

**172.** *Aromatic Polyfluoro-compounds. Part VII.*<sup>1</sup> *The Reaction of Pentafluoronitrobenzene with Ammonia.*

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Treatment of pentafluoronitrobenzene, prepared in 85% yield by the oxidation of pentafluoroaniline with peroxytrifluoroacetic acid, with ammonia gives, depending on the conditions, 2,3,4,5-tetrafluoro-6-nitro- (II) and 2,3,5,6-tetrafluoro-4-nitro-aniline (IV), and 4,5,6-trifluoro-2-nitro- (III) and 2,4,5-trifluoro-6-nitro-1,3-phenylenediamine (V), and 2,4-difluoro-6-nitrobenzene-1,3,5-triamine (VI). The ratio of *ortho*- to *para*-replacement (relative to NO<sub>2</sub>) in the initial reaction is about 7 : 3.

In a previous paper<sup>2</sup> we described the reaction of penta- and hexa-fluorobenzene with various nitrogen-containing bases to give the corresponding polyfluoro-aromatic bases by the nucleophilic release of fluoride ion. We have now found that pentafluoronitrobenzene (I) reacts with ammonia in a similar manner, but under very much milder conditions, to give a series of fluoronitroanilines as outlined in the annexed scheme.

Pentafluoronitrobenzene was prepared in 85% yield by the oxidation of pentafluoroaniline with peroxytrifluoroacetic acid: Emmons<sup>3</sup> has used this reagent to oxidise a number of aromatic primary amines to nitro-compounds.

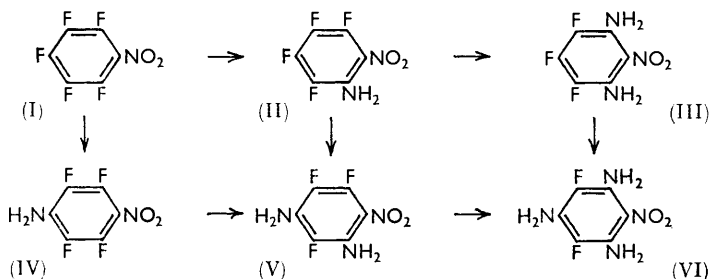
Treatment of pentafluoronitrobenzene (I) in ether with ammonia at room temperature gave, in good yield, a product which when dissolved in benzene was separated into three coloured bands on passage through a chromatographic column packed with alumina. The second of these bands was a mixture of two components (III and IV), which had to be separated by crystal-picking. The first [compound (II)] and the last [compound (V)] band were pure.

<sup>1</sup> Part VI, Robson, Stacey, Stephens, and Tatlow, *J.*, 1960, 4754.

<sup>2</sup> Brooke, Burdon, Stacey, and Tatlow, *J.*, 1960, 1768.

<sup>3</sup> Emmons, *J. Amer. Chem. Soc.*, 1954, **76**, 3470.

Two of these four components (II and IV) together made up about 95% of the product: both were tetrafluoronitroanilines. On hydrogenation over Raney nickel they gave the corresponding tetrafluorophenylenediamines, which were both different from the known <sup>2,4</sup> 2,4,5,6-tetrafluoro-1,3-phenylenediamine. The original nitroanilines must therefore have had the amino- and the nitro-group in *ortho*- and *para*-relation. They were distinguished



by condensation of one of the diamines with trifluoroacetic anhydride, with cyanogen bromide, and with carbonyl chloride to give, respectively, 4,5,6,7-tetrafluoro-2-trifluoromethylbenzimidazole, 2-amino-4,5,6,7-tetrafluorobenzimidazole and 4,5,6,7-tetrafluoro-2,3-dihydro-2-benzimidazolone. The last compound was identical with material derived <sup>5</sup> from 3,4,5,6-tetrafluorophthalic acid *via* a Curtius degradation reaction. The original diamine and the nitroaniline (II) must, therefore, have been the *ortho*-isomers and the other pair the *para*-isomers, although an attempted oxidation of the tetrafluoro-*p*-diamine to the known <sup>6,7</sup> tetrafluoro-*p*-benzoquinone was unsuccessful.

These structures were confirmed by nuclear magnetic resonance spectroscopy. The tetrafluoro-*p*-nitroaniline (IV) showed only two magnetically different types of fluorine atom, while the isomer (II) showed four. The tetrafluoro-1,4-phenylenediamine showed only one type of fluorine atom and the 1,2-isomer showed two (the 1,3-isomer shows <sup>2,8</sup> three).

Further reaction of the *p*-nitroaniline (IV) with ammonia in ether was only slow, so it was carried out in aqueous ethanol at room temperature. This gave a product which was separated into three components by chromatography of its benzene solution on alumina. The fastest-running was the unchanged nitroaniline (IV); the second, a yellow solid, was identical with one of the minor components from the original reaction. Since this was a trifluoronitrophenylenediamine and since it was also obtained by the further ammoniation of the *o*-nitroaniline (II) (see below), it could only have been the 1,3-diamine (V). Nuclear magnetic resonance was in agreement with this; three magnetically different fluorine atoms were found. Further confirmation was supplied by the nuclear magnetic resonance spectrum of the triamine (VII) obtained from this compound (V) by hydrogenation: this showed three different types of fluorine atom, which can only occur in a 1,2,4-triamine. The last component obtained from the reaction of the nitroaniline (IV) with ammonia was a deep red solid and was identical with the triamine (VI) prepared by drastic treatment of the diaminonitro-compounds (III and V) with ammonia (see below).

Reaction of the *o*-nitroaniline (II) with ammonia in ether was also slow. Reaction in ethanol gave four components which were separated by chromatography on alumina. The fastest-moving was the ethoxy-amine (VIII). This structure was indicated by analysis, by synthesis from the *o*-nitroaniline (II) and sodium ethoxide, and by analogy with the structure of the major ammoniation product (V). Presumably, in ethanol-ammonia mixtures two nucleophilic species exist: ethoxide ion and ammonia, the latter

<sup>4</sup> Robson, Roylance, Stephens, and Tatlow, unpublished work.

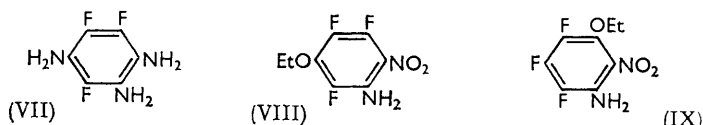
<sup>5</sup> Chaudhry, Gething, Patrick, Stephens, and Tatlow, unpublished work.

<sup>6</sup> Nield and Tatlow, *Tetrahedron*, 1960, **8**, 38.

<sup>7</sup> Wallenfels and Draper, *Chem. Ber.*, 1957, **90**, 2819.

<sup>8</sup> Homer and Thomas, unpublished work.

being more important so that attack by ethoxide ion is possible but occurs to a smaller extent. The second component, forming red crystals, was identical with one of the minor components obtained from the reaction of pentafluoronitrobenzene with ammonia in ether. It appeared to be the diamine (III) from its analysis and nuclear magnetic resonance (only two groups of fluorine resonances were shown, one twice as strong as the other); also, since



the general pattern of replacement of pentafluoronitrobenzene seems to be *ortho* and *para* to the nitro-group, it is reasonable to suppose that ammoniation of the *o*-nitroaniline (II) would give both the 1,3-diamines (III and V). The third component from the reaction of the *o*-nitroaniline (II) with ammonia was the nitro-diamine (V), that was also obtained from the *p*-nitroaniline (IV). The last component, a minor one, was the nitro-triamine (VI). A minute amount of another, red, band was found between bands two and three: it could well have been the ethoxy-analogue (IX) of the minor ammoniation product (III), but it has not been investigated in detail.

Treatment of either nitro-diamine (III or V) with ammonia in aqueous ethanol at 135° for several hours gave good yields of the deep red triamine (VI) obtained previously. If the structures of the nitro-diamines (III and V) are correct then this compound must be 2,4-difluoro-6-nitrobenzene-1,3,5-triamine (VI). Nuclear magnetic resonance confirmed this structure: only one fluorine resonance was observed. This compound was best obtained by the treatment of the *p*-nitroaniline (IV) with ammonia under similar conditions.

We have found no evidence in these reactions for displacement of the nitro-group although this could have taken place to a small extent since our isolation procedure depends on the colour of the products and any product from which the nitro-group had been displaced should be colourless.

The ratio of *ortho*- to *para*-replacement in the initial reaction of pentafluoronitrobenzene with ammonia is about 7:3. This is the first example we have found of a predominately *ortho*-reaction in the polyfluoro-aromatic field. In most other cases studied so far, such as reactions with pentafluorobenzene,<sup>1,2</sup> pentafluoroanisole,<sup>6,9</sup> and pentafluorotoluene,<sup>10</sup> replacement occurs mainly *para* to the non-fluorine position. In the reaction of pentafluoroaniline with ammonia, however, it is in the *meta*-position.<sup>2</sup> Considering the example of pentafluorobenzene, the directing of replacement almost exclusively into the *para*-position with respect to the hydrogen appears to be due to the five fluorine atoms. Electrophilic substitution in fluorobenzene takes place mainly in the *para*-position. In nucleophilic substitution, therefore, this position should be least reactive. For pentafluorobenzene then, the combined effect of the five fluorine atoms should leave the fluorine *para* to the hydrogen most susceptible to nucleophilic replacement, in accord with the experimental results. Substituents in place of hydrogen can be considered as having a modifying influence on this directing effect of the five fluorine atoms. Groups only weakly electron-attracting or -repelling would be expected only to influence the relative rate of replacement of the fluorine atom *para* to them. However, strongly electron-repelling groups should increase, by a conjugative mechanism, the electron density at the *para*- (and *ortho*-) more than at the *meta*-position; the amount of *meta*-replacement, as compared with pentafluorobenzene, should therefore increase while the overall rate of reaction decreases. A case of this occurs<sup>2</sup> in the reaction of pentafluoroaniline with ammonia,

<sup>9</sup> Godsell, Stacey, and Tatlow, *Nature*, 1956, **178**, 199.

<sup>10</sup> Coe, Barbour, Buxton, Stephens, and Tatlow, Part VIII, following paper.

from which only the *m*-diamine has been isolated. From other studies<sup>11</sup> on nucleophilic aromatic substitution it appears that the amino-group is the most deactivating group known. Since the methoxyl-group is also<sup>11</sup> powerfully deactivating and since the major substitution product of pentafluoroanisole<sup>6,9</sup> is the *para*-isomer, the influence of the five fluorine atoms must be considerable.

Strongly electron-attracting substituents, on the other hand, should decrease the electron densities at the *ortho*- and *para*-positions and increase the reaction rate. This is the case with the reaction of pentafluoronitrobenzene described in this paper. Although the *ortho*:*para* ratio in this reaction is not far from statistical, the nitro-group must nevertheless have a strong *ortho*-directing influence, since pentafluorobenzene, with its electronically neutral hydrogen substituent, is substituted almost entirely<sup>1,2</sup> in the *para*-position. The nitro-group has previously<sup>11</sup> been observed to be more activating, in most cases, from the *ortho*-position than from the *para* in nucleophilic reactions. This greater amount of *ortho*- than *para*-replacement might arise because the *ortho*- is nearer than the *para*- to the nitro-group; this proximity must also be sufficient, in the pentafluoronitrobenzene case, to overcome the *para*-directing effect of the five fluorine atoms.

That the nitroanilines (II and IV) react with ammonia under very much milder conditions than pentafluorobenzene does<sup>2</sup> suggests that the nitro-group activates much more powerfully than the amino-group deactivates.

A surprising feature of these ammoniations is that, although pentafluoronitrobenzene undergoes predominantly *ortho*-reaction, the *o*-nitroaniline (II) reacts predominantly at the position *para* to the nitro-group.

#### EXPERIMENTAL

An entry "i.r." denotes that the compound was identified by infrared spectroscopy.

*Pentafluoronitrobenzene* [with R. D. RICHARDSON].—A mixture of methylene chloride (100 ml.), trifluoroacetic anhydride (25 ml.), and ca. 90% hydrogen peroxide (10 ml.) was refluxed and stirred for 15 min. Pentafluoroaniline<sup>2</sup> (10.3 g.) in methylene chloride (50 ml.) was then added slowly at reflux temperature with stirring. The reaction mixture became dark green in a few minutes. Further hydrogen peroxide (5 ml.) was added after 1 hr., followed 2½ hr. later by more hydrogen peroxide (5 ml.) and trifluoroacetic anhydride (5 ml.). After being refluxed and stirred for 18 hr. in all, the mixture was cooled and water (100 ml.) was added slowly. The methylene chloride layer was separated, washed with water (100 ml.), and dried (MgSO<sub>4</sub>). Removal of the solvent by fractional distillation through a 6" column packed with glass helices, followed by simple distillation gave lachrymatory, golden-yellow *pentafluoronitrobenzene* (10.2 g.), b. p. 158—161° (mainly 158.5—160.0°) (Found: C, 33.9. C<sub>6</sub>F<sub>5</sub>NO<sub>2</sub> requires C, 33.8%), λ<sub>max</sub>. 224 mμ (ε 6200 in EtOH).

Removal of the methylene chloride by simple distillation caused losses of pentafluoronitrobenzene by co-distillation.

*Reaction of Pentafluoronitrobenzene with Ammonia in Ether*.—Ammonia was bubbled slowly through a solution of pentafluoronitrobenzene (3.01 g.) in ether (200 ml.) for 6 hr. After being kept at room temperature for 18 hr., the red solution was filtered to remove ammonium fluoride, and the filtrate was evaporated to dryness *in vacuo* to leave the crude product (2.91 g.). This was chromatographed on a column (20 × 1½") packed with alumina (commercial chromatography-grade alumina was used; the properties of this varied from batch to batch; sometimes the untreated material gave a satisfactory separation, but with many batches it was necessary to pre-treat the alumina with water). Benzene was used as eluant. Three bands developed. The first two were washed off with benzene and the third was removed mechanically from the column, and the component washed from the alumina with ethanol. Solvents were removed *in vacuo*, to avoid co-distillation.

*Band 1*. A bright yellow solid (1.73 g.), m. p. 35—41°, when recrystallised from benzene-light petroleum (b. p. 60—80°), gave 2,3,4,5-tetrafluoro-6-nitroaniline (II) (0.63 g.), m. p. 42.5—43.5° (Found: C, 34.4; H, 1.2; F, 36.0. C<sub>6</sub>H<sub>2</sub>F<sub>4</sub>N<sub>2</sub>O<sub>2</sub> requires C, 34.3; H, 1.0; F, 36.2%). The nuclear magnetic resonance spectrum of a 3M-solution in acetone showed four bands, of equal intensity, centred at 70.3, 73.5, 83.3, and 99.0.

<sup>11</sup> Bunnett and Zahler, *Chem. Rev.*, 1951, **49**, 273.

It gave a *trifluoroacetyl derivative*, m. p. 80—80.5° [from light petroleum (b. p. 80—100°)] (Found: C, 31.2; H, 0.6.  $C_8HF_3N_2O_3$  requires C, 31.4; H, 0.3%).

*Band 2.* An orange solid (0.78 g.), m. p. 100—106.5°, recrystallised as above, gave a yellow and a minor red component. The major component was purified by further recrystallisation and was 2,3,5,6-tetrafluoro-4-nitroaniline (IV) (0.54 g.), m. p. 106.5—108° (Found: C, 34.4; H, 1.4; F, 35.8%). Nuclear magnetic resonance of a 2.5M-solution in acetone showed two identical bands of equal intensity centred at 72.3 and 85.8.

This compound gave a *trifluoroacetyl derivative*, m. p. 107.5—108° [from benzene-light petroleum (b. p. 60—80°)] (Found: C, 31.4; H, 0.7%).

Less than 10 mg. of the minor component were formed in a single experiment. It was isolated by combination of the mother-liquors from several experiments, evaporation, recrystallisation [from benzene-light petroleum (b. p. 60—80°)], and hand-picking of the crystals. Recrystallisation from benzene-light petroleum (b. p. 60—80°) gave 4,5,6-trifluoro-2-nitro-1,3-phenylenediamine (III), m. p. 162—163.5° (Found: C, 34.5; H, 2.3; F, 27.1.  $C_8H_4F_3N_2O_2$  requires C, 34.8; H, 1.9; F, 27.5%). The nuclear magnetic resonance spectrum of a 3M-solution in acetone showed two bands of intensity 1 : 2 at 74.8, and 98.8, respectively.

*Band 3.* A bright yellow solid (0.07 g.), m. p. 139.5—145°, recrystallised from benzene to give 2,4,5-trifluoro-6-nitro-1,3-phenylenediamine (V) (0.04 g.), m. p. 146.5—148° (Found: C, 34.4; H, 1.9; F, 27.2%). A M-solution in acetone had bands of equal intensity at 72.7, 85.3, and 95.8 in its nuclear magnetic resonance spectrum.

*Treatment of the Monoamines (II and IV) with Ammonia in Ethanol.*—(a) 2,3,4,5-Tetrafluoro-6-nitroaniline (II). Ammonia was bubbled through a solution of the compound (0.47 g.) in ethanol (200 ml.) for 12 hr. The solvent was removed *in vacuo* and the crude red product was chromatographed as before. Four bands developed. The first two, bright yellow and red respectively, were washed from the column with benzene and the last two, also bright yellow and red respectively, were removed separately from the dried column and were washed from the alumina with ethanol or acetone. The solid component from each band was isolated by evaporation of the solvent *in vacuo*.

Band 1 gave 3-ethoxy-2,4,5-trifluoro-6-nitroaniline (VIII) (0.05 g.), m. p. 73—73.5° [from benzene-light petroleum (b. p. 60—80°)], unchanged on admixture with an authentic specimen; it also had an identical infrared spectrum.

Band 2 gave the diamine (III) (0.05 g.), m. p. 135—159°. Recrystallisation from light petroleum (b. p. 60—80°)-benzene gave the pure compound (0.01 g.), m. p. 157—163.5° (i.r.).

Band 3 gave the diamine (V) (0.3 g.), m. p. 146—148° (i.r.).

Band 4 gave almost pure triamine (VI) (0.01 g.), m. p. 221—228° (i.r.).

A red band followed band 2, but only a tar (0.006 g.) was isolated from it.

(b) 2,3,5,6-Tetrafluoro-4-nitroaniline (IV). The compound (0.50 g.), ethanol (4.0 ml.), and aqueous ammonia (2.0 ml.; *d* 0.88) were left at room temperature for 90 hr. The solution was diluted with ether, dried ( $MgSO_4$ ), and evaporated *in vacuo*, to leave a red residue which was separated into three bands on alumina as before.

Band 1 gave almost pure starting material (0.09 g.), m. p. 101—106° (i.r.).

Band 2 gave the diamine (V) (0.39 g.), m. p. 143—146°. The pure compound (0.27 g.), m. p. 147—148° (from benzene), had an infrared spectrum identical with that of the compound prepared previously.

Band 3 afforded almost pure triamine (VI) (0.01 g.) (i.r.).

3-Ethoxy-2,4,5-trifluoro-6-nitroaniline (VIII).—A solution of the amine (II) (0.09 g.) in ethanol (32 ml.) was treated with 0.053N-ethanolic sodium ethoxide (8.0 ml.) for 18 hr. at room temperature. Evaporation *in vacuo* left a bright yellow solid, which yielded only one band on alumina. It crystallised from benzene-light petroleum (b. p. 60—80°), to give the *ether* (VIII) (0.05 g.), m. p. 73—73.5° (Found: C, 41.0; H, 3.1.  $C_8H_5F_3N_2O_3$  requires C, 40.7; H, 3.0%).

2,4-Difluoro-6-nitrobenzene-1,3,5-triamine (VI).—The nitro-amine (IV) (0.5 g.), ethanol (4.0 ml.), and aqueous ammonia (2.0 ml.; *d* 0.88) were heated together in a sealed tube at 110° for 4 hr. The tube was allowed to cool and the deep red crystals which separated out were redissolved with acetone. Evaporation of the dried ( $MgSO_4$ ) solution left a residue (0.51 g.), m. p. 210—215°. Recrystallisation of a small sample of this from ethanol-acetone, followed by sublimation at 190°/0.05 mm., gave the *triamine*, m. p. 230.5—231° (Found: C, 35.2; H, 3.2; F, 18.8.  $C_8H_8F_2N_4O_2$  requires C, 35.3; H, 3.0; F, 18.6%). A M-solution in acetone had a single sharp peak in the nuclear magnetic resonance spectrum at 94.7.

*Treatment of the Trifluoronitrophenylenediamines (III and V) with Aqueous-ethanolic Ammonia.*—(a) The compound (V) (24 mg.), ethanol (4.0 ml.), and aqueous ammonia (2.0 ml.;  $d$  0.88) were heated together in a sealed tube at 135° for 7½ hr. The crude product, isolated as in the previous experiment, gave only one band on alumina with benzene as eluant. This was washed from the column with acetone, and the acetone was evaporated to leave the triamine (VI) (22 mg.), m. p. 229—231° (i.r.).

(b) Compound (III) (22 mg.), treated as in (a), gave almost pure triamine (VI) (15 mg.), m. p. 198—207° (i.r.).

*Hydrogenation of 2,3,4,5-Tetrafluoro-6-nitroaniline (II).*—The compound (3.79 g.), m. p. 38—40°, was hydrogenated in ethanol over Raney nickel for 18 hr. at atmospheric pressure and room temperature (uptake about 1.3 l.). After filtration and evaporation the residue (3.05 g.), m. p. 125—129°, was sublimed at 110° *in vacuo* and then recrystallised from benzene, to give 3,4,5,6-tetrafluoro-1,2-phenylenediamine (2.15 g.), m. p. 131—131.5° (Found: C, 40.2; H, 2.2. C<sub>6</sub>H<sub>4</sub>F<sub>4</sub>N<sub>2</sub> requires C, 40.0; H, 2.2%). Infrared spectroscopy showed that this compound was different from 2,4,5,6-tetrafluoro-1,3-phenylenediamine reported<sup>2</sup> previously. A 3M-solution in acetone had two, identical, bands at 87.1 and 99.3 in the nuclear magnetic resonance spectrum.

A rapid stream of carbonyl chloride was passed through a solution of the diamine (0.14 g.) in dry ether for 1 min. A white precipitate of 4,5,6,7-tetrafluoro-2,3-dihydro-2-benzimidazole (0.14 g.), m. p. 302.5—306°, was formed almost immediately: it had an infrared spectrum identical with that of a specimen prepared<sup>5</sup> by an alternative route.

The diamine (0.5 g.) was refluxed for 2 hr. with trifluoroacetic anhydride (3.0 ml.) and two drops of concentrated hydrochloric acid. The excess of anhydride was removed by co-distillation with carbon tetrachloride, and the solid residue was refluxed for 30 min. with water. Excess of aqueous ammonia ( $d$  0.88) was added and the solution was allowed to cool. A solid (0.4 g.) separated and was recrystallised from light petroleum (b. p. 80—100°) containing a small amount of benzene, to give 4,5,6,7-tetrafluoro-2-trifluoromethylbenzimidazole (0.21 g.), m. p. 163—163.5° (Found: C, 37.2; H, 0.2. C<sub>8</sub>HF<sub>7</sub>N<sub>2</sub> requires C, 37.2; H, 0.4%),  $\lambda_{\text{max}}$  (in EtOH) 228 and 248 m $\mu$  ( $\epsilon$  4400 and 4800, respectively),  $\lambda_{\text{inf}}$  267 m $\mu$  ( $\epsilon$  3400).

Cyanogen bromide (0.93 g.) was added slowly, with shaking, to a suspension of the 1,2-diamine (1.0 g.) in water (10 ml.). After being shaken for 18 hr. at room temperature the clear brown solution was made alkaline with aqueous ammonia ( $d$  0.88). The white precipitate (1.20 g.), m. p. 278.5—282.5°, was filtered off and recrystallised from aqueous ethanol to give 2-amino-4,5,6,7-tetrafluorobenzimidazole (0.52 g.), m. p. 289—290.5° (Found: C, 41.1; H, 1.6. C<sub>7</sub>H<sub>3</sub>F<sub>4</sub>N<sub>3</sub> requires C, 41.0; H, 1.5%).

*Hydrogenation of 2,3,5,6-Tetrafluoro-4-nitroaniline (IV).*—This compound (1.96 g.) was hydrogenated in the same way as the isomer (II) (uptake about 700 ml.). The product was 2,3,5,6-tetrafluoro-1,4-phenylenediamine (1.30 g.), m. p. 143.5—144° (Found: C, 40.2; H, 2.4%). Infrared spectroscopy showed that this compound differed from the isomeric 1,2- and 1,3-diamines. Nuclear magnetic resonance spectroscopy of a 2M-solution in acetone showed a single sharp peak at 86.7.

Treatment of the *p*-diamine (0.25 g.) with trifluoroacetic anhydride (2.0 ml.) gave the *bistrifluoroacetyl derivative* (0.34 g.), m. p. 274.5—275° (from aqueous ethanol) (Found: C, 32.0; H, 0.4. C<sub>10</sub>H<sub>2</sub>F<sub>10</sub>N<sub>2</sub>O<sub>2</sub> requires C, 32.3; H, 0.5%).

*Hydrogenation of 2,4,5-Trifluoro-6-nitro-1,3-phenylenediamine (V).*—This compound (4.45 g.) was hydrogenated as before to give 3,5,6-trifluorobenzene-1,2,4-triamine (VII) (1.3 g.), m. p. 164° (decomp.) (from benzene-ethanol) (Found: C, 40.7; H, 3.6. C<sub>6</sub>H<sub>6</sub>F<sub>3</sub>N<sub>3</sub> requires C, 40.7; H, 3.4%). The nuclear magnetic resonance spectrum of a 5M-solution in acetone showed three equal bands at 82.4, 87.3, and 95.0.

*Nuclear Magnetic Resonance Measurements.*—These were carried out on a Mullard SL 44 Mark I instrument at 30.107 Mc./sec. The figures quoted are fluorine chemical shifts and are in p.p.m. from trifluoroacetic acid as external reference.

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