62. *Orientation Effects in the Diphenyl Series. Part XI. A Study of the Quantitative Mono- and Di-nitration of* 4 : 4′-*Difluorodiphenyl.*

By Florence Ruth Shaw and Eustace Ebenezer Turner.

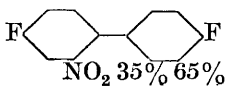
The mono- and the di-nitration of 4 : 4′-difluorodiphenyl (J., 1930, 1158) gave crude products which on qualitative examination appeared to be almost pure specimens of the 2-nitro- and the 2 : 3′-dinitro-compound, respectively. In view of the discovery (Part X, this vol., p. 285) that 4 : 4′-dichloro- and -dibromo-diphenyl, although being mononitrated solely in position 2, gave mixtures of 2 : 3′- and 2 : 2′-dinitro-compounds when nitrated further, we have investigated the difluoro-series on a quantitative basis.

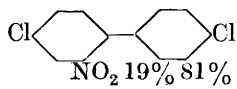
The piperidine method for determining labile halogens used in the dichloro- and dibromo-series failed in the difluoro-series owing to the uncertainty attending the precipitation of calcium or thorium fluoride from the mixtures with which we had to deal. By boiling the nitration products with a known excess of standard alcoholic

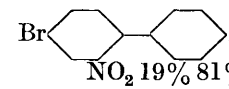
potassium hydroxide, we have obtained results which, although not accurate to the degree achieved in the dichloro- and dibromo-series, show that when 4 : 4′-difluorodiphenyl is dinitrated there is formed about 65—75% of the 2 : 3′-dinitro-compound (see below), together with 4 : 4′-*difluoro*-2 : 2′-*dinitrodiphenyl*. The latter substance had not hitherto been described, and we have prepared it from 2 : 2′-dinitrobenzidine by the diazoborofluoride method, and also by heating 4-bromo-3-nitrofluorobenzene with copper-bronze. The new compound is anomalous as regards m. p., for the melting points of the 2 : 2′-dinitro-compounds derived respectively from 4 : 4′-difluoro-, -dichloro-, and -dibromo-diphenyl are 165—166°, 138—139°, and 150°, whereas the m. p.'s of the corresponding 2-nitro-compounds are 94—95°, 102°, and 124°.

Fractional crystallisation of the dinitration product of 4 : 4′-difluorodiphenyl has now led to the isolation of a small amount of the 2 : 2′-dinitro-compound, identical with the synthetic material, but we have been unable to isolate a specimen of the 2 : 3′-isomeride essentially different from that described in Part VIII. Such a specimen has now been found to contain about 90% of the 2 : 3′-dinitro-compound, the constitution of which was previously proved by conversion into 4-fluoro-2 : 3′-dinitro-4′-piperidinodiphenyl. Further constitutive proof is given by the fact that boiling alcoholic potassium hydroxide converts the crude dinitration product into a mixture from which 4-*fluoro*-2 : 3′-*dinitro*-4′-*ethoxydiphenyl* is very readily isolated. Schiemann and Roselius (*Ber.*, 1931, **64**, 1332), in repeating our previous work, obtained a crude dinitration product which would appear, from its description, to contain phenolic material, attributable to the fact that they unduly prolonged their nitrations, which would almost certainly have produced appreciable quantities of trinitro-compounds in addition.

We have also shown that mononitration of 4 : 4′-difluorodiphenyl gives a product containing not more than 2—3% of the 3-nitro-compound. Further nitration of pure 4 : 4′-difluoro-2-nitrodiphenyl proceeds to the extent of about 64—65% in the direction of the 2 : 3′-derivative, and it is now possible to compare the mononitration of the 2-nitro-compounds in the three series :

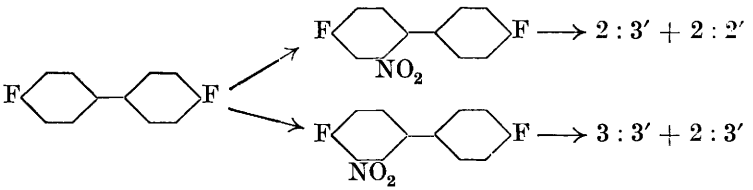






Although mononitration of 4 : 4′-dichloro(or dibromo)-2-nitro-diphenyl, and dinitration of 4 : 4′-dichloro(or dibromo)-diphenyl produced an exactly similar mixture of 2 : 3′- and 2 : 2′-dinitro-isomerides, the corresponding statement is untrue in the difluoro-

series. The results recorded in the experimental part appear to be capable of only one interpretation, namely, that the detectable 3-nitration occurring under the conditions for mononitration of difluorodiphenyl is definitely greater when mononitration occurs under the conditions of dinitration. The high 2 : 3′ content (78%) measured for the product of dinitration would then be due to the presence of the 3 : 3′-isomeride,



which in any method of determining labile fluorine would be the equivalent of twice its weight of the 2 : 3′-compound.

Experimental.

4 : 4′-*Difluorodiphenyl.*—This substance was prepared essentially by Schiemann's method (*loc. cit.* and previous papers), but sodium borofluoride was used instead of the difficultly accessible free acid, and the diazoborofluoride was decomposed by the following method, which is of general applicability. A round-bottomed litre flask was heated in a bath at 150° (in general, at a temperature 20—30° above that at which the diazo-salt blackens and swells). The dried diazoborofluoride from 74 g. of benzidine was dropped into the flask in 2—3 g. quantities as rapidly as decomposition occurred. Usually a short wide air-condenser was fitted to the flask. Finally, alkali was added and the product was distilled in steam. The average yield of difluorodiphenyl was 39 g. One crystallisation from alcohol gave a pure product, m. p. 90—91°.

4 : 4′-*Difluoro*-2 : 2′-*dinitrodiphenyl.*—(*a*) 4-Bromo-*m*-nitroaniline (52 g.) was diazotised in 20% hydrochloric acid, and the highly crystalline diazoborofluoride isolated and decomposed at 200—220°. The residue was extracted with chloroform in presence of alkali, and the chloroform solution dried and evaporated. The residue distilled at 148—150°/50 mm., and was pure 4-bromo-3-nitrofluorobenzene (16 g.), m. p. 38—39° (compare Hove, *Bull. Acad. roy. Belg.*, 1926, **12**, 801). This product (15·5 g.) was heated at 240—250°, and copper-bronze slowly added. A smooth reaction ensued, and in all 15 g. of copper were used. The hot mixture was treated with hot *o*-dichlorobenzene and filtered. On cooling, 4·5 g. of 4 : 4′-*difluoro*-2 : 2′-*dinitrodiphenyl* separated as almost colourless, hard, hexagonal plates. These, after recrystallisation from *n*-butyl alcohol, had m. p.

165—166° (Found: N, 9·9; *M*, cryoscopic in benzene, 252, 268. $C_{12}H_6O_4N_2F_2$ requires N, 10·0%; *M*, 280). (*b*) 2 : 2′-Dinitrobenzidine was prepared by the method of Täuber (*Ber.*, 1890, **23**, 794), but the crude product was crystallised from phenol containing a little alcohol, which greatly diminished the length of the preparation. The dinitro-base (15 g.) was diazotised in 20% hydrochloric acid, and the diazoborofluoride prepared as usual. It was decomposed at 200°, and gave 3 g. of crude difluorodinitrodiphenyl. This, after crystallisation from *o*-dichlorobenzene and then from butyl alcohol, had m. p. 165—166°, and did not depress the m. p. of the sample prepared by method (*a*).

A mixture of 1·000 g. of the pure difluorodinitro-compound with 50 c.c. of *N*-potassium hydroxide and 30 c.c. of absolute alcohol was boiled under reflux for 4 hours. The greater part of the alcohol was then removed by distillation, 75 c.c. of *N*-sulphuric acid added, and the whole extracted with benzene until no more coloured material was removed. The aqueous layer was then titrated with *N*-potassium hydroxide and bromothymol-blue. The mean result of two experiments was 0·15 c.c. of *N*-potassium hydroxide, corresponding to 4·2% of molecules containing reactive fluorine.

Dinitration of 4 : 4′-Difluorodiphenyl.—The difluoro-compound (6 g.) was slowly stirred into 50 c.c. of nitric acid (*d* 1·52) kept at 0°. After ½ hour, water was added very gradually until precipitation was complete, and the precipitate was filtered off and dried (8·2 g., m. p. 107—111°, cloudy until about 125°). It was twice crystallised from alcohol (6 g., m. p. 108—112°, cloudy until 140°), and the mother-liquor from the two crystallisations was concentrated to a small bulk; 1·1 g. of solid then separated, m. p. mainly 115—125°, with final clearing at 155°. After two crystallisations from *o*-dichlorobenzene, it had m. p. 163—165°, and did not depress the m. p. of 4 : 4′-difluoro-2 : 2′-dinitrodiphenyl. Despite extensive crystallisation from various solvents, no specimen of the 2 : 3′-compound could be obtained free from the 2 : 2′-isomeride, but no specimen which was mainly the 2 : 3′-compound had a m. p. much higher than 110°. At this temperature, the 2 : 2′-compound present separated from the liquid, and remained unmelted until far higher temperatures were reached, and the rate of heating materially affected the result.

Mononitration of 4 : 4′-Difluorodiphenyl.—The difluoro-compound (5 g.) was dissolved in 50 c.c. of glacial acetic acid, and 40 c.c. of nitric acid (*d* 1·46) were added. The solution was heated at 100° for ½ hour, cooled, and completely precipitated with water. The solid obtained, after being filtered and dried, weighed 5·8 g. and had m. p. 87—94°. A piperidine solution of the product was only pale yellow after some minutes' boiling, and addition of water gave a

cream-coloured precipitate, in substantiation of previous results (Part VIII).

The product (1·000 g.) was boiled with alcoholic potassium hydroxide as described under the 2 : 2′-dinitro-compound : 0·12 c.c. of *N*-potassium hydroxide were used up, corresponding to 2·8% of molecules containing reactive fluorine.

Mononitration of 4 : 4′-*Difluoro*-2-*nitrodiphenyl*.—The mononitro-compound was obtained by crystallising the crude substance from light petroleum (b. p. 60—80°), and had m. p. 94—95°. It was nitrated (6 g.) under the conditions used for difluorodiphenyl, and gave 7 g. of total nitration product, m. p. 106—112°, cloudy till 120°.

1·000 G., when boiled with standard alcoholic potassium hydroxide, was equivalent in three different experiments to 2·32, 2·26, and 2·34 c.c. of *N*-potassium hydroxide, whence the percentage of the 2 : 3′-dinitro-compound is 65·0, 63·3, and 65·6 respectively.

4-*Fluoro*-2 : 3′-*dinitro*-4′-*ethoxydiphenyl*.—The benzene extracts from the quantitative determinations just described were evaporated. The solid crystallised from alcohol in yellow matted needles, m. p. 142—143° (Found : N, 9·2. $C_{14}H_{11}O_5N_2F$ requires N, 9·1%).

Dinitration of 4 : 4′-*Difluorodiphenyl*.—Dinitration of difluoro-diphenyl under standard conditions consistently led in different experiments to a product having m. p. 108—112°, remaining turbid till about 120°. Determination of reactive dinitro-compounds by means of alcoholic potassium hydroxide gave the following results :

Nitration product No. 1 : 1·000 g. was equivalent to 2·87 c.c. of *N*-potassium hydroxide in one experiment and to 2·77 c.c. in another.

Nitration product No. 2 : 1·000 g. was equivalent to 2·83 c.c. of *N*-potassium hydroxide in one experiment and to 2·74 c.c. in another.

Mean equivalent = 2·80 c.c. of *N*-potassium hydroxide, whence the 2 : 3′-dinitro-content is 78%.

When the crude dinitration product (5 g. of No. 2) was crystallised from glacial acetic acid, 1·2 g. of flaky crystals separated, m. p. 113—120°. The mother-liquor was boiled, and water added at the boiling temperature until the volume was doubled. On cooling, 3·5 g. of hard crystalline material separated, m. p. 112—120° with turbidity. The first crop was boiled with standard alcoholic potassium hydroxide, 1·000 g. being equivalent to 3·19 c.c. of *N*-solution, corresponding to 89% of the 2 : 3′-dinitro-compound.

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