XIV.—*Transformations of Highly Substituted Nitro-aminobenzenes. II. s-Tribromo-1-nitroamino-benzene.*

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IN earlier papers (Trans., 1902, 81, 806; 1905, 87, 389) we described certain reactions which are exhibited by *s*-trichloro-1-nitroaminobenzene when treated with sulphuric acid in acetic acid solution. It was shown that within certain limits of temperature and concentration of the sulphuric acid, the nitroamine yielded some 30—35 per cent. of a *s*-trichlorophenyliminotrichlorobenzoquinone (hexachloroquinoneanil). It was found possible, in bringing about this change, to avoid any displacement of chlorine by the nitro-group, and consequent

formation of a dichloronitroaniline. In the case of the corresponding *s*-tribromo-1-nitroaminobenzene, on the other hand, it was observed that there was a far greater tendency for the bromine atom to leave the benzene nucleus, and in preliminary experiments such treatment as that described led mainly to the production of 2:6-dibromo-4-nitroaniline.

A number of experiments have, however, led to the discovery that *s*-tribromonitroaminobenzene will under narrowly-defined conditions yield phenyliminobenzoquinones analogous to those obtained from *s*-trichloronitroaminobenzene. This change is effected by solutions of sulphuric acid in acetic acid containing a certain small percentage of water. The concentration of sulphuric acid, which has been found most suitable, is 0.6 of sulphuric acid to 1 of acetic acid; with such a solution the reaction is brought to completion in one to two hours; higher concentrations of acid hasten the decomposition, but then the dibromonitroaniline is the main product. At lower concentrations the decomposition is so slow that secondary reactions greatly decrease the yield of the quinoneanil. Using the most favourable concentrations of sulphuric acid, it is only possible to obtain the quinoneanils if the temperature is kept as low as possible, that is, at the freezing point of the solution; at higher temperatures, the formation of nitroaniline again predominates. Addition of small quantities of water to the reacting mixture decreases the rate of the decomposition, but, at the same time, there is a falling off in the formation of the nitroaniline. About 4 per cent. of water is the most favourable concentration for the formation of the quinoneanil.

Although it is possible to prevent the formation of the dibromonitroaniline, the elimination of a certain proportion of bromine could not be avoided. As a result, a mixture of quinoneanils is obtained, in which the *s*-tribromophenyliminodibromobenzoquinone largely predominates over the *s*-tribromophenyliminotribromobenzoquinone.

This elimination of bromine and consequent formation of pentabromoquinoneanil is of considerable interest and throws some light on the mechanism of the formation of the quinoneanil from the nitroamine. The conversion of *s*-trichloronitroaminobenzene into a *s*-tri-

atom from one carbon atom to the neighbouring carbon atom in the benzene ring. The like holds for the formation of a hexabromo-

quinoneanil from the tribromonitroaminobenzene. But in the transformation of the bromo-compound, although the bromine is set free from its original point of attachment, only a certain proportion, and that the smaller, re-enters the benzene nucleus. In the case of the trichloronitroamine, a complete re-entrance of the chlorine may take place; nevertheless, since at higher temperatures the presence of chlorine in small quantity can be detected among the products of the reaction, the difference between the tribromo- and trichloro-nitroamines is rather one of degree.

The other characters of the decomposition of the tribromonitroaminobenzene generally resemble those of the trichloro-compound (*loc. cit.*); the quinoneanil represents some 30—35 per cent. of the nitroamine, and an equivalent amount of ammonia is produced. The remainder of the nitroamine is represented by *s*-tribromobenzene-diazonium salts. The proportion of penta- and hexa-bromoquinoneanil appears to vary considerably in different experiments, but the latter never exceeds a small percentage of the solid product of the reaction.

The constitution of the pentabromoquinoneanil partly follows from the cleavage with sulphuric acid, when it yields *s*-tribromoaniline and 2:6-dibromobenzoquinone. It is accordingly represented

The halogen derivatives of 4-hydroxydiphenylamine are, with the exception of a tetrachlorohydroxydiphenylamine (prepared indirectly by Jacobson, *Chem. Centr.*, 1898, ii, 36), unknown. Notwithstanding that hydroxydiphenylamine itself is prepared very easily by Calm's method from aniline and quinol, there is no record of attempts at chlorination and bromination. We hoped to obtain the bromohydroxydiphenylamines, which are produced from the nitroamine, by direct bromination; to that end many experiments have been made, but it has been found that the bromination is no simple matter; such results as have been achieved will be shortly recorded.

The study of the transformations of the nitroamines is being continued.

EXPERIMENTAL.

Decomposition of s-Tribromonitroaminobenzene.

The products of the decomposition of *s*-tribromonitroaminobenzene (which was prepared by the method previously recorded, *Trans.*, 1902, 81, 808) in acetic acid solution by sulphuric acid are very dependent on the conditions, namely, temperature, and the amounts of water and sulphuric acid present.

Generally speaking, the higher the temperature, and the larger the amount of sulphuric acid, the larger is the proportion of 2 : 6-dibromonitroaniline produced, and consequently of bromine eliminated. When the proportion (by weight) of the sulphuric acid to the acetic acid is above 1 : 1, the aniline is the main product; with lower proportions of sulphuric acid, but at slightly elevated temperatures, 20° to 30°, a similar result follows.

The 2 : 6-dibromo-4-nitroaniline was obtained in characteristic yellow crystals melting at 203°, and sparingly soluble in alcohol.

0.1654 gave 0.2092 AgBr. Br = 53.85.

$C_6H_4O_2N_2Br_2$ requires Br = 54.04 per cent.

As the proportion of sulphuric acid is decreased to 0.6 : 1, and rising of the temperature above freezing point of the solution prevented, the rate of the decomposition becomes slower; at the same time the yield of the nitroaniline decreases, and, with the concentration of the sulphuric acid just mentioned, is very small, a red substance (a mixture of bromoquinoneanils) being now the main solid product. Further lowering of the proportion of sulphuric acid is followed by such a decrease in the speed of the decomposition, that the nitroamine only disappears entirely after many hours' standing.

The effect of addition of water to the mixture is mainly to decrease the rate of the decomposition, but at the same time with a given concentration of sulphuric acid the production of dibromonitroaniline is less. A mixture of 30 grams of acetic acid and 18 grams of sulphuric acid, in which 1 gram of nitroamine was dissolved, contained no nitroamine after forty minutes, when so much water was present as to produce a 2 per cent. solution. If, however, the concentration of the water was 4 per cent., the time required for complete decomposition was one hour and twenty minutes. In the latter case, only a trace of dibromonitroaniline was formed, whilst in the solution containing 2 per cent. of water some 5 per cent. of the nitroamine is converted into the nitroaniline.

Preparation of the Red Solid (Mixture of Bromoquinoneanils).—In order to prepare the mixture of bromoquinoneanils as free from di-

bromonitroaniline as possible, the following procedure was finally adopted.

A solution of 50 c.c. of concentrated sulphuric acid (95 per cent.) in 50 c.c. acetic acid was slowly added to a solution of 5 grams of the nitroamine in 100 c.c. of acetic acid, the liquid being well stirred and cooled until a slight separation of the solid solvent occurred. The first addition of the sulphuric acid led to the development of a bluish-green colour, which finally changed to a deep olive-green. The liberation of bromine during the addition was very obvious. The mixture was allowed to stand, generally for about one hour, and then poured on to ice, when a red solid separated; this was collected and washed free from acid with water. Any unchanged nitroamine was removed by digestion with cold aqueous sodium carbonate; the red solid was then dried over sulphuric acid in an evacuated desiccator.

Examination of the Filtrate from the Red Solid.—The acid filtrate was of a yellow colour and had a strong odour of bromine. The estimation of the amount of bromine showed that some 26 per cent. of one atomic preparation of the bromine in the nitroamine had been eliminated.

The presence of *s*-tribromobenzenediazonium salt in the filtrate could be demonstrated by coupling, but was most clearly shown by conversion of the diazo-compound into *s*-tribromobenzene. To this end, an aliquot part of the filtrate was heated with one-third of its volume of alcohol. On cooling, *s*-tribromobenzene crystallised in long needles melting at 119—120°.

Separation of the Bromoquinoneanils.—Although it is not difficult to obtain the pure pentabromoquinoneanil, albeit with considerable loss, from the red solid, the separation of both the penta- and hexa-bromoquinoneanils is a matter of great difficulty. Repeated crystallisation from alcohol, acetic acid, or light petroleum, finally yielded a small quantity of the pentabromo-derivative of the correct melting point, 171°. The mother liquors deposited a substance, melting indefinitely between 135° and 150°, which could not be further dealt with by simple crystallisation.

The following method of treating the red solid has proved the most successful. The solid was extracted four or five times with small quantities of boiling light petroleum (b. p. 95°). The melting point of the undissolved residue gradually rose from 135—140°, the original melting point, to 160°. This residue was then dissolved in a mixture of equal volumes of benzene and petroleum, from which solution the pentabromoquinoneanil separated in the pure state, melting at 171°.

2 : 4 : 6-Tribromophenyliminodibromobenzoquinone (Pentabromo-

quinoneanil), (†), crystallises in very dark red

needles with a bronze lustre; these needles are sometimes aggregated in stellate clusters, at other times they develop into well-formed prisms. It is readily soluble in chloroform, acetone, or benzene, and very sparingly so in acetic acid, alcohol, or petroleum. It is best crystallised from petroleum (b. p. 120°) or from a mixture of benzene and petroleum. On analysis:

0.1509 gave 0.1390 CO₂ and 0.0150 H₂O. C = 25.12; H = 1.104.

0.2107 „ 0.3442 AgBr. Br = 69.35.

0.3096 „ 6.8 c.c. moist nitrogen at 8.8° and 748 mm. N = 2.625.
C₁₂H₄ONBr₅ requires C = 24.92; H = 0.7; N = 2.43; Br = 69.18 per cent.

Pentabromoquinoneanil can be hydrolysed by dissolving in excess of concentrated sulphuric acid or by boiling with a 30 per cent. solution of sulphuric acid in acetic acid. In the latter case, a few minutes' boiling is necessary. On cautious addition of water, *s*-tribromoaniline separates in a nearly pure condition; the 2:6-dibromobenzoquinone can be extracted from the diluted mother liquor by means of chloroform or ether, and purified by crystallisation from dilute alcohol; it crystallised in golden-yellow plates melting at 122°, and did not lower the melting point of a specimen of 2:6-dibromoquinone.

2:4:6-Tribromophenyl-2':6'-dibromo-4-hydroxyphenylamine,

—To a solution of the pure pentabromoquinoneanil (m. p. 171°) in acetone an equal weight of zinc dust was added, and glacial acetic acid was dropped in until the solution became colourless. After filtering, water was added, when a white solid, melting at 154°, separated; from its hot solution in petroleum it crystallised in clusters of long, silky needles melting at 155–156°:

0.1931 gave 0.3130 AgBr. Br = 68.96.

C₁₂H₆ONBr₅ requires Br = 68.94 per cent.

The pentabromohydroxydiphenylamine is readily soluble in chloroform, benzene, or alcohol, and moderately so in glacial acetic acid; in petroleum it is but sparingly soluble. Dilute aqueous sodium hydroxide dissolves it freely.

The hydroxydiphenylamine can be readily reconverted into the

quinoneanil by oxidation with mercuric oxide in benzene solution, or by chromic acid in acetic acid solution.

2 : 4 : 6-Tribromophenyliminotribromobenzoquinone (*Hexabromoquinoneanil*) and 2 : 4 : 6-Tribromophenyltribromo-4-hydroxyphenyl-

amine, $\text{Br} \begin{array}{c} \text{Br} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_2\text{Br}_3 \cdot \text{N} : \text{C}_6\text{HBr}_3\text{O} \\ \diagdown \quad \diagup \\ \text{Br} \end{array}$ and $\text{Br} \begin{array}{c} \text{Br} \\ \diagup \quad \diagdown \\ \text{C}_6\text{H}_2\text{Br}_3 \cdot \text{NH} : \text{C}_6\text{HBr}_3\text{OH} \\ \diagdown \quad \diagup \\ \text{Br} \end{array}$.—The

hexabromoquinoneanil was contained in the petroleum extracts of the original red solid. On recrystallising the material, which was obtained on evaporating this solution from petroleum, a substance was obtained melting at 143—144°. Further recrystallisation failed to change the melting point. Analysis showed that it was a mixture of the penta- and hexa-bromoquinoneanils; thus, bromine was found 70·61 and 70·74 per cent., whilst the pentabromo-derivative requires 69·18 and the hexabromo-derivative 73·04. A separation was only effected by reducing the quinoneanils to the corresponding hydroxydiphenylamines.

This reduction was carried out in the manner above described, by zinc dust in acetone solution. The hydroxydiphenylamines were precipitated by water from the acetone solution, and then extracted with small quantities of hot alcohol. A residue was left which melted at 195°; recrystallisation from chloroform or glacial acetic acid raised the melting point to 207°. Analysis showed that this was the pure hexabromohydroxydiphenylamine :

0·184 gave 0·1491 CO_2 and 0·0163 H_2O . C = 22·1; H = 0·98.

0·1935 gave 0·3304 AgBr. Br = 72·66.

$\text{C}_{12}\text{H}_5\text{ONBr}_6$ requires C = 21·86; H = 0·77; Br = 72·82 per cent.

This hexabromohydroxydiphenylamine is sparingly soluble in all solvents; it crystallises extremely well from chloroform in long, white, silky needles, and from glacial acetic acid in prisms. It dissolves freely in dilute aqueous sodium hydroxide.

The alcoholic extracts of the mixture of hydroxydiphenylamines yielded on evaporation a somewhat impure pentabromohydroxydiphenylamine; it was oxidised to the corresponding quinoneanil which, after one recrystallisation from petroleum, melted at 171°, the melting point of the pentabromoquinoneanil.

Hexabromoquinoneanil.—The hexabromohydroxydiphenylamine was converted into the corresponding quinoneanil in the following manner. 0·75 gram of the hydroxy-compound was suspended in 25 c.c. of pure benzene and a slight excess of yellow mercuric oxide added. On warming the mixture, the hydroxydiphenylamine slowly dissolved. For complete oxidation several hours warming is required. On the other hand it is inadvisable to use excess of mercuric oxide, as

other changes are thereby induced. After filtering the solution, the quinoneanil is obtained in deep red, six-sided prisms on evaporation.

This oxidation can also be conveniently carried out with chromic acid in acetic acid solution. Owing to the insolubility of the hydroxydiphenylamine a large volume of solvent must be used. A slight excess of chromic acid dissolved in acetic acid is added to the solution of the hydroxydiphenylamine, the temperature being maintained at 20—30°; a higher temperature is to be avoided. On adding water, the quinoneanil crystallises in scarlet needles.

Hexabromoquinoneanil is more readily soluble in all solvents than the pentabromo-derivative. It crystallises in prisms when its solution in cold benzene is slowly evaporated, and in small aggregates of needles from its solution in hot petroleum. It is remarkable that the latter crystals are pale red, whilst the prisms are a deep port-wine colour. The compound melts at 134—135°:

0.15 gave 0.256 AgBr. Br = 72.61.

$C_{12}H_3ONBr_6$ requires Br = 73.04 per cent.

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