LXXXII.—*Nitrogen Bromides containing the Propionyl Group.*

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NITROGEN bromides are more difficult to prepare than nitrogen chlorides, partly because hypobromous acid is less easily obtained and less stable than hypochlorous acid, and partly because they undergo transformation and are hydrolysed much more readily.

Except in colour they closely resemble the corresponding nitrogen chlorides, and undergo similar isomeric changes when an unsubstituted or partially substituted phenyl residue is also attached to the nitrogen.

Propionanilide and the bromopropionanilides readily react with hypobromous acid, the iminic hydrogen atom being replaced by bromine. A hypobromite is probably formed as an intermediate product thus :

The action is a reversible one, for when nitrogen bromides are placed in water the opposite change takes place, until a position of equilibrium is reached. The ready hydrolysis with evolution of bromine which nitrogen bromides undergo when heated with water depends

on this and on the rapidity with which hypobromous acid passes into bromine and bromic acid :

These nitrogen bromides show the characteristic behaviour of the nitrogen halogen linking, reacting readily with hydriodic acid, sulphurous acid, hydrogen sulphide, alcohol, or potassium cyanide.

When hydrogen is attached to the phenyl nucleus, either in the *para*- or *ortho*-position relatively to the nitrogen, the nitrogen bromides undergo isomeric change more readily than the corresponding chlorides. These changes are brought about in the same way as the latter by heating alone or with water or an acid. Owing to the readiness with which nitrogen bromides are hydrolysed, a little of the original anilide is generally re-formed in the process if water be present.

The following scheme shows the directions of transformation, but whilst the general course of the transformations is similar in the two cases, it is important to note that the *para*-derivative is the sole product of the transformation of propionyl phenyl nitrogen bromide :

All nitrogen bromides when treated with an excess of a solution of hydrobromic acid are decomposed, bromine is liberated, and the corresponding aniline is re-formed. On the other hand, when an anilide is treated with an excess of bromine suspended or dissolved in water, a nitrogen bromide and hydrobromic acid are produced. These changes are the related parts of a reversible action, the direction of which is determined by the conditions. An addition of halogen acid or halogen to the nitrogen probably takes place thus :—

A large excess of hydrobromic acid or the continuous removal of the free bromine causes the anilide to be re-formed, whilst on the other

hand the action proceeds in the opposite direction and a nitrogen bromide is produced when a salt of a weaker acid, as an acetate or borate, which can remove the hydrobromic acid, is added.

The reversible nature of the reaction is only seen clearly when the nucleus is already fully substituted, as otherwise isomeric change and substitution into the ring may take place.

EXPERIMENTAL.

Propionyl Phenyl Nitrogen Bromide, $C_6H_5 \cdot NBr \cdot CO \cdot CH_2 \cdot CH_3$.

This compound is prepared by shaking a solution of propionanilide in chloroform with a little more than the calculated quantity of a dilute solution of hypobromous acid* containing an equivalent weight of potassium bicarbonate, the temperature not being allowed to rise above 0° . The solution is separated, thoroughly dried over fused calcium chloride, and the chloroform completely evaporated off in a current of air, when a yellow, viscid mass is left which solidifies if cooled below 0° and stirred with a little petroleum of low boiling point. The pale yellow solid is dissolved in warm petroleum from which, on cooling, the nitrogen bromide separates in slender, very pale yellow somewhat irregularly grown pyramids. It melts at 88° .

0.3684 liberated I = 32.2 c.c. $N/10$ I.† Br as :N·Br = 34.94.

$C_9H_{10}ONBr$ requires Br as :N·Br = 35.05 per cent.

When rapidly heated above its melting point, it darkens somewhat in colour, and at about 125° is transformed almost explosively, with considerable development of heat, into a reddish-brown mass consisting mainly of *p*-bromopropionanilide. When melted and kept for some minutes at its melting point, it quietly changes into *p*-bromopropionanilide, and solidifies to a white, crystalline mass, which, on further heating, melts at 145 — 146° , or about three degrees below the melting point of the pure isomeride. This transformation takes place slowly on allowing the compound to stand exposed to moist air, or rapidly on heating it under water or on adding to its solution in chloroform a little hydrobromic or hydrochloric acid; some hydrolysis, however, takes place under these circumstances. Although a very careful search has been made, no *o*-bromopropionanilide has been isolated from the product obtained by the transformation of propionyl phenyl nitrogen

* The solutions of hypobromous acid referred to in this paper are easily made by shaking bromine with about three times its weight of precipitated mercuric oxide suspended in from 10 to 100 times its weight of water.

† All the nitrogen bromides and chlorides described in this paper were analysed in the usual way. A weighed quantity was dissolved in chloroform and shaken with an excess of a solution of potassium iodide acidified by acetic acid. The liberated iodine was then estimated by a solution of sodium thiosulphate.

bromide; *p*-bromopropionanilide is apparently the exclusive product of the change, and can be obtained pure by once crystallising from alcohol.

p-Bromopropionanilide, $C_6H_4Br \cdot NH \cdot CO \cdot CH_2 \cdot CH_3$.

This is most economically prepared by mixing *p*-chloroaniline with the calculated quantity of propionic anhydride, when much heat is developed, and heating for an hour at 120° . It is readily soluble in alcohol or chloroform, and from the latter solvent it separates in brilliant, colourless, rectangular plates with two domed edges. It melts at 149° .

0.2147 gave 0.1766 AgBr. Br = 35.

$C_9H_{10}ONBr$ requires Br = 35.05 per cent.

Propionyl p-Bromophenyl Nitrogen Bromide, $C_6H_4Br \cdot NBr \cdot CO \cdot CH_2 \cdot CH_3$.

This substance can be obtained either from propionanilide,* or better, from *p*-bromopropionanilide by shaking a chloroform solution with a strong solution of hypobromous acid containing a little potassium bicarbonate and a little precipitated mercuric oxide. On filtering and treating as described under propionyl phenyl nitrogen bromide, it is obtained in bright yellow, transparent, glistening prisms and melts at 78° :

0.3008 liberated I = 19.6 c.c. *N*/10 I. Br as $N \cdot Br$ = 26.05.

$C_9H_9ONBr_2$ requires Br as $N \cdot Br$ = 26.04 per cent.

When heated above its melting point, it darkens in colour and is transformed with development of heat at about 150 — 160° into a dark coloured mass, from which 2 : 4-dibromopropionanilide can be isolated. The transformation takes place with some little hydrolysis when the compound is heated under water to 100° , and is best effected by dissolving it in chloroform, adding a drop of propionic acid, and heating in a sealed tube for a short time at 100° .

Propionyl p-Bromophenyl Nitrogen Chloride, $C_6H_4Br \cdot NCl \cdot CO \cdot CH_2 \cdot CH_3$.

This, like all the nitrogen chlorides described in this paper, was prepared by shaking for a few hours a solution of the anilide in chloroform with a half normal solution of potassium hypochlorite containing an excess of potassium bicarbonate. The chloroform solution was separated, dried over fused calcium chloride, and the solvent evaporated. The pale yellow oil thus obtained was cooled and treated as previously

* When an excess of a strong solution of hypobromous acid is used, the transformation of the propionyl phenyl nitrogen bromide first formed takes place at the ordinary temperature, even in presence of potassium bicarbonate and mercuric oxide.

described until it solidified, when it was separated and recrystallised from light petroleum.

Propionyl *p*-bromophenyl nitrogen chloride crystallises in colourless, transparent, four-sided plates, apparently flattened rhombs, and melts at 59°:

0.4208 liberated I = 32.1 c.c. *N*/10 I. Cl as :N·Cl = 13.52.

$C_9H_9ONClBr$ requires Cl as :NCl = 13.5 per cent.

When dissolved in chloroform, to which a drop of propionic acid has been added, and heated slowly in a sealed tube to 100°, it is transformed into 2-chloro-4-bromopropionanilide.

o-Bromopropionanilide, $C_6H_4Br \cdot NH \cdot CO \cdot CH_2 \cdot CH_3$.

This is conveniently obtained by heating *o*-bromoaniline for two hours to 120° with the equivalent quantity of propionic anhydride. It is best recrystallised from dilute alcohol, and finally from petroleum (b. p. 60–80°), in which it is readily soluble. It forms slender, colourless prisms and melts at 93°:

0.1996 gave 0.1646 AgBr. Br = 35.09.

$C_9H_{10}ONBr$ requires Br = 35.05 per cent.

Propionyl o-Bromophenyl Nitrogen Bromide, $C_6H_4Br \cdot NBr \cdot CO \cdot CH_2 \cdot CH_3$

This can be prepared from *o*-bromopropionanilide by the method previously described. It is, however, not necessary to prepare hypobromous acid, as a freshly made, cooled solution of bromine in caustic potash, to which excess of a solution of potassium bicarbonate has been added, may be used. The latter may often be employed instead of hypobromous acid in the preparation of those nitrogen bromides which do not undergo transformation very readily.

Propionyl *o*-bromophenyl nitrogen bromide is very soluble in chloroform, but only sparingly so in petroleum (b. p. 60–80°). From the latter solvent, it separates in very pale yellow, long, transparent, glistening prisms and melts at 117°:

0.2296 liberated I = 14.9 c.c. *N*/10 I. Br as :N·Br = 25.94.

$C_9H_9ONBr_2$ requires Br as :N·Br = 26.04 per cent.

When slowly heated in a sealed tube to about 150° with a little propionic acid, it is transformed into 2:4-dibromopropionanilide.

Propionyl o-Bromophenyl Nitrogen Chloride, $C_6H_4Br \cdot NCl \cdot CO \cdot CH_2 \cdot CH_3$.

This substance crystallises from petroleum (b. p. 60–80°) in glistening, transparent, flattened rhombs and melts at 59°:

0.3392 liberated I = 25.8 c.c. *N*/10 I. Cl as :N·Cl = 13.48.

$C_9H_9ONClBr$ requires Cl as :N·Cl = 13.5 per cent.

When slowly heated in a sealed tube to about 150° with a little propionic acid, it is transformed into 2-bromo-4-chloropropionanilide.

2 : 4-Dibromopropionanilide, $C_6H_3Br_2 \cdot NH \cdot CO \cdot CH_2 \cdot CH_3$.

This is easily obtained by heating the aniline with the equivalent quantity of propionic anhydride for 3 hours at 150° . It is readily soluble in alcohol or chloroform, moderately so in petroleum, and crystallises from alcohol in fine, long, colourless, silky needles which melt at 136° . These become electrified on rubbing, and, when dry, the particles fly apart on drawing a platinum spatula over them :

0.1670 gave 0.2046 AgBr. Br = 52.14.

$C_9H_9NOBr_2$ requires Br = 52.08 per cent.

Propionyl 2 : 4-Dibromophenyl Nitrogen Bromide,
 $C_6H_3Br_2 \cdot NBr \cdot CO \cdot CH_2 \cdot CH_3$.

This compound can be obtained from 2 : 4-dibromopropionanilide in the ordinary way, and also by shaking for several hours a solution of the anilide in chloroform with bromine suspended in water at 0° containing an excess of sodium acetate or borax ; the chloroform solution is separated, thoroughly washed with water, dried over calcium chloride, and treated as usual. It crystallises from petroleum (b. p. $60-80^{\circ}$) in glistening, transparent, very pale yellow rhombs and melts at 87° :

0.3253 liberated I = 16.8 c.c. $N/10$ I. Br as $N \cdot Br$ = 20.64.

$C_9H_8ONBr_3$ requires Br as $N \cdot Br$ = 20.71 per cent.

When heated slowly in a sealed tube with a drop of propionic acid to about 120° , it is transformed into 2 : 4 : 6-tribromopropionanilide.

Propionyl 2 : 4-Dibromophenyl Nitrogen Chloride,
 $C_6H_3Br_2 \cdot NCl \cdot CO \cdot CH_2 \cdot CH_3$.

This crystallises from petroleum in transparent, flat, four-sided, apparently rectangular plates and melts at 71° :

0.6435 yielded I = 37.8 c.c. $N/10$ I. Cl as $N \cdot Cl$ = 10.41.

$C_9H_8ONClBr_2$ requires Cl as $N \cdot Cl$ = 10.38 per cent.

When heated in a sealed tube with a little propionic acid to about 120° , it is transformed into 2-chloro-4 : 6-dibromopropionanilide, which, however, is somewhat impure, probably owing to the formation of a little 2 : 6-dibromo-4-chloropropionanilide.

2 : 4 : 6-Tribromopropionanilide, $C_6H_2Br_3 \cdot NH \cdot CO \cdot CH_2 \cdot CH_3$.

2 : 4 : 6-Tribromoaniline was suspended in chloroform in which was dissolved the calculated quantity of propionyl chloride, an equivalent

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amount of pyridine was then added, when at once the solution became warm and the aniline dissolved. The liquid was boiled for an hour and then poured into water and heated until the chloroform had volatilised. The white solid which separated was filtered off and recrystallised from alcohol, in which it was readily soluble. It separated from this solvent in long, colourless, flattened prisms and melted at 203° :

0.1880 gave 0.2744 AgBr. Br = 62.11.

$\text{C}_9\text{H}_8\text{ONBr}_3$ requires Br = 62.14.

Propionyl 2 : 4 : 6-Tribromophenyl Nitrogen Bromide,

In the preparation of this substance from 2 : 4 : 6-tribromopropionanilide, a solution of hypobromous acid or a solution of bromine in caustic potash or bromine suspended in excess of a solution of sodium acetate or borate can be employed. The last method shows the reversible character of the reaction of a nitrogen bromide with hydrobromic acid.

This nitrogen bromide is readily soluble in chloroform, moderately so in petroleum (b. p. $60-80^{\circ}$), and crystallises from the latter in clusters of slender, flattened, bright yellow prisms melting at 82° :

0.3762 liberated I = 16.1 c.c. $N/10$ I. Br as $\text{N} \cdot \text{Br}$ = 17.11.

$\text{C}_9\text{H}_7\text{ONBr}_4$ requires Br as $\text{N} \cdot \text{Br}$ = 17.19 per cent.

When heated above its melting point, it decomposes at about 190° with evolution of bromine, leaving a dark coloured residue from which 2 : 4 : 6-tribromopropionanilide can be isolated.

Propionyl 2 : 4 : 6-Tribromophenyl Nitrogen Chloride,

This compound crystallises from petroleum in clusters of small, colourless, flattened prisms and melts at 75° :

0.2828 liberated I = 13.5 c.c. $N/10$ I. Cl as $\text{N} \cdot \text{Cl}$ = 8.46.

$\text{C}_9\text{H}_7\text{ONClBr}_3$ requires Cl as $\text{N} \cdot \text{Cl}$ = 8.43 per cent.

It may be noted that, as in the case of the nitrogen bromides of the corresponding chloropropionanilides, propionyl *p*-bromophenyl nitrogen bromide and propionyl 2 : 4 : 6-tribromophenyl nitrogen bromide are bright yellow in colour, whilst propionyl *o*-bromophenyl nitrogen bromide and propionyl 2 : 4-dibromophenyl nitrogen bromide are of a very pale yellow. Propionyl phenyl nitrogen bromide itself is, however, very pale yellow.

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