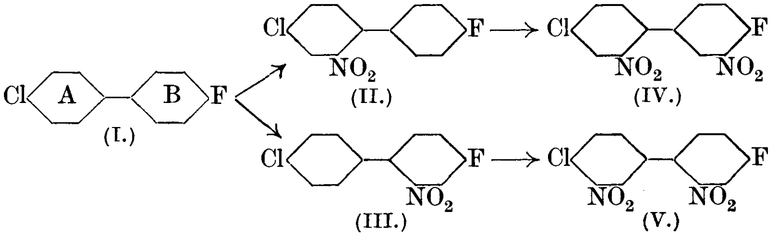
CLXXXI.—*Orientation Effects in the Diphenyl Series. Part IX. The Nitration of* 4-*Chloro*-4′-*fluoro- and* 4-*Bromo*-4′-*fluoro-diphenyl.*

By **Elizabeth Esther Jessie Marler** and **Eustace Ebenezer Turner.**

Previous work in this series has shown that the 2 : 3′-dinitration of 4 : 4′-dihalogenodiphenyls proceeds with great regularity, a fact which makes the failure (J., 1929, 509) to nitrate 4-chloro-4′-bromodiphenyl of considerable interest. The latter nitration is now being re-investigated, since we have found that 4-*chloro*-4′-*fluoro-* and 4-*bromo*-4′-*fluoro-diphenyl* are dinitrated with that facility which, apart from the exception mentioned, has been regarded as characteristic of the type in general.

The nitration of mixed dihalogenodiphenyls would be expected to take a definite course which can be predicted from a consideration of the relative deactivating effects of the various halogens. In 4-chloro-4′-fluorodiphenyl (I), nucleus B is more deactivated by the fluorine atom than is nucleus A by the chlorine atom. When mononitration is complete, therefore, the mixture of 2- and 2′-nitro-compounds (II and III) formed will consist mainly of (II). Further nitration of this substance will occur in nucleus B, and will therefore be controlled by the relative effects of the fluorine atom and the 4-chloro-2-nitrophenyl group. As a result, dinitration produces (IV), since the nitrophenyl group (whatever halogen atom it may also contain) is strongly deactivating compared with any of the halogens.

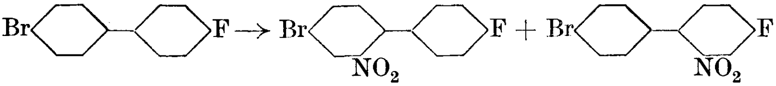


The smaller amount of mononitration giving (III) will similarly be followed in the dinitration stage by the formation of (V). There is no reason to consider the probability of (IV) and (V) being mixed with any 2 : 2′-dinitro-derivative, and satisfactory experimental vindication of this view is found in the fact that the mixture of dinitro-compounds reacted with piperidine to give a mixture the whole of which dissolved in acid.

A method for effecting the quantitative mononitration of 4 : 4′-dichloro- and 4 : 4′-dibromo-diphenyl still remains to be discovered, and it is therefore not surprising that we were unable to isolate either (II) or (III) or even a mixture of the two. Nevertheless, since (IV) can only have been formed from (II), and (V) from (III), a determination of the proportions in which (IV) and (V) are formed leads at once to quantitative information regarding the relative amounts of mononitration of (I) in nuclei A and B.

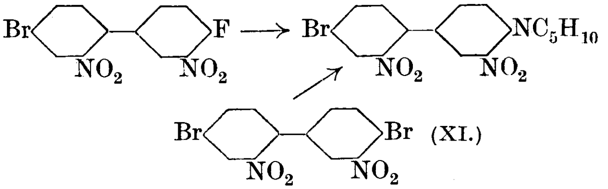
The analysis of the mixture of (IV) and (V) obtained was effected by treatment with piperidine, which gives piperidine hydrofluoride with the former and piperidine hydrochloride with the latter. Determination of the ionised chlorine formed thus provided the necessary data, which showed that 72% of mononitration occurred in nucleus A, and 28% in B.

Since the bromine atom is less deactivating than the chlorine atom (Ingold and Shaw, J., 1927, 2918), nitration of 4-bromo-4′-fluorodiphenyl (VI) should lead to even less 2′-nitration than was observed with the corresponding chlorofluoro-compound :



(VI.) (VII.) (VIII.)

Experimental investigation showed that mononitration gave 86% of (VII) and 14% of (VIII). Moreover, since the dinitration product contained so high a percentage of 4-bromo-4′-fluoro-2 : 3′-dinitrodiphenyl (IX), it was found possible to isolate from the mixture obtained after heating with piperidine an almost pure specimen of 4-bromo-2 : 3′-dinitro-4′-piperidinodiphenyl (X), capable of direct comparison with the substance obtained from 4 : 4′-dibromo-2 : 3′-dinitrodiphenyl (XI) :



(IX.) (X.) (XI.)

The 4-chloro-4′-fluorodiphenyl required for this investigation was prepared from 4 : 4′-dinitrodiphenyl, reduction of which by disodium disulphide gave 4-nitro-4′-aminodiphenyl. The method previously employed (Le Fèvre and Turner, J., 1930, 1158) for replacing an amino-group by fluorine, which has been further simplified, led to *4-fluoro-4′-nitrodiphenyl* : reduction of this gave *4-fluoro-4′-aminodiphenyl*, which was converted by the Sandmeyer reaction into 4-chloro-4′-fluorodiphenyl.

4-Bromo-4′-fluorodiphenyl was found to be more conveniently obtainable from 4-bromo-4′-nitrodiphenyl (Le Fèvre and Turner, J., 1926, 2041), followed by reduction and replacement of the amino-group by fluorine.

The results now obtained render it necessary to study the relative rates of nitration of benzene and diphenyl and similar pairs of compounds. This work is in progress.

EXPERIMENTAL.

4-*Nitro*-4′-*aminodiphenyl*.—The following method was found to be more convenient than that of Willstätter and Kalb (*Ber.*, 1906, **39**, 3479). Flowers of sulphur (14 g.) were heated with 105 g. of melted sodium sulphide nonahydrate until the sulphur had dissolved, 4 : 4′-dinitrodiphenyl (70 g.), previously ground to a paste with 300 c.c. of water, was added, and the mixture was heated on the water-bath for 5 hours, with occasional shaking. The colour gradually changed from yellow to bright orange-red. The cooled solution was filtered, and the solid well washed with boiling water and then extracted with successive small amounts of boiling dilute hydrochloric acid. The extracts were cooled, filtered, and rendered ammoniacal and the precipitated base was collected and washed with hot water. The yield of nitroaminodiphenyl, m. p. 199°, was 40 g.

In this reduction, about 1·5 times the calculated quantity of sulphide was employed. When more than this was used, benzidine was formed in considerable quantity. With the calculated amount of sulphide, reduction was far from complete.

4-*Fluoro*-4′-*nitrodiphenyl*.—A mixture of 40 g. of 4-nitro-4′-aminodiphenyl with 50 c.c. of concentrated hydrochloric acid and 50 g. of ice was diazotised with 14 g. of sodium nitrite, urea then being added to remove the excess of nitrous acid. The solution was filtered and added slowly to a cold stirred concentrated aqueous solution of sodium borofluoride which had previously been filtered. A thick cream-coloured precipitate of 4-nitrodiphenyl-4′-diazonium borofluoride separated : this was dried in the air and then over sulphuric acid in a vacuum. Considerable difficulty was experienced in the drying, as the precipitate had the consistency of mud. The complete removal of moisture is essential, otherwise some phenol is formed during thermal decomposition. The borofluoride, decomp. 130—135°, was gradually introduced into an open long-necked flask, which was heated in a metal-bath at 135—140°. Steady evolution of boron trifluoride occurred, and when this became inappreciable the coke-like residue was submitted to prolonged steam-distillation in presence of alkali : this gave 6 g. of *fluoronitrodiphenyl*, m. p.

119—121°, which crystallised from alcohol in long yellow needles, m. p. 120—121° (Found : N, 6·85. $C_{12}H_8O_2NF$ requires N, 6·45%).

4-*Fluoro-4′-aminodiphenyl*.—A solution of 4-fluoro-4′-nitrodiphenyl (5 g.) in boiling glacial acetic acid was treated with 25 c.c. of concentrated hydrochloric acid and 26 g. of stannous chloride, and the mixture was boiled for 15 minutes and cooled. After addition of excess of alkali, the mixture was extracted with ether, the ether distilled off, and the residual solid crystallised from alcohol, 4·5 g. of *fluoroaminodiphenyl*, m. p. 121°, being obtained as pale yellow, irregular leaflets (Found : N, 7·8. $C_{12}H_{10}NF$ requires N, 7·5%).

4-*Chloro-4′-fluorodiphenyl*.—4-Fluoro-4′-aminodiphenyl was diazotised in hydrochloric acid, and the solution added to cuprous chloride in hydrochloric acid. The mixture was kept for some hours, made alkaline, and steam-distilled. The *chlorofluorodiphenyl* obtained crystallised from alcohol in colourless fern-like groups of needles, m. p. 87—88° (Found : Cl, 16·9. $C_{12}H_8ClF$ requires Cl, 17·2%).

4-*Bromo-4′-fluorodiphenyl*.—4-Bromo-4′-nitrodiphenyl was obtained by brominating 4-nitrodiphenyl in glacial acetic acid (Le Fèvre and Turner, J., 1926, 2041), the condition for success being the use of not too large a quantity of the acid. The bromonitrodiphenyl was reduced with stannous chloride and hydrochloric acid.

4-*Bromo-4′-fluorodiphenyl* was prepared from 24 g. of 4-bromo-4′-aminodiphenyl, diazotised with 25 c.c. of concentrated hydrochloric acid, 25 g. of ice, and 7 g. of sodium nitrite. The filtered diazo-solution was added to a concentrated aqueous solution of 50 g. of sodium borofluoride. The dried diazonium borofluoride (35 g.) was decomposed at 100° by the method described above, and yielded, after steam-distillation, 13 g. of bromofluorodiphenyl, m. p. 97—99°. Crystallisation from alcohol gave colourless fern-like needle aggregates, m. p. 99—100° (Found : Br, 32·0. $C_{12}H_8BrF$ requires Br, 31·9%).

Dinitration of Dihalogenodiphenyls.—(a) *Qualitative*. A solution of 4-bromo-4′-fluorodiphenyl in 10 parts of nitric acid (*d* 1·5) was warmed to 100° and cooled and glacial acetic acid and water were alternately added until no further solid separated. The washed and dried material (Found : Br, 23·9. $C_{12}H_6O_4N_2BrF$ requires Br, 23·5%) was heated with piperidine for 5 minutes, and the solution diluted. The precipitate produced was completely soluble in warm hydrochloric acid, showing that mononitro- and 2 : 2′-dinitrodihalogenodiphenyl were not present. After being crystallised several times from alcohol, it gave 4-bromo-2 : 3′-dinitro-4′-piperidinodiphenyl, m. p. 134—135°, and 135—136° when mixed with the pure piperidino-compound (m. p. 136—137°). A similar experiment with 4-chloro-4′-fluorodiphenyl showed that under the above conditions none of this substance escaped dinitration; a pure specimen of an individual piperidino-derivative, however, could not be isolated.

(b) *Quantitative.* A weighed amount (about 0·01 g.-mol.) of 4-bromo-4′-fluorodiphenyl was slowly stirred with 30 c.c. of nitric acid (*d* 1·5) at room temperature. The solution obtained was heated on the water-bath for 5 minutes and allowed to cool. Water was added at such a rate that no oil was formed, and when no further precipitation occurred the solid was collected and washed with water. The solid and the filter paper were dried over sulphuric acid in a vacuum. The weighed mixture of dinitro-compounds was heated with piperidine for ½ hour at 100° and 25 c.c. of 10% potassium hydroxide solution were then added. The piperidino-compounds and the excess of piperidine were removed by thorough extraction with benzene, and the aqueous solution of potassium halides was boiled until free from traces of piperidine and benzene. It was made up to 250 c.c. and analysed by the Volhard process. In the case of 4-chloro-4′-fluorodiphenyl, approximately ⅓ of the above quantities were used throughout. The results were as follows:

Chlorofluorodinitrodiphenyl mixture.		Percentage of total chlorine.
Expt. 1	0·4701 g.	28·7
Expt. 2	0·4800 g.	28·1
		Mean 28·4

Bromofluorodinitrodiphenyl mixture.		Percentage of total bromine.
Expt. 1	2·9905 g.	14·7
Expt. 2	2·2370 g.	13·7
		Mean 14·2

Part of the cost of this investigation was defrayed from grants received from the Royal Society and the Chemical Society.

BEDFORD COLLEGE,
UNIVERSITY OF LONDON.

[*Received, March* 31*st*, 1931.]