Orientation Effects in the Diphenyl Series. Part XIV. The Thermal Decomposition of Some "Diazoperbromides."*

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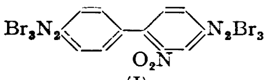
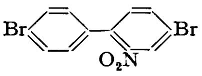
The bisdiazonium perbromide derived from 2-nitrobenzidine decomposes in hot glacial acetic acid to give 2′ : 4 : 4′-tribromo- and 4 : 4′-dibromo-2-nitrodiphenyl. The tribromo-compound appears to be formed by an intramolecular mechanism.

It was observed by Le Fèvre and Turner (*J.*, 1926, 2041) that the bisdiazonium perbromide (I) derived from 2-nitrobenzidine behaved abnormally when allowed to decompose in hot glacial acetic acid, the product most easily isolated being a tribromonitrodiphenyl, m. p. 195—196°, instead of the expected 4 : 4′-dibromo-2-nitrodiphenyl (II), m. p. 124°. Shaw and Turner (*J.*, 1932, 285) obtained the dibromo-compound and no tribromo-compound by carrying out the decomposition in boiling ethanol (cf. Saunders, *Amer. Chem. J.*, 1891, **13**, 496). The tribromo-compound was regarded by Le Fèvre and Turner as being 3′ : 4 : 4′-tribromo-2-nitrodiphenyl (III) since (*a*) it seemed inconceivable that the third bromine atom had entered the nucleus bearing the nitro-group and (*b*) by analogy with the nitration of 4 : 4′-dibromo-2-nitrodiphenyl, 3′-substitution seemed to be more probable than 2′-substitution. The most interesting thing, of course, was the entry of the third bromine atom into what would be regarded as a non-reactive system.



(I)



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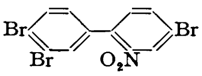
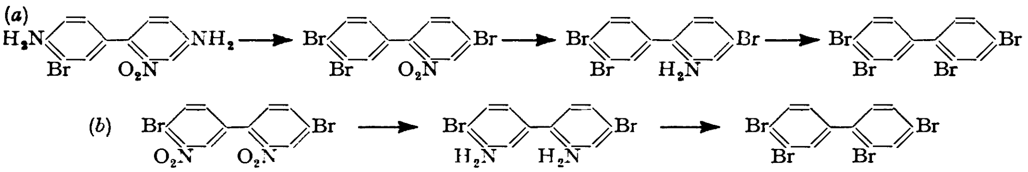
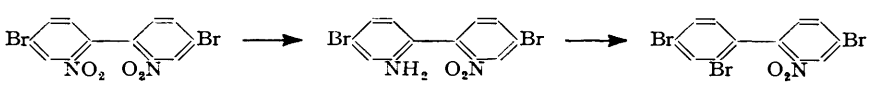


(III)

Reduction of the tribromo-compound gave a tribromo-aminodiphenyl, m. p. 154°, and replacement of the amino-group in this compound by bromine gave a tetrabromodiphenyl, m. p. 273°, different from 2 : 3′ : 4 : 4′-tetrabromodiphenyl, m. p. 124—125°, which was obtained from 3-bromo-2′-nitrobenzidine or from 2 : 3′-diamino-4 : 4′-dibromodiphenyl by routes *a* and *b*;



It thus seemed clear that the compound, m. p. 195—196°, must be 2′ : 4 : 4′-tribromo-2-nitrodiphenyl (IV). This has been proved by performing the operations shown below :



(IV)

The product was identical with the compound of m. p. 195—196° and was convertible in two stages into 2 : 2′ : 4 : 4′-tetrabromodiphenyl, m. p. 273°. The latter was also obtained by carrying out a benzidine rearrangement on 2 : 2′-dibromohydrazobenzene, followed by a diazonium perbromide replacement. It could not, however, be isolated from the mixture obtained by heating 2 : 4-dibromoiodobenzene with copper powder.

The decomposition of the bisdiazonium perbromide derived from 2-nitrobenzidine proceeds with some tar formation in boiling glacial acetic acid but has now been found to

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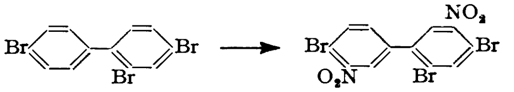
* Part XIII, *J.*, 1937, 266.

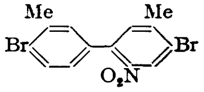
give an easily worked product when the decomposition in acetic acid is carried out at 95°. This has enabled us to make a more complete study of the decomposition, which under these conditions gives the tribromonitro-compound together with about twice its weight of 4 : 4′-dibromo-2-nitrodiphenyl. This is of some importance, as it supports the suggestion that the dibromo-compound, as such, is not the precursor of the tribromo-compound. This suggestion became more acceptable when we found that decomposition of the bisdiazonium perbromide in acetic acid in presence of one molecular proportion of the dibromo-compound gave the same yield of tribromo-compound as was obtained in absence of the dibromo-compound. Incidentally, we had already tried but failed to effect the bromination of the dibromonitro-compound by the action of bromine in boiling acetic acid solution.

It seems reasonable to conclude that in the decomposition of the bisdiazonium perbromide derived from 2-nitrobenzidine the diazonium group attached to the ring containing the nitro-group is (perhaps unexpectedly) less stable than the other diazonium group, so that bromination leading to the tribromonitro-compound occurs while the ring not containing the nitro-group retains the (*meta*-directing) diazonium grouping. Only in this way can one account for the 2′-bromination. The hitherto unknown 2 : 4 : 4′-tribromodiphenyl has been prepared from 4 : 4′-dibromo-2-nitrodiphenyl, in two stages. An attempt to obtain 2′ : 4 : 4′-tribromo-2-nitrodiphenyl by nitrating it under a number of different experimental conditions resulted in dinitration. The product appears to be 2′ : 4 : 4′-tribromo-3 : 5′-dinitrodiphenyl (V), since it reacts with hot piperidine to give a bromodinitrodipiperidinodiphenyl.

When the bisdiazonium perbromide was allowed to decompose in heated glacial acetic acid containing one molecular proportion of cinnamic acid or acetanilide or aceto-*p*-toluidide, 4 : 4′-dibromo-2-nitrodiphenyl but no tribromonitrodiphenyl was formed (cf. Bülow and Schmachtenburg, *Ber.*, 1908, **41**, 2607).



(V)



(VI)

The more general scope of the diazonium perbromide decomposition reaction has been examined in a number of cases: the perbromide derived from benzidine decomposed in boiling ethanol to give 4 : 4′-dibromodiphenyl, and in hot glacial acetic acid to give 2 : 2′ : 4 : 4′-tetrabromodiphenyl. That from 4-aminodiphenyl in boiling ethanol gave 4-bromodiphenyl, and in hot glacial acetic acid gave 4 : 4′-dibromodiphenyl. That from 2-nitro-*o*-tolidine in hot glacial acetic acid gave 4 : 4′-dibromo-3 : 3′-dimethyl-2-nitrodiphenyl (VI); this result was unexpected since the 2′-position should be more reactive than the corresponding position in the methyl-free compound. The perbromide from 4-aminodiphenyl ether in hot glacial acetic acid gave 4 : 4′-dibromodiphenyl ether.

EXPERIMENTAL

Bisdiazonium Perbromide from 2-Nitrobenzidine.—An improved method of preparing this compound was as follows: A solution of 2-nitrobenzidine (11·5 g.) in a hot mixture of 47% hydrobromic acid (72 g.) and water (144 c.c.) was cooled rapidly to about −2°. A solution of sodium nitrite (7·5 g.) in water (18 c.c.) was rapidly stirred into the paste, under the surface. After 10 min. the almost clear solution obtained was filtered and treated gradually, while being stirred, with a solution of bromine (8 c.c.) in 47% hydrobromic acid (50 c.c.). After 15 min. the orange-coloured diazonium perbromide was filtered off, washed with water, with absolute ethanol, and with dry ether and dried in a vacuum over solid potassium hydroxide and concentrated sulphuric acid (yield, 35·5 g., 96·5%).

Decomposition of the Bisdiazonium Perbromide.—(a) *In glacial acetic acid at* 95° ± 3°. The perbromide (7·33 g.) was added gradually to glacial acetic acid (40 c.c.) kept at 95° ± 3°. Then the solution was boiled until free from bromine. On cooling, a thick paste was obtained. Water was added to complete the separation of solid. The resulting paste was filtered off, washed with water, and dried at 100° and later in a vacuum (over H_2SO_4 and KOH) (yield, 3·85 g.) (Found: Br, 48·2. Calc. for $C_{12}H_6O_2NBr_3$: Br, 55·5. Calc. for $C_{12}H_7O_2NBr_2$: Br, 44·8%). By extracting twice with 50 c.c. of boiling light petroleum (b. p. 60—80°) this was freed from 4 : 4′-dibromo-2-nitrodiphenyl and gave 1·7 g. of 2′ : 4 : 4′-tribromo-2-nitrodiphenyl. Evaporation of the light petroleum extract gave 2·15 g. of almost pure dibromo-compound, which after crystallisation from ethanol had m. p. 124°, alone or mixed with 4 : 4′dibromo-2-nitrodiphenyl.

(b) *In glacial acetic acid containing* 4 : 4′-*dibromo*-2-*nitrodiphenyl.* The last experiment was repeated but with the initial addition of 3·57 g. (1 mol.) of 4 : 4′-dibromo-2-nitrodiphenyl. The yield of mixed products was 7·42 g., *i.e.*, 3·85 + 3·57 g.

(c) *In glacial acetic acid containing cinnamic acid or acetanilide or aceto*-p-*toluidide.* The perbromide was added to glacial acetic acid (at 100°) containing one of these substances (1 mol. for each mol. of perbromide). Routine methods led in each case to the isolation of 4 : 4′-dibromo-2-nitrodiphenyl, but no tribromonitrodiphenyl.

3′ : 4 : 4′-*Tribromo*-2-*nitrodiphenyl.*—3-Bromo-2′-nitrobenzidine (Lesslie and Turner, *J.*, 1933, 1590) was diazotised in hydrobromic acid solution at −4°. Addition of bromine in hydrobromic acid gave the yellow bisdiazonium perbromide. This was filtered off, washed with water, and dried in a vacuum. It was added gradually to glacial acetic acid kept at 100—110°. The solution was freed from bromine by boiling. On cooling, the *tribromonitro-compound* separated. After being crystallised from glacial acetic acid it formed leaflets, m. p. 141—142° (Found: Br, 55·0. $C_{12}H_6O_2NBr_3$ requires Br, 55·0%).

2-*Amino*-3′ : 4 : 4′-*tribromodiphenyl.*—A solution of the preceding nitro-compound in hot glacial acetic acid was treated with just over the calculated quantity of stannous chloride dissolved in concentrated hydrochloric acid. The mixture was boiled for a few minutes and then cooled, treated with excess of aqueous sodium hydroxide, and extracted with ether. The extract gave 2-*amino*-3′ : 4 : 4′-*tribromodiphenyl,* which crystallised from ethanol in needles, m. p. 78° (Found: Br, 58·8. $C_{12}H_8NBr_3$ requires Br, 59·0%).

2 : 3′ : 4 : 4′-*Tetrabromodiphenyl.*—(*a*) A solution of the aminotribromodiphenyl in glacial acetic acid was added gradually to a solution of sodium nitrite in concentrated sulphuric acid at 0°. The mixture was poured on ice and the solution obtained by filtration treated with bromine–hydrobromic acid. The precipitated perbromide was filtered off, washed, and dried in a vacuum (H_2SO_4). It was then gradually added to glacial acetic acid at 100°. The solution was freed from bromine by boiling and then cooled. The *tetrabromodiphenyl* which separated was crystallised from glacial acetic acid and formed needles, m. p. 124—125° (Found: Br, 67·5. $C_{12}H_6Br_4$ requires Br, 68·1%).

(*b*) 2 : 3′-Diamino-4 : 4′-dibromodiphenyl was diazotised in hydrochloric acid, and the bisdiazonium perbromide was precipitated in the usual way. It was decomposed in glacial acetic acid at 100°. The tetrabromodiphenyl obtained had m. p. 124—125° alone or when mixed with the product from (*a*).

2-*Amino*-2′ : 4 : 4′-*tribromodiphenyl.*—Reduction of the corresponding 2-nitro-compound, m. p. 195—196°, with stannous chloride in concentrated hydrochloric acid–glacial acetic acid, followed by normal procedure, gave the *base*, which after being crystallised from dilute alcohol (charcoal) and then from benzene formed rods, m. p. 154° (Found: Br, 58·8. $C_{12}H_8NBr_3$ requires Br, 59·1%).

2 : 2′ : 4 : 4′-*Tetrabromodiphenyl.*—(*a*) The foregoing base was diazotised by the acetic–sulphuric acid method and the diazonium perbromide formed and decomposed in the usual way. The *tetrabromo-compound* crystallised from glacial acetic acid as prisms, m. p. 273° (Found: Br, 68·2. $C_{12}H_6Br_4$ requires Br, 68·05%).

(*b*) 2 : 2′-Dibromobenzidine was diazotised and the bisdiazonium perbromide prepared, and then decomposed in hot glacial acetic acid. The tetrabromodiphenyl crystallised from the latter solvent in needles, m. p. 273° (Found: Br, 68·5%).

2-*Amino*-4 : 4′-*dibromo*-2′-*nitrodiphenyl.*—To a hot, well-stirred solution containing sulphur (1·6 g.), sodium sulphide (+$9H_2O$) (9·0 g.), and water (12 c.c.), was added an ethanolic solution of 4 : 4′-dibromo-2 : 2′-dinitrodiphenyl (10 g.). The solution was boiled for an hour, boiling water being added from time to time to maintain the volume. The solution was cooled and the orange-coloured precipitate filtered off. By extraction with dilute hydrochloric acid and precipitation with dilute aqueous ammonia and finally crystallisation from ethanol, 2-*amino*-4 : 4′-*dibromo*-2′-*nitrodiphenyl* was obtained as needles, m. p. 103—104° (Found: C, 39·8; H, 2·5; N, 7·7; Br, 42·7. $C_{12}H_8O_2N_2Br_2$ requires C, 40·0; H, 2·2; N, 7·6; Br, 43·0%).

2′ : 4 : 4′-*Tribromo*-2-*nitrodiphenyl.*—The foregoing base was diazotised by the acetic–sulphuric acid process. The diazonium perbromide was prepared, and decomposed in hot glacial acetic acid. The tribromonitrodiphenyl obtained had m. p. 195—196°, alone or when mixed with the product from 2-nitrobenzidine.

2-*Amino*-4 : 4'-*dibromodiphenyl*.—4 : 4'-Dibromo-2-nitrodiphenyl was reduced in hot acetic–hydrochloric acid solution with stannous chloride. The cooled mixture was added to excess of dilute aqueous sodium hydroxide. The solid which separated was filtered off, washed with water, and crystallised from light petroleum (b. p. 60—80°) or from ethanol. The 2-*amino*-4 : 4'-*dibromodiphenyl* formed needles, m. p. 130° (Found : Br, 48·7. $C_{12}H_9NBr_2$ requires Br, 48·9%).

2 : 4 : 4'-*Tribromodiphenyl*.—The foregoing base was diazotised by the acetic–sulphuric acid method. The diazonium perbromide was prepared and decomposed in hot acetic acid. The *tribromodiphenyl* obtained crystallised from ethanol in needles, m. p. 81° (Found : Br, 61·5. $C_{12}H_7Br_3$ requires Br, 61·4%).

Nitration of 2 : 4 : 4'-*Tribromodiphenyl*.—The tribromo-compound was dissolved in 10 parts of warm nitric acid (*d* 1·5). On cooling, a solid separated and this crystallised from ethanol in needles, m. p. 164—165° (Found : Br, 49·8. $C_{12}H_5O_4N_2Br_3$ requires Br, 49·9%). This is regarded as 2 : 4 : 4'-*tribromo*-3' : 5-*dinitrodiphenyl*. When heated with excess of piperidine for a few minutes it gave 2-*bromo*-3' : 5-*dinitro*-4 : 4'-*dipiperidinodiphenyl*(?), orange-red needles, m. p. 145—146°, from ethanol (Found : Br, 16·4. $C_{22}H_{25}O_4N_4Br$ requires Br, 16·4%).

2 : 4-*Dibromoiodobenzene*.—2 : 4-Dibromoaniline hydrochloride (29 g.) was diazotised in aqueous hydrochloric acid by aqueous sodium nitrite. The diazonium solution was added to potassium iodide solution and the solid which separated was steam-distilled from aqueous sodium hydroxide (yield, 27 g.). The dibromoiodobenzene crystallised from ethanol in needles, m. p. 45—46° (3·414 mg. gave 5·847 mg. of AgBr + AgI. Calc. for $C_6H_3Br_2I$: 5·759 mg.).

Bisdiazonium Perbromide from Benzidine.—Benzidine was diazotised in aqueous hydrochloric acid and the bisdiazonium perbromide precipitated in the usual manner, then decomposed as follows : (a) *In boiling ethanol*. The crude product after crystallisation from methanol had m. p. 164° and was identical with 4 : 4'-dibromodiphenyl. (b) *In glacial acetic acid at* 100°. The product, after crystallisation from glacial acetic acid, had m. p. 273° and was identical with 2 : 2' : 4 : 4'-tetrabromodiphenyl.

Diazonium Perbromide from 4-*Aminodiphenyl*.—The perbromide, obtained in the usual way, was decomposed as follows : (a) *In boiling ethanol*. The product, after being crystallised from benzene, had m. p. 89° and was identical with 4-bromodiphenyl. (b) *In glacial acetic acid at* 100°. The product melted at 164°, after crystallisation from methanol, and was identical with 4 : 4'-dibromodiphenyl.

Bisdiazonium Perbromide from 2-*Nitro*-o-*tolidine*.—2-Nitro-*o*-tolidine was diazotised in hydrochloric acid and the bisdiazonium perbromide prepared in the usual manner. When it was decomposed in hot glacial acetic acid it gave 4 : 4'-*dibromo*-3 : 3'-*dimethyl*-2-*nitrodiphenyl* which, after being crystallised from glacial acetic acid, formed needles, m. p. 240—241° (Found : Br, 42·2. $C_{14}H_{11}O_2NBr_2$ requires Br, 41·6%).

Diazonium Perbromide from 4-*Aminodiphenyl Ether*.—This was prepared in the normal manner. When decomposed in hot glacial acetic acid it gave 4 : 4'-dibromodiphenyl ether, which after being crystallised from ethanol had m. p. 60°.

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