

XLVII.—*Nitrogen Halogen Derivatives of the Aliphatic Diamines.*

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ALTHOUGH a few substances obtained by the direct action of the halogens on simple aliphatic primary amines were among the earliest nitrogen chlorides and bromides to be prepared, and although the quinonedichloroimides derived from aromatic diamines have long been known and have recently received important industrial applications, no compounds of this nature have hitherto been obtained from the aliphatic diamines.

The aliphatic diamines themselves, however, and the diacyldiamines readily yield compounds in which the whole of the hydrogen attached to nitrogen is replaced by halogen, and in the course of a systematic investigation of compounds of this type on which the author is engaged, a number of derivatives of ethylenediamine and trimethylenediamine have been prepared. The most noteworthy compounds obtained are those yielded by ethylenediamine itself, ethylenetetrachlorodiamine, $\text{NCl}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NCl}_2$, and ethylenetetrabromodiamine, $\text{NBr}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NBr}_2$, which approach the simple halogen derivatives of nitrogen more nearly in composition than any compounds yet known or which are likely to be prepared. Both are stable substances; the former is a limpid, yellow liquid resembling nitrogen chloride in colour, pungent odour, and explosibility, the latter a beautifully crystalline, orange-red solid which is also extremely explosive.

Ethylenetetrachloroaminodiamine, $\text{NCl}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NCl}_2$.

This compound was prepared by dissolving ethylenediamine (1 mol.) in 50 per cent. acetic acid (6 mols.) and adding this liquid slowly to a large excess of a cooled saturated solution of bleaching powder. The tetrachloroamine then separated as a pale yellow liquid and was extracted by chloroform; on separating the chloroform solution, drying it with fused calcium chloride, and evaporating off the solvent in a current of air, it was obtained anhydrous and in a pure state.

Ethylenetetrachlorodiamine is a limpid, bright yellow liquid, which does not solidify when cooled in a mixture of ice and salt; it decomposes, sometimes with explosion, when heated under the ordinary atmospheric pressure, but can be distilled unchanged under diminished pressure; it boils at 116° under 50 mm. pressure. When a small quantity contained in a capillary tube is placed directly in a flame, it explodes with great violence. It is comparatively stable at the ordinary

temperature, not undergoing any appreciable decomposition when kept for some weeks in a dry atmosphere.

It gives off a very pungent and irritating vapour, which violently attacks the eyes and has a peculiar smell very characteristic of the chloroamines and recalling that of nitrogen chloride itself.

This compound and all others described in the paper were analysed by dissolving them in acetic acid, adding to the solution potassium iodide, and titrating the iodine thus liberated with standard sodium thiosulphate.

0.1767 liberated I = 71.5 c.c. *N*/10 I. Cl (as NCl) = 71.72.

$C_2H_4N_2Cl_4$ requires Cl (as NCl) = 71.65 per cent.

Ethylenetetrabromodiamine, $NBr_2 \cdot CH_2 \cdot CH_2 \cdot NBr_2$.

A solution of ethylenediamine in the equivalent quantity of acetic acid was poured into a considerable excess of a cooled decinormal solution of hypobromous acid, when a pale yellow solid at once separated. Chloroform was then added and the whole shaken for some time, but the solid only partially dissolved. The undissolved portion was filtered off and dried over phosphoric oxide in a vacuum. It slowly evolved bromine at the ordinary temperature, and could not be recrystallised from any solvent without decomposition; it appears to be a bromine additive product of a partially substituted ethylenediamine. As its composition varied with the manner of drying and the length of time it was kept, it was not further investigated.

The filtered chloroform solution, on drying and evaporating off the solvent, deposited the ethylenetetrabromoamine as a beautifully crystalline, orange-coloured solid. When crystallised from chloroform, in which it is easily soluble, it separated in brilliant, orange-red, short, six-sided, flattened prisms with domed ends.

0.4084 liberated I = 86.8 c.c. *N*/10 I. Br (as NBr) = 84.97.

$C_2H_4N_2Br_4$ requires Br (as NBr) = 85.07 per cent.

It melts at 62°, and if heated a few degrees higher gives off gas, and almost at once explodes with a very violent detonation. It remains unchanged for some days in a dry atmosphere, but if kept for several weeks slowly decomposes giving off bromine and leaving behind a black, tarry mass.

s-Diacetythylenedichlorodiamine,
 $CH_3 \cdot CO \cdot NCl \cdot CH_2 \cdot CH_2 \cdot NCl \cdot CO \cdot CH_3$.

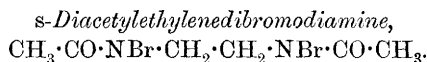
s-Diacetythylenediamine was dissolved in water and mixed with an excess of a solution of hypochlorous acid made by dissolving potass-

ium hydrogen carbonate in a solution of sodium hypochlorite. The dichloroamine produced, being soluble in water, remained dissolved, and was extracted by shaking the solution several times with chloroform. After separating and drying the chloroform solution with calcium chloride, the solvent was driven off in a current of air, when the dichloroamine was left as a white, crystalline mass; it is moderately soluble in chloroform, very sparingly so in petroleum. It was dissolved in chloroform, and a little warm petroleum added, when it crystallised in short, colourless, transparent prisms terminated by pyramids (m. p. 94°).

0.2190 liberated I = 41 c.c. $N/10$ I. Cl as $NCl = 33.18$.

$C_6H_{10}O_2N_2Cl_2$ requires Cl as $NCl = 33.27$ per cent.

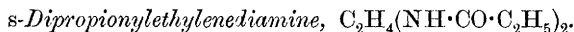
It is a comparatively stable substance, but decomposes slightly, giving off chlorine, when kept for some months, even in a dry atmosphere and when the light is excluded.



This compound was prepared and crystallised exactly as the corresponding dichloroamine, using, however, a decinormal solution of hypobromous acid made by shaking precipitated mercuric oxide suspended in water with bromine; it crystallises in short, transparent, very pale yellow prisms. On heating, it reddens and melts at about $150-155^{\circ}$, giving off bubbles of gas, and almost immediately explodes.

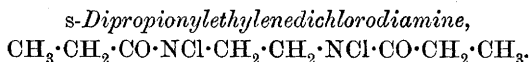
0.2418 liberated I = 31.9 c.c. $N/10$ I. Br as $NBr = 52.74$.

$C_6H_{10}O_2N_2Br_2$ requires Br as $NBr = 52.94$ per cent.



This and a number of other diacyl derivatives of the aliphatic diamines not previously described were prepared by adding the diamine cautiously to the calculated quantity of the corresponding acid anhydride or chloride dissolved in ether. After the first vigorous action, which was always accompanied by the separation of the diacyl derivative, was over the product was warmed on the water-bath to drive off the ether and the residue heated for a short time with an aqueous solution of the calculated quantity of potassium hydrogen carbonate. The product was then recrystallised from a suitable solvent, chloroform, alcohol, or glacial acetic acid being used according to the solubility of the compound.

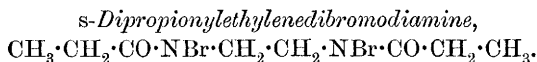
s-Dipropionylethylenediamine crystallises from alcohol, in which it is easily soluble, in small, colourless plates (m. p. 192°).



This compound was prepared by shaking a solution of *s*-dipropionylethylenediamine in chloroform with excess of a solution of hypochlorous acid and treating as before; it was obtained as a pale yellow, limpid, highly refractive liquid with a smell resembling hypochlorous acid; it showed no sign of crystallisation, even after standing in a vacuum over phosphoric oxide for several weeks. When strongly heated, it decomposes almost explosively.

0.3244 liberated I = 53.7 c.c. *N*/10 I. Cl as NCl = 29.34.

$\text{C}_8\text{H}_{14}\text{O}_2\text{N}_2\text{Cl}_2$ requires Cl as NCl = 29.41 per cent.

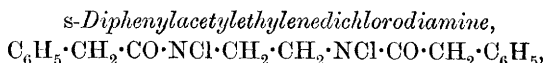


This compound, prepared as previously described, crystallises in transparent, slender, flattened, pale yellow prisms; it melts at 112° and when more strongly heated decomposes explosively at about 160°.

0.2306 liberated I = 27.9 c.c. *N*/10 I. Br as NBr = 48.37.

$\text{C}_8\text{H}_{14}\text{O}_2\text{N}_2\text{Br}_2$ requires Br as NBr = 48.44 per cent.

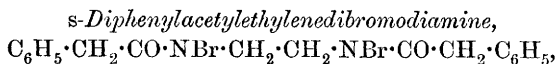
s-Diphenylacetylenediamine, $\text{C}_2\text{H}_4(\text{NH} \cdot \text{CO} \cdot \text{CH}_2 \cdot \text{C}_6\text{H}_5)_2$, crystallises from alcohol, in which it is moderately soluble, in large, thin, glittering, six-sided, colourless plates (m. p. 207°).



prepared as previously described, is obtained as a viscid, oily, pale yellow liquid which very slowly solidifies; it crystallises from a mixture of chloroform and light petroleum in small, colourless, four-sided plates which melt at 65°.

0.3978 liberated I = 43.1 c.c. *N*/10 I. Cl as NCl = 19.2.

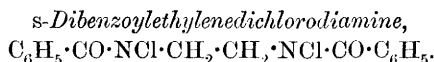
$\text{C}_{18}\text{H}_{13}\text{O}_2\text{N}_2\text{Cl}_2$ requires Cl as NCl = 19.42 per cent.



crystallises from a mixture of chloroform and petroleum in clusters of transparent, very pale yellow plates; it melts at 128°, and if heated rapidly above this temperature explodes at about 150°.

0.2272 liberated I = 19.8 c.c. *N*/10 I. Br as NBr = 34.84.

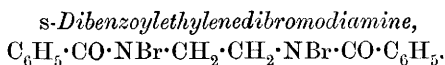
$\text{C}_{18}\text{H}_{18}\text{O}_2\text{N}_2\text{Br}_2$ requires Br as NBr = 35.21 per cent.



This compound was prepared by slowly adding an excess of a solution of bleaching powder to a well-cooled solution of *s*-dibenzoylthylenediamine in glacial acetic acid. The dichloroamine, which separated at first as a yellow, viscid liquid, was extracted with chloroform, and this solution shaken with a fresh solution of hypochlorous acid made from potassium hydrogen carbonate and sodium hypochlorite. On separating and drying the solution, and driving off the chloroform in a current of air, the dichloroamine was left as a beautifully crystalline solid. It crystallises from chloroform, in which it is sparingly soluble, in glittering, transparent, colourless, four-sided, rhombic plates, which are apparently flattened rhombs. It melts at 162° , and when heated a few degrees higher decomposes, giving off bubbles of gas.

0.3160 liberated I = 37.7 c.c. $N/10$ I. Cl as NCl = 21.14 .

$\text{C}_{16}\text{H}_{14}\text{O}_2\text{N}_2\text{Cl}_2$ requires Cl as NCl = 21.03 per cent.

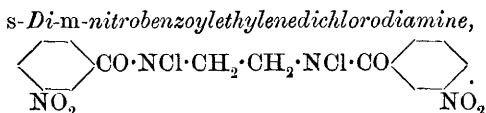


This compound was prepared by adding a solution of *s*-dibenzoylthylenediamine in glacial acetic acid to a well-cooled solution of hypobromous acid. The solid which separated was dissolved in glacial acetic acid and the solution again added to well-cooled hypobromous acid solution. The dibromoamine was then dried and recrystallised from chloroform, in which it is sparingly soluble; it crystallises in small, brilliant, transparent, four-sided, very pale yellow plates. When quickly heated at about 180 – 182° , it melts with reddening and decomposition, but the melting point varies with the time taken in heating, as decomposition begins before the compound melts.

0.3032 liberated I = 28.4 c.c. $N/10$ I. Br as NBr = 37.45 .

$\text{C}_{16}\text{H}_{14}\text{O}_2\text{N}_2\text{Br}_2$ requires Br as NBr = 37.53 per cent.

s-Di-*m*-nitrobenzoylthylenediamine, $\text{C}_2\text{H}_4(\text{NH} \cdot \text{CO} \cdot \text{C}_6\text{H}_4 \cdot \text{NO}_2)_2$, crystallises from glacial acetic acid, in which it is very sparingly soluble, in small, colourless needles with a faint yellow tint (m. p. 257°).



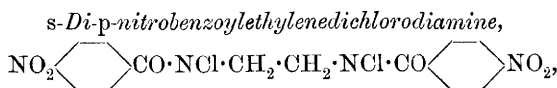
This and the other dichloroamines derived from diacyl compounds only sparingly soluble in glacial acetic acid were prepared by rapidly

adding bleaching-powder solution to a warm solution of the amide in glacial acetic acid. It crystallises from chloroform, in which it is very sparingly soluble, in brilliant, small, transparent, colourless plates with a slight yellow tint. It melts at 173° , and on further treating remains apparently unchanged up to 220° , but when heated rapidly in a flame decomposes explosively.

0.2236 liberated I = 20.8 c.c. $N/10$ I. Cl as $NCl = 16.49$.

$C_{16}H_{12}O_6N_4Cl_2$ requires Cl as $NCl = 16.6$ per cent.

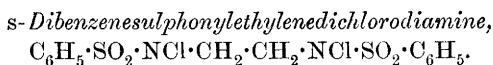
s-Di-*p*-nitrobenzoylethylenediamine, $C_2H_4(NH \cdot CO \cdot C_6H_4 \cdot NO_2)_2$, crystallises from glacial acetic acid, in which it is sparingly soluble, in pale yellow, irregularly grown prisms (m. p. 254°).



is very sparingly soluble in chloroform, from which it crystallises in small, colourless plates with a faint yellow tint (m. p. 207°). When heated more strongly, it decomposes with evolution of gas at about 215° , and explodes when rapidly heated in a flame.

0.1325 liberated I = 12.4 c.c. $N/10$ I. Cl as $NCl = 16.59$.

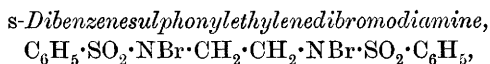
$C_{16}H_{12}O_6N_4Cl_2$ requires Cl as $NCl = 16.6$ per cent.



This compound was prepared by adding bleaching-powder solution to a solution of the amide in glacial acetic acid, extracting with chloroform, and treating as before described; it crystallises from a mixture of chloroform and light petroleum in clusters of slender, colourless prisms. It melts at 113° and can be heated to 200° with very slight decomposition; when heated strongly in a flame, it decomposes explosively.

0.2787 liberated I = 27.2 c.c. $N/10$ I. Cl as $NCl = 17.3$.

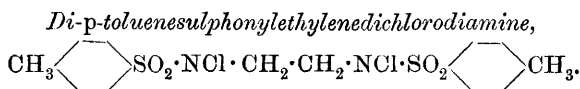
$C_{14}H_{14}O_4N_2Cl_2S_2$ requires Cl as $NCl = 17.32$ per cent.



crystallises from a mixture of chloroform and light petroleum in clusters of pale yellow prisms (m. p. 134°). On heating above this temperature, it decomposes, reddening and evolving gas at about 160 — 175° . When heated rapidly in a flame, it explodes.

0.3667 liberated I = 29.4 c.c. *N*/10 I. Br as NBr = 32.05.

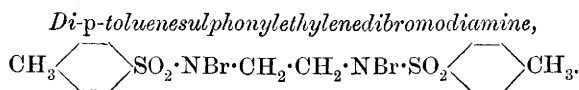
$C_{14}H_{14}O_4N_2Br_2S_2$ requires Br as NBr = 32.1 per cent.



This compound is moderately easily soluble in chloroform, and crystallises in long, colourless, very slender prisms. It melts at 136° and can be heated to 200° with no apparent change, but at 200—210° it decomposes rapidly with evolution of gas.

0.3524 liberated I = 32.3 c.c. *N*/10 I. Cl as NCl = 16.24.

$C_{16}H_{18}O_4N_2Cl_2S_2$ requires Cl as NCl = 16.21 per cent.

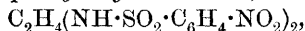


This compound crystallises extremely well in clusters of pale yellow, transparent, glittering plates; it melts at 165°, and, on heating to about 170°, it reddens and begins rapidly to decompose, evolving bubbles of gas; if heated rapidly at about 180°, it explodes.

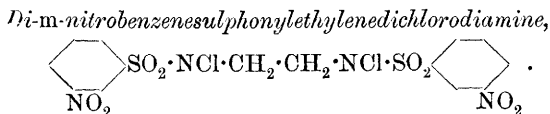
0.3087 liberated I = 23.4 c.c. *N*/10 I. Br as NBr = 30.31.

$C_{16}H_{18}O_4N_2Br_2S_2$ requires Br as NBr = 30.39 per cent.

Di-m-nitrobenzenesulphonylethylenediamine,



crystallises from glacial acetic acid in very small, colourless plates with a faint yellow tint and melts somewhat indefinitely at 189—191°.



This compound, which was prepared by adding bleaching-powder solution in excess to a hot solution of the amide in glacial acetic acid, is so sparingly soluble in chloroform that it was recrystallised from glacial acetic acid, in which it is moderately soluble; it crystallises in very small, short, pale yellow prisms (m. p. 198°). When heated to 220°, it apparently undergoes little decomposition, the melted substance only slightly reddening; it explodes, however, when heated in a flame.

0.2820 liberated I = 22.4 c.c. *N*/10 I. Cl as NCl = 14.08.

$C_{14}H_{12}O_8N_4Cl_2S_2$ requires Cl as NCl = 14.26 per cent.

Dibenzoyltrimethylenedichlorodiamine,
 $\text{C}_6\text{H}_5 \cdot \text{CO} \cdot \text{NCl} \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{NCl} \cdot \text{CO} \cdot \text{C}_6\text{H}_5.$

The trimethylene-dichlorodiamines and -dibromodiamines are prepared as easily as those derived from ethylenediamine and by similar methods. Dibenzoyltrimethylenedichlorodiamine is easily soluble in chloroform, and crystallises from a mixture of this with light petroleum in brilliant, colourless plates; it melts at 84° and decomposes violently when rapidly heated to about 160° .

0.3005 liberated I = 34.3 c.c. *N*/10 I. Cl as NCl = 20.23.

$\text{C}_{17}\text{H}_{16}\text{O}_2\text{N}_2\text{Cl}_2$ requires Cl as NCl = 20.19 per cent.

Dibenzenesulphonyltrimethylenediamine, $\text{C}_3\text{H}_6(\text{NH} \cdot \text{SO}_2 \cdot \text{C}_6\text{H}_5)_2.$

This compound crystallises from alcohol, in which it is very easily soluble, in long, colourless plates (m. p. 96°).

Dibenzenesulphonyltrimethylenedichlorodiamine,
 $\text{C}_3\text{H}_6(\text{NCl} \cdot \text{SO}_2 \cdot \text{C}_6\text{H}_5)_2.$

This compound is easily soluble in chloroform; it crystallises from this solvent mixed with light petroleum in small, transparent, colourless plates (m. p. 134°).

0.2668 liberated I = 25.3 c.c. *N*/10 I. Cl as NCl = 16.81.

$\text{C}_{15}\text{H}_{16}\text{O}_4\text{N}_2\text{Cl}_2\text{S}_2$ requires Cl as NCl = 16.75 per cent.

Other diamines, for example, pentamethylenediamine, and their acyl derivatives yield similarly chloroamino- and bromoamino-derivatives. These resemble in general properties the compounds previously described, but have not been yet obtained in a well-crystallised form, probably on account of the diamines used not being perfectly pure, for it has been noted with all other classes of substituted nitrogen chlorides and bromides that the difficulty of obtaining a crystalline product is very greatly increased by quite an insignificant amount of impurity.

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