

964. *Aromatic Polyfluoro-compounds. Part XIX.¹ The Preparation of Some Polyfluorodi- and Polyfluorotri-phenylamines.*

By J. BURDON, J. CASTANER, and J. C. TATLOW.

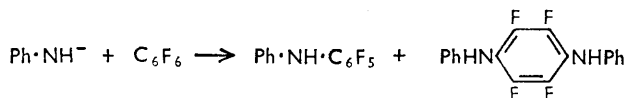
Di- and tri-arylamines, $C_6F_5 \cdot NHR$ and $C_6F_5 \cdot NRR'$ ($R, R' = Ph$ or C_6F_6), have been prepared by reaction of the sodium salt of the appropriate aniline or diphenylamine with hexafluorobenzene. Further reaction, that is replacement of two fluorine atoms from the hexafluorobenzene, occurred in some cases.

In a previous Paper,² we showed that aniline is not a sufficiently powerful nucleophile to displace fluorine from hexafluorobenzene. However, in the reaction of sodamide with hexafluorobenzene, besides the major product, pentafluoroaniline, there was also formed² a little decafluorodiphenylamine. The primary product, pentafluoroaniline, is a weaker base than ammonia and so $C_6F_5 \cdot NH^-$ should be generated and should be an effective nucleophile. We have now extended this type of replacement and by use of strong bases have promoted reactions between aniline or various diphenylamines and hexafluorobenzene. In every case we believe that the effective nucleophiles were anionic species of the type $Ar \cdot NH^-$ or Ar_2N^- .

¹ Part XVIII, Aroskar, Chaudry, Stephens, and Tatlow, *J.*, 1964, 2975.

² Brooke, Burdon, Stacey, and Tatlow, *J.*, 1960, 1768.

With sodium hydride, aniline gave a sodio-derivative which, with hexafluorobenzene, afforded two products, pentafluorodiphenylamine (49%) and 2,3,5,6-tetrafluoro-*NN'*-diphenyl-1,4-phenylenediamine (1%):

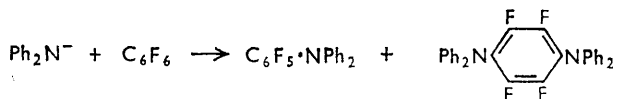


The structure of the di-replacement product was established by its preparation from pentafluorodiphenylamine and sodium anilide, and by its oxidation to the known³ tetrafluoro-*p*-benzoquinone. While we cannot completely rule out the possibility of the formation of isomers other than the *para*, they could only have been present in very small proportion. That the di-replacement compound has the *para*-orientation is in agreement with other results^{2,4,5} on the nucleophilic replacement reactions of *N*-substituted pentafluoroanilines. Pentafluoroaniline itself directs nucleophiles into the position^{2,4} *meta* to the amino-group. *N*-Substitution distorts the NHR group out of planarity with the ring by steric interaction with the *ortho*-fluorine atoms, and hence reduces the conjugation of the lone pair of electrons on the nitrogen with the ring; this conjugation is the probable cause of *meta*-replacement in pentafluoroaniline.

Anilinomagnesium iodide and hexafluorobenzene gave only 1% of pentafluorodiphenylamine under even more drastic conditions than were used in the reaction with sodium anilide. This could be due to the lower ionic character of the magnesium than of the sodium reagent.

We have improved the yield of decafluorodiphenylamine to 17% in the reaction of pentafluoroaniline with hexafluorobenzene in the presence of sodium in liquid ammonia.² No di-replacement products were isolated; this could be due both to the milder conditions used here than in the aniline reaction, and to the weaker nucleophilicity of the $\text{C}_6\text{F}_5\cdot\text{NH}^-$ than of the $\text{Ph}\cdot\text{NH}^-$ ion. Surprisingly, no reaction occurred between pentafluoroaniline and hexafluorobenzene in the presence of sodium hydride. Pentafluoroaniline would be expected to form a sodium salt with sodium hydride more readily than does aniline, as it is presumably a stronger acid; the lack of reaction could, however, be due to a physical effect, as the pentafluoroaniline-sodium hydride reaction is heterogeneous.

Diphenylamine, however, reacted with hexafluorobenzene in the presence of sodium hydride, presumably by way of an ion Ph_2N^- , to give 2,3,4,5,6-pentafluorotriphenylamine (48%) and a di-replacement product (14%) which we suggest, by analogy with the aniline product, is the *para*-isomer:



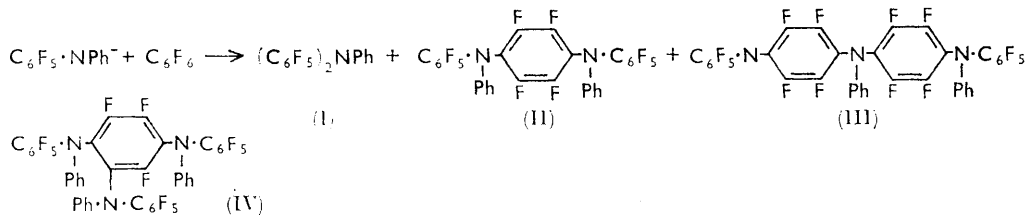
Pentafluorodiphenylamine and hexafluorobenzene reacted in the presence of *p*-tolyl-sodium to give three products. The first was the expected decafluorotriphenylamine (I) (21%) and the second, from molecular-weight measurements, was a di-replacement product (14%), which, from previous results, we suggest is the *para*-isomer (II). From its elemental analysis, the third product (5%) appeared to be a tri-replacement compound. We suggest, very tentatively, that it is compound (III) and not the branched compound (IV): both compounds could theoretically be formed from the di-replacement product (II), by replacement either in the C_6F_4 ring, to give (IV), or in one of the two C_6F_5 rings to give compound (III). We consider the last possibility more likely as the C_6F_5 rings have only one deactivating nitrogen-containing substituent.

³ Nield and Tatlow, *Tetrahedron*, 1959, **8**, 38; Wallenfels and Draber, *Chem. Ber.*, 1957, **90**, 2819.

⁴ Allen, Burdon, and Tatlow, unpublished work.

⁵ Robson, Smith, Stephens, and Tatlow, *J.*, 1963, 3692.

Some of the triphenylamine (I) was formed when either sodium hydride or sodium-liquid ammonia was used instead of *p*-tolylsodium. We have not investigated these reactions fully, but there seems no reason why these reagents should not be as effective as *p*-tolylsodium.



Very drastic conditions were required to cause reaction of decafluorodiphenylamine with hexafluorobenzene in the presence of *p*-tolylsodium. This is reasonable in that the ion $(C_6F_5)_2N^-$ would be expected to be a weaker nucleophile than any of the other amine anions described in this Paper. The sole product isolated was pentadecafluorotriphenylamine (24%).

The ultraviolet spectra of the fluorinated di- and tri-phenylamines show a decrease in extinction coefficient and λ_{\max} , as compared with those of the non-fluorinated analogues ($m\mu$; ϵ in parentheses):

Ph ₂ NH	283 (17,800)	Ph ₃ N	299 (25,500) ⁶
Ph·NH·C ₆ F ₅	266 (11,900)	Ph ₂ N·C ₆ F ₅	282 (14,500)
(C ₆ F ₅) ₂ NH	251 (12,200)	Ph·N(C ₆ F ₅) ₂	265 (13,200)
		N(C ₆ F ₅) ₃	255 (13,200)

The end-absorptions showed a similar decrease in extinction coefficient. We attribute these decreases in ϵ and λ to steric inhibition of resonance caused by interactions between the *ortho*-fluorine atoms and the substituents on the nitrogen.

EXPERIMENTAL

Recrystallisations were carried out from light petroleum (b. p. 40–60°).

2,3,4,5,6-Pentafluorodiphenylamine.—A 50% w/w sodium hydride–hydrocarbon oil dispersion (2.20 g.), aniline (7.70 g.), and dioxan (175 ml.) were refluxed for 1½ hr. Hexafluorobenzene (7.70 g.) in dioxan (25 ml.) was then added, the mixture was refluxed for a further 5 hr., then poured into *n*-hydrochloric acid (1.5 l.), and the organic products were extracted with methylene chloride. Evaporation of the dried (MgSO₄) extracts (gas-phase chromatography showed that the distillate contained some hexafluorobenzene) left a residue, the light petroleum (b. p. 40–60°)–soluble portion (7.05 g.) of which was chromatographed on alumina (30 cm. × 3.5 cm.). Elution with light petroleum (b. p. 40–60°)–ether (4 : 1 v/v) gave 2,3,4,5,6-pentafluorodiphenylamine (5.28 g.), m. p. 71–73° (Found: C, 55.7; H, 2.5; F, 37.0; N, 5.4. C₁₂H₆F₅N requires C, 55.6; H, 2.3; F, 36.7; N, 5.4%), ν_{\max} 3400 cm.⁻¹, λ_{\max} 266 $m\mu$ (ϵ 11,900) in cyclohexane; at 210 $m\mu$ ϵ was 13,600.

Further elution with ether–chloroform (1 : 1 v/v) gave the pale pink 2,3,5,6-tetrafluoro-*NN'*-diphenyl-1,4-phenylenediamine (0.19 g.), m. p. 149–152° (Found: C, 65.1; H, 3.8; F, 22.5; N, 8.5. C₁₈H₁₂F₄N₂ requires C, 65.0; H, 3.6; F, 22.9; N, 8.4%), ν_{\max} at 3400 cm.⁻¹.

On treatment with acetic anhydride, pentafluorodiphenylamine gave an *N*-acetyl derivative, m. p. 91–93° (Found: C, 56.1; H, 2.7. C₁₄H₈F₅NO requires C, 55.8; H, 2.7%).

No reaction occurred between hexafluorobenzene and anilinomagnesium iodide in refluxing diethyl ether; reaction in boiling dioxan for 20 hr. gave about 1% of crude pentafluorodiphenylamine.

Reaction of Aniline with 2,3,4,5,6-Pentafluorodiphenylamine.—Sodium anilide [prepared as in

⁶ Kortum and Dreesen, *Chem. Ber.*, 1951, **84**, 182.

the last experiment from aniline (1.00 g.), 50% w/w sodium hydride-oil (0.20 g.), and dioxan (10 ml.)], 2,3,4,5,6-pentafluorodiphenylamine (1.00 g.), and more dioxan (5 ml.) were heated in an atmosphere of nitrogen in a sealed tube at 190–200° for 19 hr. The product was isolated as in the previous experiment and chromatographed on alumina (20 cm. × 2 cm.). Elution with light petroleum (b. p. 40–60°)-ether (5 : 1) gave unchanged 2,3,4,5,6-pentafluorodiphenylamine (0.09 g.), m. p. 71–73°; further elution with ether alone gave 2,3,5,6-tetrafluoro-*NN'*-diphenyl-1,4-phenylenediamine (0.45 g.), m. p. and mixed m. p. with the specimen obtained in the previous experiment, 148–151°.

*Oxidation of 2,3,5,6-Tetrafluoro-*NN'*-diphenyl-1,4-phenylenediamine.*—The diamine (0.040 g.) in dioxan (10 ml.) was heated on a steam-bath with concentrated nitric acid (5 ml.) for 30 min., and then poured into water. Ether-extraction gave a product which was purified by sublimation to give 2,3,5,6-tetrafluorobenzoquinone (0.003 g.), m. p. 165–170° (sealed tube) (lit.,³ 179°), having the reported infrared spectrum.³

Decafluorodiphenylamine.—Pentafluoroaniline (3.07 g.) was added to a stirred solution of sodium (0.40 g.) in liquid ammonia (175 ml.); the colour changed from violet to orange. After 15 min., hexafluorobenzene (5.06 g.) was added to the resulting solution, and then, during 1 hr., the ammonia was evaporated while ether (150 ml.) was added. After being refluxed for 1 hr. more, the red solution was washed with 2*N*-hydrochloric acid and water and dried (MgSO₄). Distillation gave, besides ether, unchanged pentafluoroaniline (0.36 g.); several crystallisations of the residue gave decafluorodiphenylamine (0.90 g.), m. p. 85–87° (lit.,² 81–82°) (Found: C, 41.5; H, 0.3; N, 4.4. Calc. for C₁₂HF₁₀N: C, 41.3; H, 0.3; N, 4.0%), having the reported infrared spectrum.² It had λ_{\max} . 251 m μ (ϵ 12,200) in cyclohexane; at 210 m μ , ϵ was 8200.

Reaction of Diphenylamine with Hexafluorobenzene.—50% w/w sodium hydride-oil (1.22 g.) and diphenylamine (4.31 g.) were refluxed in dioxan (200 ml.) with a small amount of copper powder for 2 hr., with stirring. Hexafluorobenzene (10.00 g.) was then added and the refluxing was continued for 2 hr. more. The mixture was poured into *n*-hydrochloric acid (750 ml.) and the product isolated by extraction with methylene chloride. It was extracted with hot light petroleum (b. p. 40–60°; 200 ml.) and this solution was shaken with 6*N*-hydrochloric acid (200 ml.). The precipitate was treated with aqueous potassium hydroxide, to give diphenylamine (1.96 g.), identified by infrared spectroscopy. The light petroleum layer was dried (MgSO₄) and evaporated and the residue was chromatographed on alumina (30 cm. × 3.5 cm.). Elution with light petroleum (b. p. 40–60°)-ether (5 : 1) gave, first, 2,3,4,5,6-pentafluorotriphenylamine (2.26 g.), m. p. 101–103° (Found: C, 64.3; H, 3.0. C₁₈H₁₀F₅N requires C, 64.5; H, 3.0%), λ_{\max} . 282 m μ (ϵ 14,500) in cyclohexane (at 210 m μ , ϵ 25,500) and, secondly, pale yellow 2,3,5,6-tetrafluoro-*NNN'*-tetraphenyl-1,4-phenylenediamine (0.91 g.), m. p. 198–200° (Found: C, 73.8; H, 4.1; N, 6.1; F, 15.8. C₃₀H₂₀F₄N₂ requires C, 74.4; H, 4.2; N, 5.8; F, 15.5%).

Reaction of 2,3,4,5,6-Pentafluorodiphenylamine with Hexafluorobenzene.—A suspension of *p*-tolylsodium [from sodium (0.50 g.) and *p*-chlorotoluene (1.39 g.) in heptane (6 ml.)] was added, with stirring and in nitrogen, to a solution of 2,3,4,5,6-pentafluorodiphenylamine (2.62 g.) in dioxan (125 ml.). After a few minutes, hexafluorobenzene (5.12 g.) was added and the solution was refluxed for 3 hr. More hexafluorobenzene (2.00 g.) was then added and the refluxing was continued for 21 hr. more. Isolation as in the first experiment left a residue which was chromatographed on alumina (30 cm. × 3.5 cm.). Elution with light petroleum (b. p. 40–60°)-ether (9 : 1) gave 2,2',3,3',4,4',5,5',6,6'-decafluorotriphenylamine (I), (0.36 g.), m. p. 119–121° (Found: C, 50.8; H, 1.4; N, 3.6. C₁₈H₅F₁₀N requires C, 50.8; H, 1.2; N, 3.3%), λ_{\max} . 265 m μ (ϵ 13,200) in cyclohexane (at 210 m μ , ϵ was 21,600). Further elution, with light petroleum (b. p. 40–60°)-ether (5 : 1), gave 2,3,5,6-tetrafluoro-*NN'*-bis(pentafluorophenyl)-*NN'*-diphenyl-1,4-phenylenediamine (II) (0.19 g.), m. p. 176–178° [Found: N, 3.9; *M*, 698, 681 (by a modified Barger's method). C₃₀H₁₀F₁₄N₂ requires N, 4.2%; *M*, 664]. Elution with a 1 : 1 mixture of the same solvents gave 2,2',3,3',5,5',6,6'-octafluoro-4,4'-bis-(2,3,4,5,6-pentafluorodiphenylamino)triphenylamine (III) (0.05 g.), m. p. 262–264° (Found: C, 55.6; H, 1.5. C₄₂H₁₅F₁₈N₃ requires C, 55.7; H, 1.7%). Finally, elution with ether alone gave pentafluorodiphenylamine (1.49 g.), identified by mixed m. p. and infrared spectroscopy.

When this reaction was repeated, but with a 3 hr. reflux, 1.5% conversion into the decafluorotriphenylamine was obtained.

Pentadecafluorotriphenylamine.—*p*-Tolylsodium [from sodium (0.16 g.) and *p*-chlorotoluene (0.45 g.) in heptane (2 ml.)], a solution of decafluorodiphenylamine (1.09 g.) in dioxan (15 ml.),

[1964]

Evans, Owen, and Phillips.

5021

and hexafluorobenzene (7.20 g.) were heated in nitrogen in a sealed tube at 230° for 42 hr. Isolation as in previous experiments and chromatography on alumina (15 cm. × 3.5 cm.), with light petroleum (b. p. 40–60°) as eluent gave *pentadecafluorotriphenylamine* (0.09 g.), m. p. 97–99° (Found: C, 41.9. C₁₈F₁₅N requires C, 42.0%), λ_{\max} 255 m μ (ϵ 13,200) in cyclohexane (at 210 m μ , ϵ was 18,800). Further elution with light petroleum (b. p. 40–60°)–ether (10 : 1) gave small amounts of aromatic hydrocarbons which infrared spectroscopy indicated were mainly 4,4'-dimethylbiphenyl. Finally, elution with a 1 : 1 mixture of the same solvents gave unchanged decafluorodiphenylamine (0.81 g.), identified by infrared spectroscopy and mixed m. p.

No reaction occurred when the same reactants were refluxed in dioxan for 24 hr.; decafluorodiphenylamine was recovered in 94% yield.

CHEMISTRY DEPARTMENT, THE UNIVERSITY,
EDGBASTON, BIRMINGHAM 15.

[Present address (J. C.): DEPARTMENT OF ORGANIC CHEMISTRY,
C.S.I.C., UNIVERSITY OF BARCELONA, SPAIN.]

[Received, March 20th, 1964.]
