Org.

## Aromatic Polyfluoro-compounds. Part XXXVII.<sup>1</sup> Nitration of Some **Polyfluoro-benzenes and -biphenyls**

By P. L. Coe, A. E. Jukes, and J. C. Tatlow

Pentafluorobenzene, 1,2,3,4- and 1,2,3,5-tetrafluorobenzenes, 1-bromo-2,3,4,5-tetrafluorobenzene, and 2Hnonafluorobiphenyl have been nitrated (replacement of H) in high yields to the corresponding mononitro-compounds by use of a mixture of fuming nitric acid, boron trifluoride, and tetramethylene sulphone.

ALTHOUGH nucleophilic displacement of fluorine is well known among aromatic polyfluoro-compounds,<sup>2</sup> examples of electrophilic substitution are limited. Pentafluorobenzene has been sulphonated and halogenated <sup>3</sup> to the corresponding sulphonic acid and pentafluorohalogenobenzenes, but there has been no report of its nitration and only one of nitration of a tetrafluorobenzene.<sup>4</sup> We have now found a method of nitration of highly fluorinated aromatic compounds, involving replacement of hydrogen, which seems to have wide application and gives high yields.

Previously 1,2,3,5-tetrafluorobenzene was nitrated <sup>4</sup> with a concentrated sulphuric acid-concentrated nitric acid mixture, but attempts to nitrate other tetrafluorobenzenes produced quinones. Earlier attempts to nitrate pentafluorobenzene also produced quinones.<sup>5</sup>

We have investigated many nitration conditions using all the possible combinations of both concentrated and fuming nitric and sulphuric acids with and without solvents such as sulpholane, nitromethane, and N-methyl-2-pyrrolidone, and also additions of metal salts such as mercuric nitrate and ferrous sulphate. The best yields of nitrated products, found to be with concentrated sulphuric acid and fuming nitric acid, were from pentafluorobenzene (28%), 1,2,3,4-tetrafluorobenzene (68%), and 1,2,3,5-tetrafluorobenzene (70%). Since the reactions are less satisfactory than those reported below they will not be described in detail. There seemed to be two modifications which might improve the yields of nitro-product; first, use of a homogeneous solution, and secondly the use of a more powerful " catalyst."

The solvent should dissolve both polyfluoroaromatic compounds and fuming nitric acid and be largely unaffected by the latter. Tetramethylene sulphone (sulpholane) has been used frequently in exchange reactions with chlorofluoro-compounds and is largely unaffected by nitric acid. Experimentally, it is the best solvent we have tried. The work of Olah and his co-workers<sup>6</sup> on Lewis acids in nitration, and the report that boron trifluoride is a good " catalyst " for difficult nitrations," suggested its use.

We found that a mixture of fuming nitric acid and sulpholane saturated with boron trifluoride gave high yields of nitro-derivatives from a variety of polyfluoro-

<sup>1</sup> Part XXXVI, J. Burdon, D. R. King, J. C. Tatlow, Tetrahedron, in the press.
<sup>2</sup> J. C. Tatlow, Endeavour, 1963, 22, 89.
<sup>3</sup> E. Nield, R. Stephens, and J. C. Tatlow, J. Chem. Soc., 1959,

166. <sup>4</sup> G. C. Finger, F. H. Reed, and R. E. Oesterling, J. Amer. Chem. Soc., 1951, 73, 152.

aromatic compounds. Thus pentafluorobenzene gave pentafluoronitrobenzene in 82% yield unaccompanied by oxidation, 1,2,3,4-tetrafluoro- and 1,2,3,5-tetrafluoro-benzenes gave similarly their mononitro-derivatives in 90 and 86% yields, respectively, and 1-bromo-2,3,4,5-tetrafluorobenzene and 2H-nonafluorobiphenyl are nitrated in 85 and 72% yields, respectively. Attempts to dinitrate the tetrafluorobenzenes resulted in very small conversions (ca. 10%) and further work is needed to increase these yields. 1,2,4,5-Tetrafluorobenzene and its derivatives behaved in an anomalous and so far unexplained manner on attempted nitration. In general the substrate was either totally unreactive or totally degraded.

The importance of the solvent is clearly shown since pentafluorobenzene is nitrated in 35% yield only, during a comparable time and at similar temperatures, when fuming nitric acid and boron trifluoride are used alone.

The function of boron trifluoride is not clear. It has been suggested 7 that it is solely to remove water as BF<sub>3</sub>,2H<sub>2</sub>O; this complex has been isolated from a nitration. A second possibility is the formation of  $[BF_3OH]^-NO_2^+$  which acts as the nitrating species; against this we have shown that  $NO_2^+BF_4^-$  (made by Olah, Kuhn, and Flood's method <sup>6</sup>) in sulpholane nitrates the polyfluorobenzenes in only trivial yield, although this could be accounted for by the low solubility of the complex in sulpholane.

Work is in progress to investigate the scope of the new nitration system, to measure relative reactivities of the polyfluorobenzenes, and to study the use of Lewis acids as "catalysts" for other electrophilic substitutions.

## EXPERIMENTAL

Nitration of Pentafluorobenzene.-Boron trifluoride was bubbled through a mixture of sulpholane (20 c.c.) and fuming nitric acid (95%, d 1.5, 5 c.c.) at 0° until a saturated solution was obtained (ca. 1 hr.). Pentafluorobenzene (10.9 g.) was added and the mixture stirred at 60-70° for 2 hr. The homogeneous yellow solution was poured on crushed ice (200 g.), diluted with water (100 c.c.), and steam-distilled. The lower organic layer of the distillate was separated, the aqueous layer was extracted with methylene chloride  $(2 \times 25$  c.c.), and the methylene chloride was distilled off through a 6 in. vacuum-jacketed column packed with glass helices. The concentrated extract and the original organic

<sup>&</sup>lt;sup>5</sup> P. Robson, E. Nield, R. Stephens, unpublished results.

<sup>&</sup>lt;sup>6</sup> G. A. Olah, S. J. Kuhn, and S. Flood, J. Amer. Chem. Soc., 1961, 83, 4564, and following Papers.

<sup>7</sup> R. J. Thomas, W. F. Anzilotti, and G. F. Hennion, Ind. Eng. Chem., 1940, 32, 408.

layer were combined and distilled *in vacuo* from phosphoric oxide to yield pentafluoronitrobenzene (11.4 g.) identical with an authentic sample.<sup>8</sup>

Nitration of 1,2,3,5-Tetrafluorobenzene.—Sulpholane (10 c.c.) and fuming nitric acid (2.5 c.c.) were saturated at 0° with boron trifluoride, 1,2,3,5-tetrafluorobenzene (5 g.) was added, and the mixture warmed at 65° for 1.5 hr. Isolation as before yielded 1,2,3,5-tetrafluoro-4-nitrobenzene <sup>4</sup> (5.6 g.), b. p. 177—178° (Found: C, 37.2; H, 0.7. Calc. for C<sub>6</sub>HF<sub>4</sub>NO<sub>2</sub>: C, 36.9; H, 0.5%). Hydrogenation of the nitrobenzene (1 g.) over 10% palladium-on-charcoal gave 2,3,4,6-tetrafluoroaniline (0.5 g.), b. p. 80°/50 mm. (Found: C, 43.3; H, 2.0. C<sub>6</sub>H<sub>3</sub>F<sub>4</sub>N requires C, 43.6; H, 1.8%).

Nitration of 1,2,3,4-Tetrafluorobenzene.—Sulpholane (20 c.c.) and fuming nitric acid (8·4 c.c.) were saturated with boron trifluoride at 0°, 1,2,3,4-tetrafluorobenzene (19 g.) was added, and the mixture heated at 70° for 1 hr. Isolation as before afforded 1,2,3,4-tetrafluoro-5-nitrobenzene (22·3 g.) b. p. 179° (Found: C, 37·2; H, 0·7. C<sub>6</sub>HF<sub>4</sub>NO<sub>2</sub> requires C, 36·9; H, 0·5%). Hydrogenation of the nitrobenzene (1·1 g.) over 10% palladium-on-charcoal in the usual way gave 2,3,4,5-tetrafluoroaniline (0·8 g.), m. p. 27—28° (Found: C, 43·7; H, 1·8. C<sub>6</sub>H<sub>3</sub>F<sub>4</sub>N requires C, 43·6; H, 1·8%).

Nitration of 2H-Nonafluorobiphenyl.—Sulpholane (20 c.c.) and fuming nitric acid ( $2\cdot 4$  c.c.) were saturated at 0° with boron trifluoride. 2H-Nonafluorobiphenyl ( $7\cdot 6$  g.) in

<sup>8</sup> G. M. Brooke, J. Burdon, and J. C. Tatlow, J. Chem. Soc., 1961, 802.

sulpholane (5 c.c.) was added and the mixture heated at  $65^{\circ}$  for 3 hr. Isolation as before afforded nonafluoro-2-nitrobiphenyl (6·3 g.), m. p.  $75-75\cdot5^{\circ}$  (lit.,  $9,77-...77\cdot5$ ) with similar infrared spectrum to an authentic sample. The nitrobiphenyl was hydrogenated using 10% palladised charcoal to give 2-aminononafluorobiphenyl, m. p.  $77-...78^{\circ}$  (Found: C, 43·7; H, 0·8.  $C_{12}H_2F_9N$  requires C, 43·5; H, 0·6%).

Nitration of 1-Bromo-2,3,4,5-tetrafluorobenzene.—Sulpholane (10 c.c.) and fuming nitric acid (1.8 c.c.) were saturated with boron trifluoride at 0°. 1-Bromo-2,3,4,5-tetrafluorobenzene (4.4 g.) was added and the mixture heated at 65° for 2 hr. The resulting solution was poured into water (100 c.c.) and the aqueous phase steam-distilled. The organic layer from the distillate was distilled from phosphoric oxide to give 1-bromo-2,3,4,5-tetrafluoro-6-nitrobenzene (4.5 g.), b. p. 200° (Found: C, 26.6; H, 0.1. C<sub>6</sub>BrF<sub>4</sub>NO<sub>2</sub> requires C, 26.2; H, 0%) identical with an authentic sample prepared by bromination of 1,2,3,4-tetrafluoro-5-nitrobenzene.<sup>10</sup>

We thank Imperial Smelting Corporation for a grant (to A. E. J.).

CHEMISTRY DEPARTMENT,

THE UNIVERSITY, EDGBASTON,

BIRMINGHAM 15. [6/888 Received, July 13th, 1966]

<sup>9</sup> G. M. Brooke and W. K. R. Musgrave, J. Chem. Soc., 1965, 1864.

<sup>10</sup> M. W. Buxton and L. J. Belf, personal communication.