CXLVII.—*Orientation Effects in the Diphenyl Series. Part VIII. The Nitration of* 4 : 4′-*Difluorodiphenyl.*

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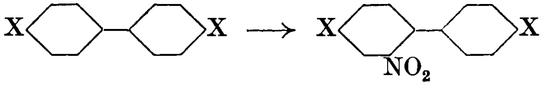
The earliest papers in this series were concerned with showing that certain 4 : 4′-disubstituted diphenyl derivatives underwent unsymmetrical dinitration. This was notably so with the dichloro- and the dibromo-compound, each of which formed first the 2-nitro-derivative, which then gave, on further nitration, the corresponding 2 : 3′-dinitro-compound.* Attention was directed to the fact that these substitutions were as nearly quantitative as possible.

At the above period, similar and comparative experiments on 4 : 4′-difluoro- and 4 : 4′-di-iodo-diphenyl had not been reported. Nevertheless it was felt that a simple application of results, obtained in other investigations of the phenomena of aromatic substitution, to the mechanism of nitration of disubstituted diphenyl derivatives consistently envisaged in this series (compare Parts I and IV) would give an accurate forecast of the facts. For instance, in a 4 : 4′-disubstituted diphenyl compound (I), the position in which the first nitro-group enters is determined only by the relative powers of X and p-X·C_6H_4 in facilitating ortho-substitution. When X is chlorine or bromine, it happens that p-chloro- or p-bromo-phenyl easily outweighs chlorine or bromine in this respect, and the 2-nitro-derivative is therefore produced (I ⟶ II). Similarly, the second entrant nitro-group is affected only by the competing ortho-facilitations of p-X-o-NO_2·C_6H_3 and X; in the examples cited, it enters the 3′-position.

(I.)


(II.)

From what is known regarding the relative orienting influences of the halogens, it would be expected that 3-mononitration should become less likely as one passes down the series: 4 : 4′-di-iodo-, 4 : 4′-dibromo-, 4 : 4′-dichloro-, 4 : 4′-difluoro-diphenyl. Actually, Hodgson (J., 1926, 2384), by the dinitration of 4 : 4′-di-iododiphenyl, obtained only the 2 : 3′-dinitro-derivative, indicating that the first nitro-group enters only the 2-position. Since, therefore,

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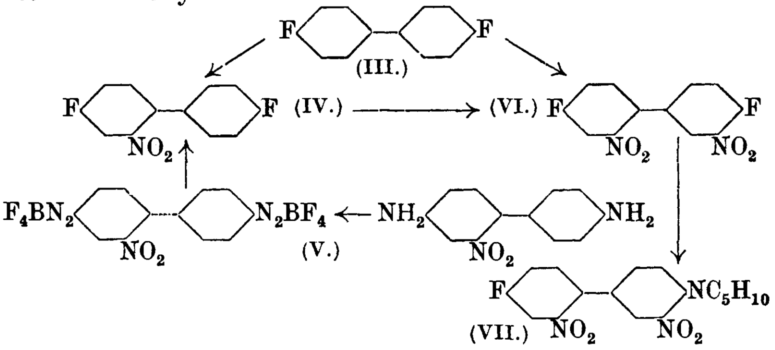
* Borsche and Scholten (*Ber.*, 1917, **50**, 609) state that the product of dinitrating 4 : 4′-dichlorodiphenyl is identical with the 4 : 4′-dichloro-2 : 2′ dinitrodiphenyl obtained by heating 2 : 5-dichloronitrobenzene with copper powder. Actually, a mixture of the two compounds concerned melts at a temperature well below the m. p. of either individual.

4 : 4′-dibromo- and -dichloro-diphenyl undergo no 3-mononitration, it seems certain that 4 : 4′-difluorodiphenyl would be nitrated quantitatively in position 2.

In the further nitration of 4 : 4′-difluoro-2-nitrodiphenyl, we should expect the second nitro-group to enter the 3′-position for three reasons : (1) By analogy with the three parallel cases in which the other halogens are present, (2) because, although it may be the weakest ortho-directing halogen, fluorine still possesses this power, and (3) because this substitution would be more open to the steric influence of the 2-nitro-group.

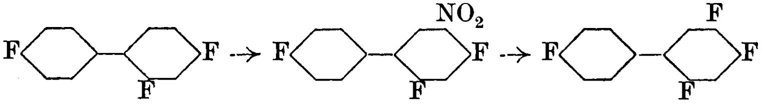
With these considerations before us, we had no doubt that Schiemann and Bolstad's statement (*Ber.*, 1928, **61**, 1403), that the nitration of 4 : 4′-difluorodiphenyl gives a 3-mononitro-derivative only, was inaccurate. Their evidence for this constitution was that by the action of potassium methoxide a methoxy-derivative was formed. For this, however, they give neither preparative details nor analyses.



We accordingly reinvestigated this problem, with the following results : 4 : 4′-Difluorodiphenyl (III), prepared by a process analogous to but simpler than that described by Schiemann and co-workers, was shown not to react with boiling piperidine. It gave a mononitro-derivative melting at 94—95°, as described by the previous investigators. This substance did not react with boiling piperidine, and was identical with 4 : 4′-difluoro-2-nitrodiphenyl (IV) obtained by thermal decomposition of the *bisdiazonium borofluoride* (V) obtained from 2-nitrobenzidine. The mononitro-compound was therefore the 2-nitro-derivative. This conclusion was confirmed by the production, on further nitration of the mononitro-compound, of a substance (also produced by dinitration of 4 : 4′-difluorodiphenyl) which rapidly reacted with piperidine, even in the cold, to give a fluorodinitropiperidinodiphenyl. The dinitro-compound must therefore be 4 : 4′-*difluoro*-2 : 3′-*dinitrodiphenyl* (VI), and that no appreciable quantity of any isomeride accompanies it is shown by the fact that the crude nitration product melts only 1° lower than the pure compound.

As the scheme on p. 1159 indicates, the nitration of 4 : 4′-difluorodiphenyl follows a course exactly similar to that of the analogous chloro- and bromo-compounds.

Schiemann and Bolstad (*loc. cit.*) converted their supposed 4 : 4′-difluoro-3-nitrodiphenyl into the corresponding amino-compound and thence into a trifluorodiphenyl by the diazoborofluoride method. These two compounds must be respectively 4 : 4′-difluoro-2-amino- and 2 : 4 : 4′-trifluoro-diphenyl. Schiemann and Roselius (*Ber.*, 1929, **62**, 1805) nitrated the trifluoro-compound, reduced the product, and again replaced the amino-group by fluorine. Their evidence for the constitution of the trifluoronitrodiphenyl consisted in showing that the derived tetrafluorodiphenyl was oxidised to *p*-fluorobenzoic acid, and they accordingly regarded it as 3 : 4 : 5 : 4′-tetrafluorodiphenyl. Accepting the evidence of oxidation, it seems probable that the reactions in question are more correctly represented as follows :



but further investigation appears desirable.

EXPERIMENTAL.

4 : 4′-*Difluorodiphenyl*.—The method described by Balz and Schiemann (*Ber.*, 1927, **60**, 1186) for the replacement of amino-groups by fluorine atoms considerably simplifies this process. We have found that the difficultly accessible hydroborofluoric acid may be replaced by the readily obtainable sodium borofluoride. The following method gave excellent results : A solution of benzidine (46 g.) in concentrated hydrochloric acid (150 c.c.) and water (150 c.c.) was bisdiazotised, a solution of 35 g. of sodium nitrite in 60 c.c. of water being used and 200 g. of ice added during the process. The solution was filtered and added to a filtered solution of 85 g. of sodium borofluoride in 150 c.c. of water. On stirring, the bisdiazonium borofluoride separated in cream-coloured needles; a further quantity was obtained on addition of more sodium borofluoride. The precipitate was collected, dried at 100°, and decomposed by being heated in an open flask, fitted with an air-condenser, the temperature being slowly raised to 150°. Steam distillation of the product gave 21 g. of pure difluorodiphenyl. After being crystallised from alcohol, it had m. p. 92—93°.

Mononitration of 4 : 4′-*Difluorodiphenyl.*—A solution of 5 g. of difluorodiphenyl in 10 c.c. of warm glacial acetic acid was cooled and treated with a mixture of 7 c.c. of nitric acid of *d* 1·4 and 2 c.c. of nitric acid of *d* 1·52. The whole was left over-night, then warmed to 60°, cooled, and glacial acetic acid added; 4·5 g. of a product, m. p. 85—95°, were obtained. After crystallisation from light petroleum–benzene, the substance had m. p. 94—95°. The 4 : 4′-difluoro-2-nitrodiphenyl so obtained depressed the m. p. of 4 : 4′-difluorodiphenyl (Found : C, 61·4; H, 2·9; N, 6·1. Calc. : C, 61·3; H, 3·0; N, 6·0%). The nitro-compound was recovered unchanged from a piperidine solution which had been boiled for several minutes.

4 : 4′-*Difluoro*-2-*nitrodiphenyl.*—2-Nitrobenzidine (11·5 g.) was warmed with 35 c.c. of concentrated hydrochloric acid until it was completely converted into the hydrochloride; 30 c.c. of water were then added. The suspension was bisdiazotised (7 g. of sodium nitrite in 12 c.c. of water) and the solution was filtered and added to a filtered solution of 30 g. of sodium borofluoride in 50 c.c. of water. After a few minutes, 2-*nitro*-4 : 4′-*diphenylylbisdiazonium borofluoride* separated as matted needles which, after being dried at 100°, became a yellow sandy powder; this turned brown at about 125° and decomposed with effervescence at 129° (Found : N, 16·5. $C_{12}H_7O_2N_5F_8B_2$ requires N, 16·4%).

Conversion of the diazonium borofluoride into the difluoronitrodiphenyl was effected by mixing it with fine purified sand, or with barium sulphate, and heating gradually in a bath to 190°, the whole operation occupying ½ hour. The mixture obtained was distilled in steam, and the cooled distillate filtered. The 4 : 4′-difluoro-2-nitrodiphenyl so isolated melted at 94—95°, either alone or when mixed with the substance obtained by the nitration of difluorodiphenyl (Found : N, 6·4, 6·3. Calc. : N, 6·0%).

Dinitration of 4 : 4′-*Difluorodiphenyl.*—The difluorodiphenyl (2 g.) was gradually added to 15 c.c. of nitric acid (*d* 1·5), kept cool in tap water. The solution was warmed to 100° during 5 minutes, cooled slightly, and treated with 2 vols. of glacial acetic acid and a little water. On being kept, it deposited crystals, which, after being crystallised from diluted acetic acid, formed cream-coloured leaflets, m. p. 109—110° (Found : C, 51·4; H, 2·1; N, 9·7. $C_{12}H_6O_4N_2F_2$ requires C, 51·4; H, 2·1; N, 10·0%).

Mononitration of 4 : 4′-*Difluoro*-2-*nitrodiphenyl.*—(*a*) The nitro-compound obtained from 2-nitrobenzidine was added to 20 parts of nitric acid (*d* 1·5), the solution obtained being heated to 100° during 5 minutes. On cooling, crystallisation set in. Glacial acetic acid was added, the whole warmed, and then allowed to cool slowly. The dinitro-compound so obtained was crystallised from diluted acetic acid, and then melted at 109—110°, either alone or when mixed with the product of the same m. p. described above.

(*b*) The mononitration product of difluorodiphenyl was gradually added to 20 parts of nitric acid (*d* 1·5), and the solution was slowly heated to 100° during 5 minutes. An equal volume of glacial acetic acid was now added, and then water, until no further precipitation occurred. The crude filtered and washed product melted at 108—109°. Crystallisation from diluted acetic acid raised the m. p. to 109—110°. A mixture of this substance with the dinitration product of difluorodiphenyl also melted at 109—110°.

Action of Piperidine on 4 : 4′-*Difluoro*-2 : 3′-*dinitrodiphenyl*.—A solution of the dinitro-compound (2 g.) in 5 c.c. of piperidine was boiled for 2 minutes to complete the reaction which began in the cold. Water was added and the solid precipitated was crystallised from alcohol, 4-*fluoro*-2 : 3′-*dinitro*-4′-*piperidinodiphenyl* being obtained as orange rhombohedra, m. p. 126·5—127·5° (Found : C, 59·0; H, 4·6; N, 12·2. $C_{17}H_{16}O_4N_3F$ requires C, 59·1; H, 4·6; N, 12·2%).

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[*Received, March* 18*th*, 1930.]