

Journal of Fluorine Chemistry 75 (1995) 169-172



# Reactions of polyfluoroarenes with hexamethyldisilazane and with 1,1,1-trimethyl-*N*,*N*-bis(trimethylsilyl)stannaneamine in the presence of caesium fluoride

Alexey O. Miller, Georgii G. Furin

Institute of Organic Chemistry, Siberian Branch of the Russian Academy of Sciences, Novosibirsk 630090, Russian Federation

Received 28 February 1995; accepted 7 March 1995

#### Abstract

Hexamethyldisilazane and 1,1,1-trimethyl-N,N-bis(trimethylsilyl) stannaneamine aminate pentafluoropyridine, octafluorotoluene, pentafluorobenzonitrile, pentafluoronitrobenzene and pentafluorobenzene sulphonyl fluoride in the presence of caesium fluoride with formation of the corresponding perfluorinated aryl amines (ArNH<sub>2</sub>), diarylamines (Ar<sub>2</sub>NH) and triarylamines (Ar<sub>3</sub>N) (where the amine functions are in positions 4 relative to the arene substituent).

Keywords: Polyfluoroarenes; Hexamethyldisilazane; Caesium fluoride; Silylated amines

#### 1. Introduction

Silylated amines are widely used in organic synthesis for the introduction of nitrogen-containing groups [1]. Hexamethyldisilazane is the simplest stable ammonia derivative containing trimethylsilyl groups, but the possibilities of its synthetic applications are limited because of the considerable decrease in nitrogen nucleophilicity under the influence of the neighbouring trimethylsilyl groups. Nevertheless, the use of sodium or lithium hexamethyldisilylamide in the reactions with polyfluoroaromatic compounds allows the corresponding arylamines and diarylamines to be obtained [2]. Fluoride ion is a very strong base in bipolar aprotonic solvents and is able to abstract protons even from very weak acids [3]. Caesium fluoride can be assumed to bind protons of the NH group of hexamethyldisilazane under certain conditions to form a highly reactive N anion.

The present work is devoted to the study of the possibility of amination of polyfluoroaromatic compounds with hexamethyldisilazane in the presence of caesium fluoride.

#### 2. Results and discussion

Polyfluoroaromatic compounds 2a-2e have been shown by us to react with hexamethyldisilazane in the presence of caesium fluoride in dimethylformamide at 100 °C, leading, after aqueous hydrolysis, to the corresponding arylamines 3 and diarylamines 4 (Scheme 1). In more drastic conditions (150 °C, excess of CsF) triarylamines 5 are yielded together with compounds 3 and 4. These reactions do not occur under the described conditions in the absence of CsF.

$$HN(SiMe_3)_2 + Ar - F \xrightarrow{(1) CsF}_{(2) H_2O, HCl}$$

su c

$$Ar - NH_2 + Ar_2NH + Ar_3N$$

$$3a - e \qquad 4a - e \qquad 5a - c$$

Ar = 
$$\bigvee_{F} F_{F}$$
 (a), 4-CF<sub>3</sub>C<sub>6</sub>F<sub>4</sub>- (b), 4-NC-C<sub>6</sub>F<sub>4</sub>- (c),  
4-O<sub>2</sub>N-C<sub>6</sub>F<sub>4</sub>- (d),  
4-FSO<sub>2</sub>-C<sub>6</sub>F<sub>4</sub>- (e).

Scheme 1.

Caesium hexamethyldisilylamide can be assumed to be generated primarily, reacting further with polyfluoroaromatic compounds to give N,N-bis(trimethylsilyl) arylamines **6**. The nucleophilicity of the nitrogen atoms in various N-trimethylsilyl derivatives increases under CsF coaction, facilitating subsequent substitution of active fluorine atoms in the aromatic rings [4,5]. The consecutive addition of electron-withdrawing polyfluoroaryl substituents to nitrogen promotes the subsequent coordination of fluoride ion with the silicon atom of silylamines 6 and 7 and generation of N anions, but decreases the nucleophilicity of the latter.

The participation of caesium trimethylsilylamide  $Cs^+$  NHSiMe<sub>3</sub> in the reaction also cannot be completely excluded, although it seems to be less probable because of the difficult formation of the complex between the fluoride ion and silanes without electron-withdrawing substituents [6].

The reaction seems to occur through the formation of N anions (as shown in Scheme 2) or corresponding polar complexes of the  $[Ar-N(X)--SiMe_3--F]^-$  type.





Hydrogen fluoride, obtained in the reaction, binds CsF of caesium fluoride which is needed as catalyst. This decreases the yields of arylamines. The generation of caesium hexamethyldisilylamide under these conditions, in the absence of HF, was of interest.

As mentioned above, diarylamines are the main products of reaction of hexamethyldisilazane with polyfluoroarenes. That could arise from the difficulty of generation of  $(Ar_F)_2N^-$  anions from the intermediate  $(Ar_F)_2NSiMe_3$ . We assumed that the use of the tin fragment  $-SnMe_3$  instead of the silicon fragment  $-SiMe_3$  will favour the generation of the  $(Ar_F)_2N^-$  anion and its further reaction with polyfluoroarenes. This should be expected from the lower reactivity and solubility of FSnMe<sub>3</sub> relative to FSiMe<sub>3</sub>. Indeed, polyfluorinated triarylamines together with diarylamines were obtained in the CsF-catalysed reaction of 1,1,1-trimethyl-*N*,*N*bis(trimethylsilyl)stannaneamine (**8**) with polyfluoroarenes in DMF (Scheme 3).

$$\begin{array}{c} \text{Me}_{3}\text{Sn-N}(\text{SiMe}_{3})_{2} + 2\text{a-c,e} \xrightarrow[2]{\text{H}_{2}\text{O},\text{HCl}} \\ 8 & 2 \end{array}$$

3a-c,e+4a-c,e+5a-c,e

Scheme 3.

The reactions occur even at room temperature. Diarylamines and arylamines are the main products as found before [2]. As the reaction temperatures rises to 150 °C, the degree of conversion of reagents increases, leading to the formation of triarylamines, although arylamines and diarylamines are also yielded in considerable amounts. That fact can be associated with the ability of amides of alkaline metals, being strong bases, to eliminate protons from various CH acids [7,8].

In the case of pentafluoronitrobenzene (2d) the yields of the corresponding diarylamine 4d are substantially lower than for other polyfluoroarenes. Probably side reactions, involving the nitro group, and also reactions at the *ortho* positions of the aromatic ring are taking place.

The main advantages found in this work in comparison with methods described earlier are the following. The synthesis of polyfluoronated diarylamines is executed without application of amides and hydrides of alkali metals [2,9] using accessible reagents. Polyfluorinated triarylamines unknown earlier are made by reaction of polyfluoroarenes with 1,1,1-trimethyl-N,N-bis(trimethylsilyl)stannaneamine.

#### 3. Experimental details

The <sup>1</sup>H and <sup>19</sup>F nuclear magnetic resonance (NMR) spectra were recorded on a Bruker WP 200 SY spectrometer at frequencies of 200 MHz and 188.28 MHz respectively (hexamethyldisiloxane and  $C_6F_6$  were internal standards), mass spectra on a Finnigan MAT MS-8200 mass spectrometer (EI, 70 eV), and UV spectra on a Specord UV-visible spectrophotometer.

Caesium fluoride was calculated directly before use. All the syntheses were carried out in dry DMF in a nitrogen atmosphere.

The spectral characteristics of compounds **3a-3e** and **4a-4d** and analytical data for **4a-4d** correspond to those described previously [2]. Summaries of the results of preparation according to the methods described in the following sections are given in Table 1.

## 3.1. 1,1,1-Trimethyl-N,N-bis(trimethylsilyl)stannaneamine (8)

This was synthesized similarly to procedures described previously [10,11]. A solution of 18.93 g (0.095 mol) of Me<sub>3</sub>SnCl in 10 ml of THF was added to the solution of bis(trimethylsilyl)aminomagnesium bromide (obtained according to Refs. [12,13] from 10.90 g (0.1 mol) of EtBr, 2.43 g (0.1 mol) of magnesium chips and 16.14 g (0.1 mol) of hexamethyldisilazane). The mixture was boiled for 1 h, the solvent was distilled off, and the residue was distilled twice in vacuum. Yield was 22.00 g (71%).

Approximate content (per cent) of amination products 3:4:5 in reaction mixtures (according to <sup>19</sup> F nuclear magnetic resonance)					
Method of preparation	Initial arene				
	2a	2b	2c	2d	2e
A	10:80:0	15:75:0	15:60:0	15:40:0	10:70:0
B <sup>a</sup>	10:50:0	10:30:0	_	15:35:0	-
С	10:40:15	10:50:30	10:25:30	-	10:40:15
D	10:50:10	10:50:15	10:40:5	-	-

Table I

<sup>a</sup> Considerable amounts of the initial arenes 2a and 2b are observed in the reaction mixture.

#### 3.2. Polyfluorodiarylamines 4

#### Method A

A mixture of 8.07 g (0.05 mol) of hexamethyldisilazane, polyfluoroaromatic compound 2a (or 2b-2e) (0.1 mol) and 1.52 g (0.1 mol) of CsF in 150 ml of DMF was stirred at 100 °C for 5 h, cooled, poured into water, acidified with HCl and extracted with diethyl ether. The organic solution was washed with water and dried with CaCl<sub>2</sub>. The <sup>19</sup>F NMR spectra of the resulting solutions were recorded. After solvent distilling, the residue was recrystallized from petroleum ether (70-100 °C) (in the case of compound 4b the residue was pre-distilled in vacuum, the fraction with boiling point 160–170 °C at 11 Torr being sampled; compound 4d was isolated through column chromatography on Al<sub>2</sub>O<sub>3</sub>, eluting with a 1:1 mixture of benzene and ethanol. The yields of products were as follows: **4a**, 11.03 g (70%), melting point 149–150 °C; **4b**, 14.60 g (65%), melting point 76-77 °C; 4c, 9.08 g (50%), melting point 171-172. 5 °C; 4d, 6.45 g (32%), melting point 164-166 °C; 4e, 14.80 g (62%), melting point 169–171 °C.

#### Method B

The polyfluoroaromatic compound 2a (or 2b, 2d) (0.03 mol) and 3.24 g (0.01 mol) of amine 8 were added to a suspension of 1.52 g (0.01 mol) of CsF in 50 ml DMF at 20 °C and the mixture was stirred for 24 h and treated as described above for method A. The yields of products were as follows: 4a, 1.36 g (43%); 4b, 0.99 g (22%); 4d, 1.21 g (30%).

Bis(2,3,5,6-tetrafluoro-4-fluorosulphonylphenyl)amine (4e)

• Melting point 169–171 °C (heptane)

• NMR: <sup>1</sup>H (MeCN),  $\delta = 8.14$ ; <sup>19</sup>F (MeCN),  $\delta = 14.06$ (4F), 26.91 (4F), 237.37 (2F)

- UV (heptane):  $\lambda_{\text{max}}$  (log  $\epsilon$ ) = 307 nm (4.568)
- C<sub>12</sub>HF<sub>10</sub>NO<sub>4</sub>S<sub>2</sub> (477.3): calculated, C 30.20, H 0.21, F

39.81, N 2.93, S 13.44; found, C 30.75, H 0.31, F 39.58, N 2.67, S 13.00

Molecular mass 477 (mass spectrometry)

#### 3.3. Polyfluorotriarylamines 5

#### Method C

A mixture of 3.24 g (0.01 mol) of amine 8 and polyfluoroaromatic compound 2a (or 2b, 2, 2e) (0.03 mol) was added dropwise to a boiling suspension of 1.52 g (0.01 mol) of CsF in 50 ml of DMF during a period of 3-5 h. The mixture was cooled, poured into water, acidified with HCl and extracted with diethyl ether. The organic solution was washed with water and dried with CaCl<sub>2</sub>. The <sup>19</sup>F NMR spectra of the resulting solutions were recorded. After solvent distilling, the residue was consecutively recrystallized from ethanol and heptane (or chloroform). The yields of products were as follows: 5a, 0.56 g (12%); 5b, 1.53 g (23%); 5c, 1.39 g (26%); **5e**, 0.85 g (12%).

#### Method D

A mixture of 1.61 g (0.01 mol) of hexamethyldisilazane and polyfluoroaromatic compound 2a (or 2b, 2c) (0.03 mol) was added dropwise to a boiling suspension of 4.56 g (0.03 mol) of CsF in 50 ml of DMF during a period of 3-5 h. The mixture was treated as described above for method C. The yields of products were as follows: 5a, 0.23 g (5%); 5b, 0.80 g (12%); 5c, 0.11 g (2%).

#### Tris(2,3,5,6-tetrafluoro-4-pyridyl)amine (5a)

- Melting point 215–220 °C (heptane)
- NMR: <sup>19</sup>F (CHCl<sub>3</sub>),  $\delta$  = 13.04 (6F), 76.12 (6F)
- UV (heptane):  $\lambda_{\text{max}}$  (log  $\epsilon$ ) = 262 nm (4.491)

•  $C_{15}F_{12}N(464.2)$ : calculated, C 38.81, F 49.12, N 12.07; found, C 38.61, F 49.89, N 12.00

• Molecular mass 463.9931 (mass spectrometry) (calculated, 463.9931)

#### Tris[2,3,5,6-tetrafluoro-4-(trifluoromethyl)phenyl]amine (5b)

• Melting point 153–155 °C (heptane)

• NMR: <sup>19</sup>F (CCl<sub>4</sub>),  $\delta$  = 14.55 (6F), 23.88 (6F), 105.32 (9F)

- UV (heptane):  $\lambda_{\text{max}}$  (log  $\epsilon$ ) = 271 nm (4.553)
- C<sub>21</sub>F<sub>21</sub>N (665.2): calculated, C 37.92, F 59.98, N 2.11;

found, C 37.86, F 59.42, N 2.05

Molecular mass 665 (mass spectrometry)

### Tris(2,3,5,6-tetrafluoro-4-cyanophenyl)amine (5c)

- Melting point 293–295 °C (CHCl<sub>3</sub>)
- NMR: <sup>19</sup>F (CHCl<sub>3</sub>),  $\delta = 16.37$  (6F), 32.52 (6F)
- UV (heptane):  $\lambda_{\text{max}}$  (log  $\epsilon$ ) = 299 nm (4.643)
- $C_{21}F_{12}N_4$  (536.2): calculated, C 47.04, F 42.51, N 10.45; found, C 46.75, F 42.94, N 10.24

• Molecular mass 535.9942 (mass spectrometry) (calculated, 535.9931)

#### Tris(2,3,5,6-tetrafluoro-4-fluorosulphonylphenyl)amine (5e)

- Melting point 244–246 °C (CHCl<sub>3</sub>)
- NMR: <sup>19</sup>F (MeCN),  $\delta = 19.57$  (6F), 30.47 (6F), 237.05 (3F)
- UV (heptane):  $\lambda_{\text{max}}$  (log  $\epsilon$ ) = 286 nm (4.550)
- C<sub>18</sub>F<sub>15</sub>NS<sub>3</sub>O<sub>6</sub> (707.4): calculated, C 30.56, F 40.29, N 1.98; found, C 30.47, F 40.58, N 2.00
- Molecular mass 707 (mass spectrometry)

#### Acknowledgement

This work was carried out with the financial support of the Russian Foundation for Fundamental Research (Project 93-03-4725).

#### References

- I. Fleming, in D. Barton and D. Ollis (eds.), Comprehensive Organic Chemistry, Pergamon, Oxford, 1979, p. 600.
- [2] G.G. Furin, A.O. Miller and G.G. Yakobson, Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim., 1 (1985) 127.
- [3] K.O. Christe, W.W. Wilson, R.D. Wilson, R. Bau and J. Feng, J. Am. Chem. Soc., 112 (1990) 7619.
- [4] A.V. Zibarev, A.O. Miller, M.M. Shakirov and G.G. Furin, Zh. Obshch. Khim., 61 (1991) 951.
- [5] A.V. Zibarev and A.O. Miller, J. Fluorine Chem., 50 (1990) 359.
- [6] V.V. Bardin, O.N. Loginova and G.G. Furin, Izv. Sib. Otd. Akad. Nauk SSSR, Ser. Khim., 5 (1989) 53.
- [7] A.O. Miller and G.G. Furin, Synth. Commun., 24 (17) (1994), in press.
- [8] H. Ahlbrecht and G. Schneider, Tetrahedron, 42 (1986) 4729.
- [9] R. Koppang, J. Fluorine Chem., 9 (1977) 449; 8 (1979) 389; Acta Chem. Scand., 25 (1971) 3067; 25 (1972) 3872.
- [10] G. Bahr and S. Pawlenko, Methoden der Organische Chemie (Houben-Weyl), Vol. 13/6, 4th edn., 1978, p. 358.
- [11] A.O. Miller, A.V. Zibarev, M.A. Fedotov and G.G. Furin, Zh. Obshch. Khim., 59 (1989) 586.
- [12] U. Wannagat, H. Autzen, H. Kuckertz and H.J. Wismar, Z. Anorg. Allg. Chem., 394 (1972) 254.
- [13] G. Schubert and G. Gattow, Z. Anorg. Allg. Chem., 572 (1989) 126.