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REACTION OF DIFLUOROCARBENE AND HEXAFLUOROPROPENE
WITH POLYFLUORINATED N-METAL-DIPHENYLAMIDES

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SUMMARY

N-difluoromethyl and N-(perfluoropropenyl)-decafluorodiphenylamine together with N-(perfluoropropenyl)-2,3,4,5,6-pentafluorodiphenylamine have been prepared by reacting N-lithium or sodium diphenylamides with difluorocarbene or hexafluoropropene. The amines were hydrolyzed to the respective N,N-decafluorodiphenyl amides with sulphuric acid. The ^{19}F NMR spectra of the N,N-decafluorodiphenylamides showed a set of resonances for each of the phenyl groups indicating hindered internal rotation around the N-C(O) bond.

INTRODUCTION

A growing amount of reports dealing with carbenes, but only few concerning reactions on anilino derivatives have been published in recent years.

Diphenylformamide has been obtained from a reaction between diphenylamine and dichlorocarbene [1,2], while N-methylaniline and dichlorocarbene gave N,N',N''-trimethyl-N,N',N''-triphenylamino methane. The latter product was obtained also in a reaction between N-methyl-N-sodium anilide and chlorodifluoromethane [3], while 1,1,2,2,-tetra-N-methylanilino ethene resulted from a reaction between N-methylaniline and dibromocarbene [4]. In the present work reactions between pentafluoroaniline or polyfluorodiphenylamines and difluorocarbene have been investigated. The difluorocarbene was generated by the method of Miller et al. [5,6]

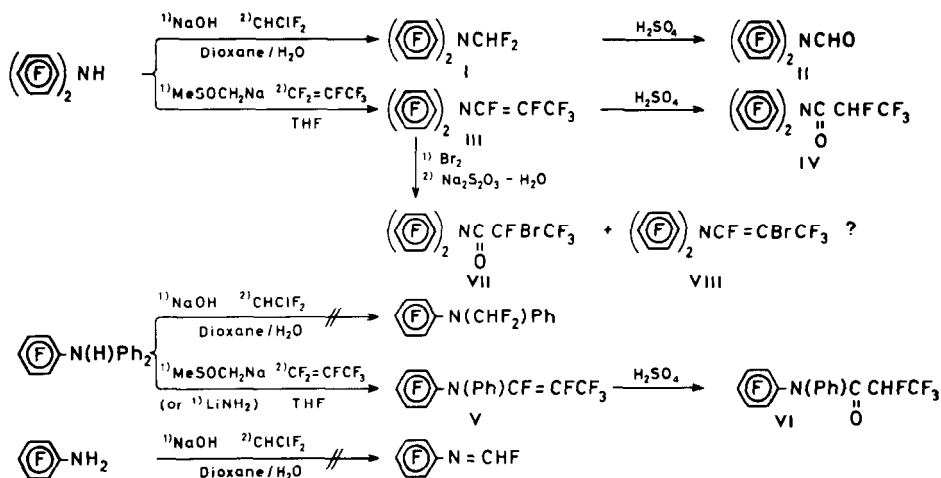
Reactions between tetrafluoro or chlorotrifluoro ethylenes and diphenylamine in presence of catalytic amounts of potassium gave the substituted products [7] or with N-lithium or N-potassium diphenylamide the substituted vinyl compounds [8]. The reactions have been performed in pressure vessels. The prepared diphenylamino compounds hydrolyzed easily to the respective amides [8].

In this paper the preparation of N-difluoromethyl and N-perfluoropropenyl polyfluorodiphenylamines is reported. These compounds are likely to hydrolyze very slowly to the respective amides without giving fluorinated acetic acids by further hydrolysis.

RESULTS AND DISCUSSION

A direct insertion of difluorocarbene into an amine with an isolable difluoromethyl amino compound as a result has been obtained with decafluorodiphenylamine in a mixture of dioxane and diluted sodium hydroxide by adding chlorodifluoromethane. With pentafluoroaniline and 2,3,4,5,6-pentafluorodiphenylamine no reaction seemed to occur. The reaction with decafluorodiphenylamine may result from the ability of this compound to form a sodium salt in water from the base, thus paralleling the reactions of thiols and phenols under identical conditions [5,6]. The proton magnetic resonance of N-difluoromethyl-decafluorodiphenylamine, I, gave a triplet at δ 6.54 ppm with a proton-fluorine coupling constant of 60.3Hz. Each of the resonances seems to be a pentet with coupling constant $J(H, F_o)$ 0.8Hz [9]. The ^{19}F NMR spectrum of the difluoromethyl group gave a doublet with a proton-fluorine coupling constant of 60.3Hz, at 73.1 ppm downfield to C_6F_6 . Each resonance was splitted into a pentet, most probably through a coupling with the orthofluorines [9], with a coupling constant of 6.2Hz. The amine, I, was hydrolyzed quantitatively to decafluorodiphenylformamide, II, with concentrated sulphuric acid, see Scheme 1.

Reactions between N-lithium or N-sodium decafluorodiphenylamide or 2,3,4,5,6-pentafluorodiphenylamide and hexafluoropropene, gave the desired compounds, N-(perfluoro-



Scheme 1. Performed reactions.

propenyl)-decafluorodiphenylamine, III, and N-(perfluoropropenyl)-2,3,4,5,6-pentafluorodiphenylamine, V, respectively in good yield. The reactions occurred at normal pressure in a reaction vessel with a reflux cooler at -70° . Treatment of the prepared amines with concentrated sulphuric acid, see Scheme 1, gave the corresponding amides (II, IV, and VI). No hydrolysis of compound V took place with the method described for N-trifluorovinylidiphenylamine [10].

Treatment of III with bromine seemed to give the normal addition product since N,N-(decafluorodiphenyl)-2-bromo-tetrafluoropropanamide, VII, was the main product obtained after hydrolysis of the reaction mixture utilizing sodium thiosulphate. Two other compounds were also present, see the Experimental part.

The ^{19}F NMR spectra for the N,N-decafluorodiphenylamides, II, IV and VII, gave a set of resonances for each of the phenyl groups in the ratio 1:1, Table 1. Different chemical shifts for the N-methyl groups in compounds as N,N-dimethylacetamide and N,N-dimethyltrifluoroacetamide are known to result from the double bond character in the N-C(O) bond [11]. No shift differences have been detected, however, between the N-trifluoromethyl groups in perfluoro-N,N-dimethylacetamide or in methyl-N,N-bis-(trifluoromethyl)-carbamate [11].

Table 1. Spectral data

Compound	Chemical shifts (ppm)	IR (cm ⁻¹)	¹ H shifts at (ppm) downfield to internal TMS in CDCl ₃	Skeletal vibrations of fluorinated ring	Bands in C-F region
I (C ₆ F ₅) ₂ NCH ₂	C ₆ F ₅ : 17.8 (c), 9.0 (p), 1.0 (m) CH ₂ : 73.1 dp J(H,F) 60.3 and J(F,F _o) 16.2 Hz	6.54 tp J (H,F) 160.3 and (H,F _o) 10.8 Hz		1515 (sb) 1505 (s)	1225 (m), 1203 (w), 1114 (s) 1047 (sb), 1042 (s), 1025 (sb), 945 (s), 926 (w), 807 (m)
III (C ₆ F ₅) ₂ NCF=CFCF ₃			1748 (s)	1520 (s, br)	1300 (s), 1210 (s), 1185 (m), 1150 (s), 1045 (s), 048 (s), 993 (s)
VIII (C ₆ F ₅) ₂ NCF=CBrCF ₃ ^a				1520 (s)	1245 (m), 1212 (m), 1160 (m), 1130 (w), 1110 (w), 1095 (w), 1047 (s), 993 (s), 805 (w)
V (C ₆ F ₅ N(Pn))CF=CFCF ₃	C ₆ F ₅ : 16.2 (o), 7.9 (p), 1.2 (m)		1737 (s)	1515 (s)	1250 (m), 1205 (s), 1177 (w), 1143 (s), 1065 (w), 1050 (s), 1032 (m), 993 (s)
II (C ₆ F ₅) ₂ NCHO	C ₆ F ₅ : 16.1 (o), 10.2 (p), 1.1 (m) J _{2,4} 2.6 Hz 18.9 (c), 10.9 (p), 2.4 (m) J _{2,4} 2.1 Hz	8.35 br	1737 (s)	1513 (s, br)	1237 (m), 1198 (w), 1100 (m), 1045 (w), 1028 (w), 1017 (w), 986 (s), 918 (w), 805 (m)

IV (C ₆ F ₅) ₂ NC(O)CHFCF ₃	C ₆ F ₅ : 18.4 (o), 11.2 (p), 1.6 (m) 13.0 (p), 3.1 (m) CH ₂ : 39.4 dq J(H,F) 46.2 and J(F,F) 12.3 Hz	5.34 dq J(H,F) 46.4 and J(H,F) 5.8 Hz	1742 (s)	1520 (s, br)	1253 (m), 1205 (m), 1151 (w), 1133 (w), 1109 (m), 1059 (m), 999 (s), 900 (w), 875 (m), 806 (m)
VII (C ₆ F ₅) ₂ NC(O)CFBrCF ₃	C ₆ F ₅ : 19.6 (o), 11.6 (p), 2.0 (m) 21.6 (o), 13.4 (p), 2.4 (m)	1729 (s)	1523 (s)	1224 (m), 1201 (w), 1119 (w), 1056 (s), 1036 (m), 1026 (w), 999 (s), 912 (w), 896 (w), 809 (m)	
VI C ₆ F ₅ N(Ph)COCHFCF ₃	5.33 dq J(H,F) 145.9 and J(H,F) 5.7 Hz Ph: 7.49	1712 (s)	1519 (s)	1267 (m), 1188 (m), 1129 (m), 1119 (m), 1109 (m), 996 (s), 978 (m), 874 (w), 854 (w)	

a. See experimental part.

b. Center of overlapping signals.

c. Internal CF₃CCl₃: C₆F₆ = -CF₃CCl₃ + 80.67 ppm in CCl₄.
br, broad; d, doublet; p, pentet; q, quartet; t, triplet

It is therefore believed that the strongly electron withdrawing trifluoromethyl groups bonded directly to nitrogen, suppress the double bond character of the N-C(O) bond in these compounds [11]. It is emphasized that when the trifluoromethyl groups bonded to nitrogen are changed with pentafluorophenyl groups, two sets of resonances are obtained in the ^{19}F NMR spectra. Magnetic non-equivalence for the phenyl groups in decafluorodiphenylamino compounds has previously not been reported. The shift differences found for the phenyl groups in the N,N-decafluorodiphenylamides are therefore believed to result from hindered rotation around the N-C(O) bond as shown for N,N-dimethylacetamide and N,N-dimethylformamide [11,12].

EXPERIMENTAL

The reactions with hexafluoropropene were carried out under an atmosphere of dry oxygen-free nitrogen. Tetrahydrofuran was dried and distilled from sodium benzophenone ketyl prior to use. IR and NMR spectra were determined employing Perkin-Elmer IR 225 spectrophotometer, Bruker HFX 60 and Varian 60 and 100 MHz NMR instruments, respectively. MS spectra were recorded on an AEI MS 902 instrument attached to an AEI DS30 data system.

N-Difluoromethyl-decafluorodiphenylamine (I)

To decafluorodiphenylamine (10.47g, 0.03 mol) in a mixture of 1,4-dioxane/water (25/25 ml) sodiumhydroxide (6.0g, 0.15 mol) was added. The temperature in the mixture was raised to 60°, and chlorodifluoromethane (40g) was slowly bubbled through the mixture. The mixture was cooled, diluted with water (100 ml), extracted with ether, dried, concentrated and chromatographed on neutral alumina (Woelm) with light petroleum (40-60°). This gave an oil and 4.45g recovered decafluorodiphenylamine. The oil (5.12g) contained approximately 27.5% decafluorodiphenylamine and 60.5% N-difluoromethyl-decafluorodiphenylamine (n.c.) by G.L.C. An analytical sample was obtained by preparative G.L.C.

Found: C, 38.96; H, 0.03; m/e, 399 (75), 380 (12.5), 349 (100), 348 (13), 51 (27.5). Calc. for $C_{13}HF_{12}N$: C, 39.12; H, 0.25; M, 399.0).

N-(Perfluoropropenyl)decafluorodiphenylamine (III).

Decafluorodiphenylamine (5.34g, 0.015 mol) in THF (15 ml) was added at 0° to sodium dimethyl sulphoxide [dimethylsulphoxide (3 ml) and sodium hydride (0.39g, 0.016 mol)]. The mixture was warmed to 50° and the hexafluoropropene (4.2g) was added slowly until no more was consumed, and stirred for still 1 h (a -70° reflux condenser was used). The light red mixture was cooled, hydrolyzed with 5% HCl and worked up to give a red oil which was chromatographed on neutral alumina (Woelm), and subsequently vacuum distilled ($110^{\circ}/15$ mm Hg). This gave N-(perfluoropropenyl)decafluorodiphenylamine (n.c.) 4.93g of an approximate purity 94% from G.L.C. An analytical sample was obtained by preparative G.L.C. Found: C, 37.45; H, 0; m/e, 479 (52), 460 (13.5), 410 (12), 217 (67.5), 212 (100), 167 (20.5), 117 (22.5), 69 (26.5), Calc. for $C_{15}F_{15}N$: C, 37.60; H, 0; M, 479.2.

N-(Perfluoropropenyl)2,3,4,5,6-pentafluorodiphenylamine (V).

Through the reaction mixture from 2,3,4,5,6-pentafluorodiphenylamine (5.18g, 0.02 mol) and lithium amide (0.52g) in THF (15 ml) [13], nitrogen was bubbled for 20 min. More THF (50 ml) was added, and the mixture was placed on a bath (15°) with tap water. Hexafluoropropene (8.6g) was added until saturation (15 min.). The mixture was stirred over night at ambient temperature, concentrated, diluted in light petroleum ($40-65^{\circ}$), filtered and concentrated again and chromatographed on neutral alumina with light petroleum ($40-65^{\circ}$). The oily product obtained after vacuum distillation ($105^{\circ}/0.25$ mm Hg, 3.09 g) contained 98% N-(perfluoropropenyl)2,3,4,5,6-pentafluorodiphenylamine (n.c.) from G.L.C. An analytical sample was obtained by preparative G.L.C. Found: C, 46.05; H, 1.07; m/e, 389 (88), 370 (11.5), 320 (24.5), 77 (100). Calc.

for $C_{15}H_5F_{10}N$: C, 46.29; H, 1.30; M, 389.2.

2.15 g 2,3,4,5,6-pentafluorodiphenylamine was recovered.

Addition of bromine to N-(perfluoropropenyl)decafluoro-
diphenylamine.

To N-(perfluoropropenyl)decafluorodiphenylamine (2.40g) in carbontetrachloride (4 ml) with some steel wool, bromine (0.27 ml) was added. The mixture was stirred at 60° for 1 h, then over night at ambient temperature. After the addition of traces of benzoylperoxide the mixture was stirred for another hour at 60° . The dark, bromine coloured mixture was cooled, treated with aqueous sodium thiosulphate, separated, washed and treated with carbon-tetrachloride. The carbontetrachloride layers were gathered, dried and concentrated to a yellow oil which, as found from G.L.C. analysis, contained three new compounds ($\sim 13\%$, $\sim 23\%$ and $\sim 40\%$ of the oil) with the main one slowly precipitating from the mixture. Analytical samples were obtained by preparative G.L.C.

1. N-(1 or 2-bromo-tetrafluoropropenyl)decafluorodiphenylamine (VIII) 23%. Found: C, 33.30; H, 0.22; m/e, 541 (13.6), 539 (13.5), 522 (3.6), 520 (3.6), 472 (3.3), 470 (3.3), 460 (21), 274 (16.4), 272 (14.8), 267 (76), 217 (100), 167 (25), 111 (37), 93 (14), 69 (13), 31 (18).

Calc. for $C_{15}BrF_{14}N$: C, 33.36; H, 0; M, 540.1. No double bond stretch in the proximity of 1700 cm^{-1} in IR was present.

2. N-(2-bromo-hexafluoropropyl)decafluorodiphenylamine (IX) (n.c.), 13%. Identification has been done from M.S. data only Found: m/e, 579 (16.3), 577 (16.8), 560 (2.8), 558 (2.9), 479 (12), 410 (15), 399 (19), 398 (100), 349 (13), 348 (35), 298 (17), 231 (12), 217 (25), 181 (2.2), 179 (4.5), 167 (14), 155 (51), 131 (17), 117 (32), 100 (3.2), 98 (4.7), 93 (15), 69 (52), 31 (11). Calc. for $C_{15}BrF_{16}N$: M, 578.1.

3. N,N-(decafluorodiphenyl)2-bromotetrafluoropropanamide (VII) (n.c.), 40%, m.p. $100-102^\circ$. Found: C, 32.56; H, 0.16; m/e, 557 (6.1), 555 (6.3), 457 (15), 374 (4.4), 372 (4.8), 348 (21), 181 (12.4), 179 (12.7), 155 (24), 117 (9), 109

(100), 98 (1), 93 (5), 69 (10). Calc. for $C_{15}BrF_{14}NO$:
C, 32.4%; H, 0; M, 556.1.

Hydrolysis

The hydrolysis were performed in conc. sulphuric acid at ambient temperature for 20 h. The reaction mixture was added to water (100 ml), extracted with ether, dried (sodium sulphate and sodium carbonate), concentrated to a white crystalline material and recrystallized from ether/light petroleum (40-60°). Analytical samples were obtained from preparative G.L.C.

N,N-Decafluorodiphenylformamide (II)

An oil (1.36g) containing 30.6% N-difluoromethyldecafluorodiphenylamine and 67.6% decafluorodiphenylamine gave a crude product which as found from G.L.C. analysis, contained 67.9% decafluorodiphenylamine and 31.3% decafluorodiphenylformamide (n.c.), m.p. 70.5-72.5°. Found: C, 41.56; H, 0.41; m/e, 377 (18), 350 (12), 349 (100), 330 (33), 311 (11), 310 (43), 299 (11), 298 (11), 280 (21), 279 (22), 210 (3), 182 (10), 167 (6), 156 (13), 155 (52). Calc. for $C_{13}HF_{10}NO$: C, 41.4%; H, 0.27; M, 377.1.

N,N-(Decafluorodiphenyl)2,3,3,3-tetrafluoropropanamide (IV).

N-(Perfluoropropenyl)decafluorodiphenylamine (0.7g) gave, as found from G.L.C. analysis of the crude product, 20.7% recovered material and 71% N,N-(decafluorodiphenyl)2,3,3,3-tetrafluoropropanamide (n.c.), m.p. 110-111°. Found: C, 38.02; H, 0.36; m/e, 478 (5), 477 (36), 376 (8), 350 (8), 349 (64), 348 (16), 330 (6), 310 (7), 298 (24), 294 (18), 279 (9), 155 (46), 129 (87), 117 (23), 101 (100), 93 (11.5), 69 (28), 51 (22).
Calc. for $C_{15}HF_{14}NO$: C, 37.76; H, 0.21; M, 477.2.

N,N-(2,3,4,5,6-Pentafluorodiphenyl)2,3,3,3-tetrafluoropropanamide (VI).

N-(Perfluoropropenyl)2,3,4,5,6-pentafluorodiphenylamine (0.80g) gave 0.52g N,N-(2,3,4,5,6-pentafluorodiphenyl)-2,3,3,3-tetrafluoropropanamide (n.c.), m.p. 79-80.5°.

Found: C, 46.68; H, 1.73; m/e, 388 (16), 387 (99), 294 (100)
259 (51), 258 (60), 257 (14), 240 (13), 239 (28), 238 (49),
208 (15), 204 (23), 167 (3), 129 (13), 101 (28), 93 (4),
77 (46), 65 (54).

Calc. for $C_{15}H_6F_9NO$: C, 46.53; H, 1.56; M, 387.2.

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N,N-Dimethyl- and N-methylpentafluoroaniline gave
triplets at δ 2.90 and δ 3.06 ppm with 1.8 Hz and
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