

LXX.—*Ortho-substituted Nitrogen Chlorides and Bromides and the Entrance of Halogen into the Ortho-position in the Transformation of Nitrogen Chlorides.*

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IN our earlier papers (Trans., 1899, 75, 1046; Ber., 1899, 32, 3573) on substituted nitrogen chlorides and bromides, it was stated that we had so far not observed the simultaneous formation of ortho- and para-derivatives in their isomerisation. The transformation products of phenyl acetyl nitrogen chloride and phenyl acetyl nitrogen bromide, for example, melted within a degree or so of the isomeric *p*-chloro- and *p*-bromo-acetanilides, and could be obtained perfectly pure by one crystallisation from alcohol.

In order, however, to decide this point definitely, we have prepared larger quantities of phenyl acetyl nitrogen chloride, phenyl acetyl nitrogen bromide, and phenyl benzoyl nitrogen bromide, and have made a careful search, in the products of their transformation, for small amounts of *o*-chloroacetanilide, *o*-bromoacetanilide and *o*-bromobenzanilide respectively.

When phenyl acetyl nitrogen chloride is transformed, we find that *o*-chloroacetanilide is produced together with *p*-chloroacetanilide. The transformation product consists of about 95—96 per cent. of the para- and 4—5 per cent. of the ortho-compound.

We have failed to isolate any *o*-bromoacetanilide or *o*-bromobenzanilide from the transformation products of the isomeric nitrogen bromides, and although from analogy these probably are formed, the amount produced must be exceedingly small, certainly less than one per cent. under the conditions of transformation which we have studied.

When these nitrogen bromides are worked with on a large scale, the problem is complicated by a certain amount of hydrolysis occurring, and by the consequent reformation of a small amount of unsubstituted anilide.

The behaviour of these nitrogen halogen compounds is in marked contrast with that of the nitramines (Bamberger, Ber., 1897, 30, 1248), which, when this is possible, always undergo transformation into both ortho- and para-derivatives, the former often being the chief, if not the only, product.

We have also prepared *o*-chlorophenyl acetyl nitrogen chloride and *o*-bromophenyl acetyl nitrogen bromide by the action of hypochlorous

and hypobromous acid respectively on the corresponding substituted anilides.

The physical and general chemical properties of these compounds are typical of the nitrogen chlorides and nitrogen bromides, but they are relatively more stable and may be heated moderately or kept for a long time without alteration. Isomeric change can, however, be effected readily, and they then undergo transformation into the 2:4-disubstituted acetanilides.

Transformation of Acetylchloraminobenzene (Phenyl Acetyl Nitrogen Chloride).

One hundred grams of acetanilide were converted into the nitrogen chloride by the method already described (Trans., 1899, **75**, 1046). The pure chloride was placed under water, acidified with acetic acid, and ice added to prevent the temperature rising. In an hour transformation was complete; the product was then hydrolysed by boiling for six hours with alcohol and sulphuric acid. On cooling, the larger part of the *p*-chloroaniline separated out as sulphate. This was filtered off and the alcohol evaporated from the mother liquor, which was then subjected to steam distillation after partially neutralising the acid. A liquid base came over in small quantity. This was acetylated and the crude anilide, which melted at 72°, was recrystallised from benzene and light petroleum (b. p. 50—80°) until it melted constantly at 87°, the melting point of *o*-chloroacetanilide. A yield of between 4 and 5 per cent. of the theoretical amount was obtained. As a confirmation, the percentage of chlorine was determined.

0.1411 yielded 0.1204 AgCl. Cl = 21.1.

$C_6H_4Cl \cdot NH \cdot CO \cdot CH_3$ requires Cl = 20.9 per cent.

A similar method of procedure was adopted in studying the transformation products of phenyl acetyl nitrogen bromide and phenyl benzoyl nitrogen bromide. Five hundred grams of the former were transformed by rapidly heating with water, and 60 grams of the latter by allowing it to stand for a few hours in a moist state at the ordinary temperature. After treating the transformed products as above, the small quantity of material distilling over after partial neutralisation was in each case shown to be a mixture of *p*-bromoaniline and aniline by acetylating and benzoylating respectively, finding the percentage of bromine in the recrystallised product, and comparing its melting point with that of a similar mixture crystallised from a prepared solution containing anilide and *p*-bromoanilide. The product obtained from the transformed material melted within a degree or so of the melting point of the known mixture.

Acetylchloramino-2-chlorobenzene (o-Chlorophenyl Acetyl Nitrogen Chloride), $C_6H_4Cl \cdot NCl \cdot CO \cdot CH_3$.

o-Chloroacetanilide is treated with an excess of a solution of potassium hypochlorite containing potassium hydrogen carbonate. After about 1 hour the conversion into the nitrogen chloride is complete. The latter is very soluble in chloroform, benzene, or acetic acid, but only moderately so in hot petroleum (b. p. 50—80°). It forms long, flattened, exceedingly lustrous prisms which melt at 88°.

0.2901 liberated I = 28.8 c.c. *N*/10 iodine. Cl, as $:NCl$, = 17.59.

$C_6H_4Cl \cdot NCl \cdot CO \cdot CH_3$ requires Cl, as $:NCl$, = 17.38 per cent.

On heating the molten substance, no sudden transformation takes place, but decomposition with darkening occurs about 170°.

This nitrogen chloride is unusually stable and can be recrystallised from glacial acetic acid; even heating its solution in glacial acetic acid for several hours at 100° does not complete the isomeric change, a mode of treatment which would have caused the immediate transformation of any other nitrogen chloride with the para-position unoccupied. On heating under boiling water, it partially hydrolyses and partially transforms into 2:4-dichloroacetanilide. Heated in a sealed tube at 140° in the presence of a little acetic acid, 2:4-dichloroacetanilide is rapidly formed. No 2:6-dichloroacetanilide has been recognised in the product of transformation.

Acetylbromamino-2-bromobenzene (o-Bromophenyl Acetyl Nitrogen Bromide), $C_6H_4Br \cdot NBr \cdot CO \cdot CH_3$.

o-Bromoacetanilide in a finely powdered state was suspended in a dilute solution of potassium hydrogen carbonate containing an excess of hypobromous acid, and the whole stirred for several hours. The nitrogen bromide was then recrystallised from chloroform and light petroleum. It separates in pale yellow, four-sided prisms with domed ends, and melts at 150—152° with slight decomposition. Heated above this temperature, the yellow liquid darkens in colour and at 160° decomposes suddenly, bromine being evolved and a dark brown mass left.

0.1968 liberated I = 13.4 c.c. *N*/10 iodine. Br, as $:NBr$, = 27.22.

$C_6H_4Br \cdot NBr \cdot CO \cdot CH_3$ requires Br, as $:NBr$, = 27.29 per cent.

On heating for some hours at 100° with a little water, it is partially hydrolysed and partially transformed into 2:4-dibromoacetanilide melting at 146°. This latter transformation alone takes place when the nitrogen bromide is heated in a sealed tube with a

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few drops of glacial acetic acid at 140° for about an hour. *o*-Chloroformanilide and -benzanilide and *o*-bromoformanilide and -benzanilide also yield nitrogen chlorides and nitrogen bromides.

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