminary notice of this reaction has already appeared (Proc., 1901, 17, 262). We have now supplemented these experiments by extending the reaction to a number of other sulphonamides.

instance enters the para-position with respect to the amino-group if this position is free, but otherwise becomes attached to an ortho-carbon atom. The orientating effect of the sulphonic group is different; in the first instance, the halogen seeks the ortho-position with respect to the amino-group, thus the benzenesulphonamides of aniline, *p*-toluidine, *m*-4-xyldine, and β -naphthylamine form ortho-compounds almost exclusively. If, however, a methyl group is present and the para-position to the amino-group is free, the conditions are modified and the halogen enters either the ortho-position to the methyl group or the para-position to the amino-group. Thus, the sulphonamide of *m*-toluidine gives a derivative of 6-chloro-*m*-toluidine. There is a considerable difference also in the readiness with which the different sulphonamides react. This is very marked in the case of those bases which are substituted in the ortho-position to the amino-group. The sulphonamides of *o*-toluidine and *m*-4-xyldine are only acted on slowly, whereas the sulphonamide of α -naphthylamine, which may be regarded as an *o*-substituted compound, is quite unchanged by the hypochlorite. The following table gives a list of the compounds which have been studied:

$\text{ArNH}\cdot\text{SO}_2\cdot\text{C}_6\text{H}_5$ ArNH_2	Melting point of the sulphonamide.	Position of the halogen relative to the amino-group.	Melting point of the chloro- sulphonamide.
Aniline.....	110°	<i>o</i> -	129—130°
<i>o</i> -Toluidine	123—124	<i>p</i> -	124—125
<i>m</i> -Toluidine.....	95	<i>p</i> -	130
		<i>op</i> -dichloro- compound	114
<i>p</i> -Toluidine	120	<i>o</i> -	110
<i>m</i> -4-Xyldine	124—125	<i>o</i> -	148—149
α -Naphthylamine	168	no action	—
β -Naphthylamine	97—98	<i>o</i> -	130—131

The Action of Sodium Hypochlorite on Benzenesulphonanilide.

Twenty grams of benzenesulphonanilide were dissolved in 200 c.c. of a solution of sodium hypochlorite (1 c.c. = 0.03 gram Cl) in the cold and left for 12 hours; the brown solution was acidified with acetic acid and the semi-solid precipitate was filtered and washed. It was then dissolved in about twice its weight of glacial acetic acid, to which a few drops of strong sulphuric acid were added, and digested for an hour on the water-bath. The product was poured into water, from which a crystalline compound separated, and, when purified by recrystallisation from dilute acetic acid, melted at 129—130°; 18 grams of the crude product or 11 grams of purified substance were obtained.

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The mother liquor contained a small quantity of a semi-solid substance which slowly became crystalline, and after recrystallisation from benzene and petroleum melted at 116° . This substance is probably benzenesulphon-*p*-chloroanilide (m. p. 121°), but it is not readily freed from oily impurity. On analysis, the substance melting at 129 – 130° gave the following numbers :

0.292 gave 14.15 c.c. moist nitrogen at 15.5° and 758 mm. $N = 5.66$.

0.3185 „ 0.1764 AgCl. $Cl = 13.57$.

0.2097 „ 0.1820 BaSO₄. $S = 11.93$.

C₁₂H₁₀O₂NCIS requires $N = 5.23$; $Cl = 13.27$; $S = 11.90$ per cent.

The constitution of the substance was determined by hydrolysis ; two grams were heated with about 8 c.c. of concentrated hydrochloric acid in a sealed tube at 190° for 4–5 hours. On opening the tube there was a strong odour of benzene, the presence of which was confirmed by conversion into aniline, with which sodium hypochlorite gave the usual reaction. The appearance of benzene in the decomposition of the sulphonanilide is readily accounted for, seeing that Armstrong and Field (*Ber.*, 1874, 7, 406) and Jacobsen (*Ber.*, 1876, 9, 258) have shown that sulphonic acids are converted into hydrocarbons by strong hydrochloric acid under pressure. The acid solution, after extracting with light petroleum, was made alkaline with sodium carbonate and distilled in steam ; the distillate was extracted with ether, the ether removed, and the residue dehydrated in a vacuum desiccator, when a yellow oil weighing 0.8 gram remained. The substance did not solidify on introducing a crystal of *p*-chloroaniline, even when cooled in ice ; it yielded an acetyl derivative melting at 85 – 86° and a benzoyl derivative melting at 102° . This corresponds with *o*-chloroaniline, which was prepared for comparison and converted into the acetyl, benzoyl, and benzenesulphonyl derivatives.

The reaction probably occurs in two stages, as in the chlorination of the acetyl derivatives studied by Chattaway and Orton, although the intermediate chloroamide was too unstable to be isolated in a pure state.

The main product is therefore the *o*-chloroanilide, together with a very small quantity of the para-compound. Wallach (*Ber.*, 1877, 9, 424) found that benzenesulphonanilide, when heated at 100° with phosphorus pentachloride, yields benzenesulphon-*p*-chloroanilide (m. p. 121°), but no reference is made to an ortho-compound. We

have repeated and confirmed Wallach's work. The product is difficult to purify, and only a small quantity of pure substance could be obtained, but we failed to detect any ortho-compound. We have also synthesised Wallach's compound from *p*-chloroaniline and benzenesulphonic chloride, and to complete the series we have also prepared benzenesulphon-*m*-chloroanilide from *m*-chloroaniline.

This anilide, which has not been previously described, melts at 121° like the para-compound.

0.2576 gave 12.85 c.c. moist nitrogen at 13° and 761 mm.; N = 5.76.

$C_{12}H_{10}O_2NClS$ requires N = 5.23 per cent.

The Action of Sodium Hypochlorite on Benzenesulphon-o-toluidide.

Benzenesulphon-*o*-toluidide was described by Beckmann and Fellrath (*Annalen*, 1893, 273, 13); it crystallises from alcohol in rectangular tablets which melt at 123—124°. When treated with sodium hypochlorite in the manner already described, it gave an uncrystallisable product, but in acetic acid solution a colourless crystalline substance was obtained. If warmed with alcohol for any length of time, this compound decomposed, a portion of the alcohol being oxidised to aldehyde. From a mixture of benzene and light petroleum, the substance crystallised without any decomposition, and a product was obtained which melted at 99—100°.

0.1951 gave 0.1000 AgCl; Cl = 12.92.

$C_{13}H_{12}O_2NClS$ requires Cl = 12.61 per cent.

On crystallising the foregoing compound from acetic acid solution, it becomes transformed into an isomeride melting at 124—125°.

0.1014 gave 0.0530 AgCl; Cl = 12.93.

0.1014 „ 0.0843 BaSO₄; S = 11.41.

$C_{13}H_{12}O_2NClS$ requires Cl = 12.61; S = 11.39 per cent.

This substance was identified as benzenesulphon-5-chloro-*o*-toluidide, also obtained from benzenesulphonic chloride and 5-chloro-*o*-toluidine; The chlorine therefore enters the para-position to the amino-group. The isomeric substance melting at 99—100° is probably the chloroamide, $C_7H_7 \cdot NCl \cdot SO_2 \cdot C_6H_5$, for on heating with alcohol it loses chlorine and reverts to the original substance. This explains both the conversion effected by acetic acid and the decomposition produced by alcohol, in which the latter reagent is oxidised to aldehyde in eliminating chlorine.

The Action of Sodium Hypochlorite on Benzenesulphon-m-toluidide.

Benzenesulphon-*m*-toluidide has not been previously described; it crystallises from alcohol in colourless plates melting at 95°. The action of the hypochlorite solution on this substance is much more vigorous than in the preceding cases, both mono- and di-chloro-derivatives being formed.

The *monochloro*-compound was obtained by using the theoretical quantity of sodium hypochlorite and keeping the mixture cold; after 12 hours, a large quantity of crystalline substance separated, which melted at 275—280°. This is probably a sodium derivative having the formula $C_6H_3Cl(CH_3) \cdot NNa \cdot SO_2 \cdot C_6H_5$; it crystallises from ethyl acetate in fine needles.

0.8808 required 28.87 c.c. N/10 H_2SO_4 ; Na = 7.54.

$C_{13}H_{11}O_2NCISNa$ requires Na = 7.58 per cent.

When digested for a few minutes with glacial acetic acid, the sodium compound is easily decomposed, yielding the mono-chloro-derivative, which crystallises in long, colourless prisms and melts at 130°. Five grams of the toluidide yielded 3.2 grams of the pure mono-chloro-compound.

0.3790 gave 0.1970 AgCl; Cl = 12.86.

0.3790 „ 0.3144 $BaSO_4$; S = 11.39.

$C_{13}H_{12}O_2NCIS$ requires Cl = 12.60; S = 11.37 per cent.

The constitution of the substance was determined by hydrolysis as in the previous cases. A crystalline base was obtained which melted at 83° and gave an acetyl derivative melting at 89°. These numbers correspond with the melting points of 6-chloro-*m*-toluidine and its acetyl derivative. The formula of the original compound is therefore

No other mono-chloro-compound could be detected.

The Dichloro-compound.—Five grams of the sulphon-*m*-toluidide were dissolved in excess of the hypochlorite solution; the whole mass subsequently solidified and was collected at the pump. After crystallisation from acetic acid, 3 grams of pure substance (m. p. 114°) and 1.7 grams of an impure product melting at about 80° were obtained. The latter is probably a mixture of the mono- and di-chloro-compounds, which are separated with difficulty. A better yield of the dichloro-compound was obtained either by warming the mixture of hypochlorite

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and *m*-toluidide at about 40° for a short time or by adding sodium hypochlorite solution to the monochloro-compound. The substance melting at 114° was analysed with the following result:

0.2640 gave 0.2303 AgCl. Cl = 21.60.

0.2640 „ 0.2030 BaSO₄. S = 10.53.

C₁₃H₁₁O₂NCl₂S requires Cl = 22.4; S = 10.10 per cent.

On hydrolysis, a crystalline base was obtained, which was recrystallised from alcohol and melted at 58°, its acetyl derivative melting at 121°. The base was further identified by successive conversion into 2:3:6-trichlorotoluene (m. p. 45—46°), 2:3:6-trichlorobenzoic acid (m. p. 165°), and dinitro-2:3:6-trichlorotoluene (m. p. 141—142°) (compare Cohen and Dakin, *Trans.*, 1902, 81, 1333). The structure of the sulphonidichloro-*m*-toluidide is accordingly represented as follows:

It is interesting to compare the action of the hypochlorite on the benzenesulphonyl and acetyl derivatives of *m*-toluidine. In the acetyl derivative, the hypochlorite produces substitution in the ortho- and para-positions to the methyl group (Cohen and Dakin, *Trans.*, 1902, 81, 1332); in the sulphonamide, the chlorine atoms enter the two ortho-positions.

Action of Sodium Hypochlorite on Benzenesulphon-p-toluidide.

Benzenesulphon-*p*-toluidide was described by Wallach (*Ber.*, 1876, 9, 424), who states that it does not yield a halogen derivative with phosphorus pentachloride, and attributes the fact to the presence of the methyl group in the para-position to the amino-group. With sodium hypochlorite, the reaction goes quite smoothly, and benzenesulphon-3-chloro-*p*-toluidide (m. p. 110°) is obtained, 5 grams of the toluidide giving 3.5 grams of pure product.

0.4020 gave 0.2068 AgCl. Cl = 12.73.

0.4020 „ 0.3383 BaSO₄. S = 11.54.

C₁₃H₁₂O₂NClS requires Cl = 12.60; S = 11.37 per cent.

On hydrolysis with hydrochloric acid, 2 grams of the compound gave 0.9 gram of a yellow, oily base, which solidified on cooling in ice, and yielded an acetyl derivative melting at 118°. These properties agree with those of the 3-chloro-*p*-toluidine. The chlorine, therefore, enters the ortho-position to the amino-group. An excess of hypochlorite produced no further substitution.

The Action of Sodium Hypochlorite on Benzenesulphon-m-4-xylylide.

Benzenesulphon-*m-4*-xylylide, which has not been previously described, is prepared in the usual way, and crystallises in colourless prisms melting at 124—125°. When treated with sodium hypochlorite solution, it remained unchanged, but in acetic acid a small amount of chlorination product was obtained, the yield being augmented by carrying out the reaction at about 50°. The white solid which separated was recrystallised from alcohol and melted at 148—149°. Six grams of the *m*-xylylide gave 4.2 grams of pure product.

0.1293 gave 0.0619 AgCl. Cl = 11.84.

0.1293 „ 0.1004 BaSO₄. S = 10.66.

C₁₄H₁₄O₂NClS requires Cl = 11.89 ; S = 10.72 per cent.

On hydrolysis, 2 grams of the chlorination product gave 0.8 gram of a colourless, crystalline base melting at 39—40°, which formed an acetyl derivative melting at 200—201°. The base obtained on hydrolysis is identical with 5-chloro-*m-4*-xylylidine.* The sulphon-5-chloro-*m-4*-xylylide has therefore the following structure :

An excess of sodium hypochlorite had no further action.

Sodium Hypochlorite and Benzenesulphon-α-naphthalide.

The sulphon-α-naphthalide obtained by the action of benzenesulphonic chloride on α-naphthylamine crystallises from alcohol in colourless needles melting at 168°; it dissolves in aqueous sodium hypochlorite forming a deep brown solution, which, when poured into acetic acid, yielded a precipitate of the original substance. No change was effected by the hypochlorite in the presence of acetic acid.

The Action of Sodium Hypochlorite on Benzenesulphon-β-naphthalide.

Benzenesulphon-β-naphthalide crystallises from alcohol in colourless plates, which melt at 97—98°. On adding sodium hypochlorite, a yellow oil separated, which quickly solidified, the product being a

* For purposes of identification, the preparation of the three isomeric monochloro-derivatives of *m-4*-xylylidine was undertaken, and an account of these substances will appear separately.

sodium derivative of benzenesulphonchloro- β -naphthalide, which crystallises in glistening needles from benzene containing about 5 per cent. of alcohol.

0.8837 required 2.45 c.c. NH_2SO_4 . $\text{Na} = 6.38$.

$\text{C}_{16}\text{H}_{11}\text{O}_2\text{NClSNa}$ requires $\text{Na} = 6.76$ per cent.

The sodium compound was decomposed by boiling for a few minutes with dilute mineral acid; the product dissolved in alcohol, from which it crystallised in colourless needles melting at $130-131^\circ$; 5 grams of β -naphthalide gave 4 grams of pure substance.

0.1843 gave 0.0840 AgCl . $\text{Cl} = 11.28$.

0.1843 „ 0.1355 BaSO_4 . $\text{S} = 10.10$.

$\text{C}_{16}\text{H}_{12}\text{O}_2\text{NClS}$ requires $\text{Cl} = 11.18$; $\text{S} = 10.08$ per cent.

The compound is more easily hydrolysed than the benzenesulphon-toluidides, a temperature of 140° for one hour being sufficient for the purpose; 1.8 grams gave 0.7 gram of solid base, which melted at 60° and formed an acetyl derivative melting at $147-148^\circ$. These data correspond with the melting points of 1-chloro- β -naphthylamine and its acetyl derivative. The sulphonamide, therefore, has the following structure:

In this case, the chlorine atom enters the α -position contiguous to the amidic nitrogen.

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