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Fluorodenitration of activated diphenyl sulphones using tetramethylammonium fluoride

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Abstract

Fluorodenitration of nitro-substituted diphenyl sulphones occurs readily in dipolar aprotic solvents using tetramethylammonium fluoride as the source of fluoride, although other reactions including fluorodesulphonylation can sometimes occur in competition.

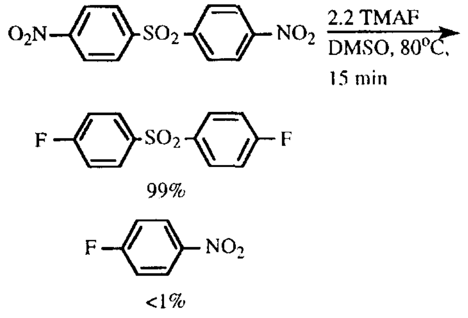
Keywords: Fluorodenitration; Diphenyl sulphones; Tetramethylammonium fluoride; NMR spectroscopy; Mass spectrometry

1. Introduction

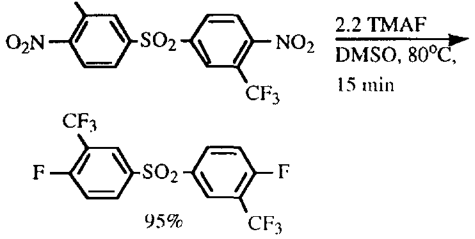
Aromatic fluorodenitrations are often attractive alternatives to halogen exchange for the synthesis of selectively fluorinated aromatic molecules via nucleophilic fluorination [1]. Unfortunately these reactions are often accompanied by formation of significant amounts of phenolic and diaryl ether by-products. We have reported recently the first use of tetramethylammonium fluoride (TMAF) as an efficient reagent for the fluorodenitration of nitroaromatics [2]. As part of our work on the use of fluorine-containing diphenyl sulphones to modify the thermal, electrical, mechanical and hydrophobic properties of poly(aryl ether sulphone)s (PES), we have studied the reactions of *p*-nitro-substituted diphenyl sulphones with TMAF as possible routes to sulphone monomers [3,4].

2. Results and discussion

The simplest nitroaryl sulphone studied was 4,4′-dinitrodiphenyl sulphone, which undergoes rapid fluorodenitration with a small excess of TMAF in DMSO giving complete conversion of the substrate within 15 min.



This demonstrates the clear preference for fluorodenitration over fluorodesulphonylation under conditions of equal activation. Unsurprisingly, the first perfluoroalkyl-substituted nitroaryl sulphone we studied, i.e. 3,3′-bis(trifluoromethyl)-4,4′-dinitrodiphenyl sulphone (a precursor to halide-ended monomers previously used in the synthesis of poly(aryl ether sulphone)s [4,5]), also gave rapid and clean fluorodenitration with TMAF:



On changing to the more useful 2,2′-bis(trifluoromethyl)-4,4′-dinitrodiphenyl sulphone – a unit which gives stable and water-resistant PES-type polymers [4,5] – the added activation of the 2-trifluoromethyl group

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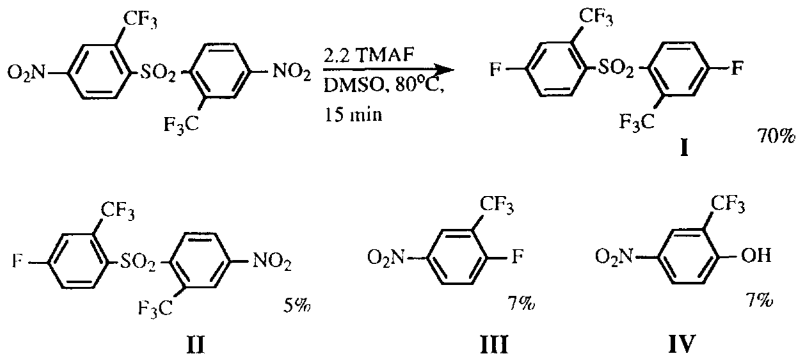


allows fluorodesulphonylation to occur in competition with the normal fluorodenitration reaction (see above).

The phenol observed is likely to result from attack of traces of fluoride-activated water (from the highly hygroscopic TMAF) attacking the 2-fluoro-5-nitrobenzofluoride. Fluorodenitration continues to be the dominant route (75:12 expressed as total product %) under these standard conditions but interestingly, by reducing the amount of TMAF present, fluorodesulphonylation becomes more significant (Table 1). This is the case over a range of temperatures. We believe that this is probably due to the particular ability of the TMA^+ cation to stabilise the NO_2^- anion as we originally suggested in a preliminary communication [2].

The most remarkable results came from studying the reaction of TMAF with 4-chloro-4′-nitro-2′-trifluoromethyldiphenyl sulphone [3]. Consistent with the earlier observation, fluorodesulphonylation occurred in competition with fluorodenitration, but a third type of product – an isomer of the fluorodenitration product – was also observed. The isomerisation accompanying fluorodenitration can be explained by attack of the sulphinate (produced in the fluorodesulphonylation reaction) on the starting material giving an intermediate triphenyl disulphone which can then undergo fluorodesulphonylation to give the third observed product.

The triphenyl disulphone was observed during substrate synthesis with extended reaction periods. Synthesis of this triaryl sulphone via an alternative route followed by fluorination under identical conditions gave the isomeric product exclusively. Changing the solvent to sulpholane had only a small effect on the product distributions – all three products were again observed.

It is apparent that TMAF is an excellent source of nucleophilic fluorine for the fluorodenitration of nitroaryl sulphones to give useful monomers for the synthesis of polysulphones. Fluorodesulphonylation will, however, occur in competition when this process is subject to sufficient electronic activation.

Table 1
Fluorination of 2,2′-bis(trifluoromethyl)-4,4′-dinitrodiphenyl sulphone

Reaction conditions[a]		Observed products after 30 min (% by GC)				
Temp. (°C)	TMAF[b] concentration (mol equiv. w.r.t. substrate)	I	II	III	IV	Others[c]
80	2.2	70	5	5	7	–
80	2.2 added over 30 min	45	–	51	–	–
60	1.1	27	39	21	–	13
115	1.1	22	25	41	9	12
130	2.2 KF, 0.2 PPh_4Br	11	18	67	4	–

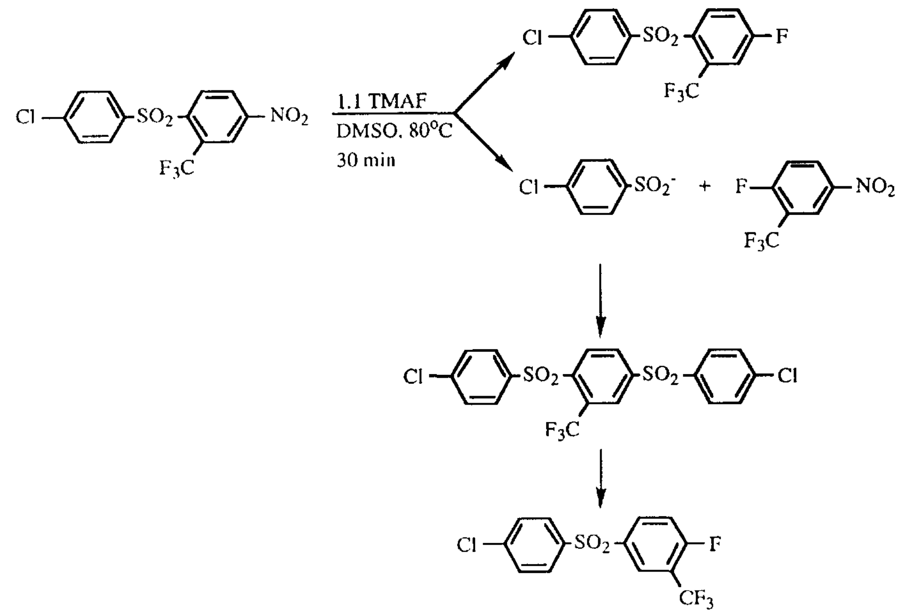
[a] DMSO solvent.
[b] TMAF was dried.
[c] Including substrate.

3. Experimental details

Gas–liquid chromatograms were obtained using a Phillips PU4500 instrument equipped with an FID detector and a Hewlett Packard 3396A integrator. GC–MSs were obtained using a Hewlett Packard 589011GC interfaced to a VG Analytical Autospec mass spectrometer. ^1H and ^{19}F NMR spectra were obtained on a JEOL FX90Q instrument operating at 90 MHz (^1H) and 84.3 MHz (^{19}F). Spectra are referenced to TMS (^1H) or $CFCl_3$ (^{19}F).

3.1. Typical fluorodenitration procedure

Approximately 0.76 g (5 mmol) of TMAF tetrahydrate (Fluka) and 20 ml of DMSO were azeotropically dried with 40 ml of cyclohexane under nitrogen for at least 6 h. For reactions at or below the azetrope temperature,



the required amount of substrate was then added and azeotroping continued during the reaction. For reactions above the azeotrope temperature, the cyclohexane was distilled out prior to substrate addition. Reactions were monitored by GC and the products identified by high-resolution GC–MS.

3.2. *4,4′-Dinitrodiphenyl sulphone*

Synthesis

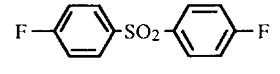
Sodium sulphide nonahydrate (12.0, 0.05 mol) [6] was dissolved in 50 ml of NMP under nitrogen and heated to 50 °C. 4-Chloronitrobenzene (15.8 g, 0.125 mol) was added and heating continued for 15 min. The sulphide was recovered by pouring on to ice, filtering and recrystallising from ethanol. Yield 13.5 g (98%).

4,4′-Dinitrodiphenyl sulphone: MS [*m*/*z* (intensity)]: 276 (100); 246 (17); 184 (36); 171 (12); 152 (9); 139 (22); 69 (10); 50 (9). ^{1}H NMR ($CDCl_3$) δ: 8.28 (2H, d, $J=9$ Hz); 7.79 (2H, d, $J=9$ Hz) ppm.

Fluorodenitration

The sulphide (10 g) was dissolved in 115 ml of glacial acetic acid and 12.04 g of chromium trioxide added cautiously. The mixture was then heated to 100 °C for 16 h. The sulphone was isolated by pouring on to crushed ice, and was washed with hot water to remove chromium residues and recrystallised from acetone. Yield 6.5 g (59%). MS [*m*/*z* (intensity)] 308 (22); 186 (8); 170 (100); 122 (19); 92 (11); 76 (31); 63 (10); 50 (26). ^{1}H NMR (DMSO-d_6) δ: 8.55 (2H, d, $J=9$ Hz); 8.49 (2H, d, $J=$ 9 Hz) ppm. M.p. 250–252 °C (lit. value [7]: 251–254 °C).

Fluorodenitration product:

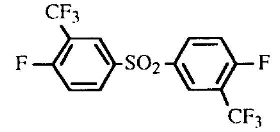


MS [*m*/*z* (intensity)]: 254 (39); 143 (100); 115 (9); 95 (54); 83 (10); 75 (29); 69 (7); 50 (8). Analysis: $C_{12}H_8F_2N_2O_2S$ requires: 254.0213. Found: 254.0201.

3.3. *4,4′-Dinitro-3,3′-bis(trifluoromethyl)diphenyl sulphone*

This substrate was obtained from Dr. J.E. Denness [4].

Fluorodenitration product:



MS [*m*/*z* (intensity)]: 390 (27); 37 (14); 227 (6); 211 (100); 163 (58); 144 (11); 113 (7). Analysis: $C_{14}H_6F_8O_2S$ requires: 389.9961. Found: 389.9955.

3.4. *4,4′-Dinitro-2,2′-bis(trifluoromethyl)diphenyl sulphone*

Synthesis

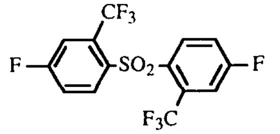
The synthesis of this substrate has been reported previously [8]. Sodium sulphide nonahydrate (7.2 g, 0.03 mol) and 3.38 g (0.015 mol) of 2-chloro-5-nitrobenzotrifluoride were heated in 30 ml of *N*,*N*-dimethylacetamide (DMAc) at 140 °C for 15 min using similar reaction and recovery conditions to those for 4,4′-dinitrodiphenyl sulphone.

4,4′-Dinitro-2,2-bis(trifluoromethyl)diphenyl sulphone: Analysis: $C_{14}H_6F_6N_2O_6S$ requires: C, 37.8; H, 1.4; N, 6.3%. Found: C, 37.7; H, 1.2; N, 6.2%. MS [*m*/*z* (intensity)]: [M^+ 444(2)]; 238 (100); 144 (40); 268 (25); 190 (11); 75 (11); 125 (9); 254 (9); 287 (9). ^{19}F NMR ($CDCl_3$) δ: −57.22 (CF_3, s) ppm. M.p. 205–207 °C.

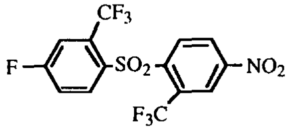
Fluorodenitration

The crude sulphide (9.0 g, 73%) was oxidised with 24 g of chromium trioxide in 100 ml of glacial acetic acid for 16 h, poured on to ice, washed with hot water and recrystallised from ethanol. Yield 6.64 g (68%).

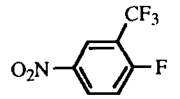
Fluorodenitration products:



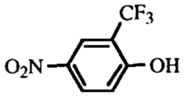
MS [*m*/*z* (intensity)]: 390 (13); 227 (12); 211 (100); 163 (58); 144 (17); 113 (9); 94 (5); 63 (5). Analysis: $C_{14}H_6F_8O_2S$ requires: 389.9961. Found: 389.9948.



MS [*m*/*z* (intensity)]: 417 (28); 238 (44); 227 (39); 211 (100); 179 (77); 163 (88); 144 (35); 125 (8). Analysis: $C_{14}H_6F_8O_2S$ requires: 416.9906. Found: 416.9913.



MS [*m*/*z* (intensity)]: 209 (42); 163 (100); 143 (17); 113 (23); 101 (21); 94 (16); 75 (30); 63 (16). Analysis: $C_7H_3F_4NO_2$ requires: 209.0100. Found: 209.0093.



MS [*m*/*z* (intensity)]: 207 (100); 187 (32); 157 (20); 141 (18); 129 (30); 113 (76); 107 (27); 63 (59). Analysis: $C_7H_4FNO_3$ requires: 207.0143. Found: 207.0148.

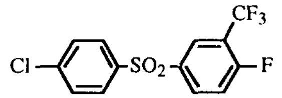
3.5. 2,5-Bis(4-chlorobenzenesulphonyl)benzotrifluoride

Synthesis

Sodium 4-chlorobenzene sulphinate (5.0 g, 25 mmol) [9] and 5.63 g (25 mmol) of 5-chloro-2-nitrobenzotrifluoride were heated in 25 ml of DMAc to 140 °C for 15 min under nitrogen. The sulphone was isolated by pouring on to ice, filtering and recrystallisation from ethanol. Yield 4.6 g (74%).

2,5-Bis(4-chlorobenzenesulphonyl)benzotrifluoride: Analysis: $C_{19}H_{11}Cl_2F_3O_4S_2$ requires: C, 46.1; H, 2.2%. Found: C, 46.0; H, 2.1%. MS [*m*/*z* (intensity)]: 494 (28); 175 (63); 159 (44); 144 (10): 127 (100); 111 (98); 99 (15). ^{19}F NMR ($CDCl_3$) δ: −57.48 (CF_3, s) ppm. M.p. 222–224 °C.

Fluorodenitration product:



MS [*m*/*z* (intensity)]: 338 (70); 319 (10); 211 (100); 159 (51); 127 (64); 111 (56); 99 (22); 75 (43). Analysis: $C_{13}H_7ClF_4O_2S$ requires: 337.9791. Found: 337.9807.

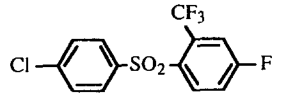
3.6. 4-Chloro-4′-nitro-2′-trifluoromethyldiphenyl sulphone

Synthesis

Sodium 4-chlorobenzene sulphinate (15.0 g, 0.076 mol) and 17.0 g (0.076 mol) of 2-chloro-5-nitrobenzotrifluoride were heated to 70 °C in 50 ml of DMAc for 15 min. The sulphone was isolated by pouring on to ice, filtering and recrystallisation from ethanol. Yield 21.0 g (75%).

4-Chloro-4′-nitro-2′-trifluoromethyldiphenyl sulphone: Analysis: $C_{14}H_6ClF_6N_2O_6S$ requires: C, 42.7; H, 1.9; N, 3.8%. Found: C, 43.2; H, 1.9; N, 3.4%. MS [*m*/*z* (intensity)]: 365 (33); 175 (62); 159 (15); 144 (7); 127 (57); 111 (100); 99 (16); 75 (36). ^{19}F NMR ($CDCl_3$) δ: −57.13 (CF_3, s) ppm. M.p. 139–140 °C.

Fluorodenitration products: 2-fluoro-5-nitrobenzotrifluoride, 2-trifluoromethyl-4-nitrophenol and 4-chloro-4′-fluoro-2′-trifluoromethyldiphenyl sulphone, identical to the products obtained above.



MS [*m*/*z* (intensity)]: 338 (44); 211 (84); 175 (39); 159 (22); 127 (62); 111 (100); 99 (16); 75 (44). Analysis: $C_{13}H_7ClF_4O_2S$ requires: 337.9791. Found: 337.9806.

Acknowledgements

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