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On reactions of carbon disulphide induced by 'naked' fluoride Part 1: Reactions with fluoroaromatics [1]

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Abstract

On reaction with carbon disulphide and tetramethylammonium fluoride in dimethylformamide, pentafluorobenzonitrile undergoes nucleophilic substitution reactions, resulting eventually in trifluoromethylthio substituted polyfluorobenzonitrile. 2,4-Dinitrofluorobenzene and pentafluorobenzene undergo similar substitutions, however, the product mixtures are much more complex.

Keywords: Carbon disulphide; Fluoroaromatics

1. Introduction

Fluoroaromatics are known [1] to undergo nucleophilic substitution of fluorine atoms by strong nucleophiles. In principle, the nucleophilicity of the FCS_2 anion (**1**), formed on the reaction of carbon disulphide with highly nucleophilic fluoride ion [2], should be sufficiently high for such a substitution reaction too. Therefore, pentafluorobenzonitrile, 2,4-dinitrofluorobenzene, and pentafluorobenzene were reacted with carbon disulphide + tetramethylammonium fluoride in order to provoke nucleophilic substitution on the aromatic ring.

2. Results and discussion

When pentafluorobenzonitrile (F_5PhCN, **2**) was reacted with carbon disulphide and tetramethylammonium fluoride (TMAF) in dimethylformamide (DMF) at room temperature, red to reddish brown liquid mixtures were obtained, the composition of which depended on the molar ratio of the reactants. A common characteristic of these mixtures is the occurrence of comparatively strong new signals at about −41 ppm in the respective ^{19}F NMR spectra. Attempted reactions in acetonitrile failed, the ^{19}F NMR signal is that of F_5PhCN only, even after prolonged heating. Likewise, no reactions could be observed using CsF or KF instead of TMAF.

A mixture of TMAF, CS_2 and F_5PhCN (molar ratio 1:8:5) in DMF showed a new, intensive, sharp signal at −41.9 ppm (in addition to several others) but no longer any F_5PhCN in the ^{19}F NMR spectrum after 3 days stirring at room temperature. From this reaction mixture, 3-(trifluoromethylthio)tetrafluorobenzonitrile (**4**) together with DMF could be separated by distillation. The residue, which is partially soluble in diethyl ether but completely soluble in acetonitrile, contains other trifluoromethyl substituted compounds, as indicated by several strong NMR peaks between −41.3 and −45.7 ppm. Using GC/MS, bis(trifluoromethylthio)trifluorobenzonitrile and tris(trifluoromethylthio)difluorobenzonitrile were detected.

The unexpected formation of trifluoromethylthio groups from carbon disulphide and TMAF, which proceeds under very gentle conditions, can be rationalized by a reaction sequence, as shown in Scheme 1.

The first step, the formation of the dithiofluoroformic acid anion (**1**), has already been described [2]. In separate experiments, we could not detect the anion in DMF solution (nor in acetonitrile solution), therefore it might be formed in the sequence as an intermediate only. Nucleophilic attack of **1** on pentafluorobenzonitrile (**2**) should result in **3**, with the attack oriented primarily to the para (sterically favoured) or ortho positions. A possible indication for –SC(S)F formed intermediately in the course of the reaction could be the ^{19}F NMR peak at −5.8 ppm observed temporarily. The third step in Scheme 1 must be more complex. It involves nucleophilic replacement of one sulphur atom by two fluoride ions, prob-

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[1] Dedicated to Professor A. Haas on his 65th birthday.

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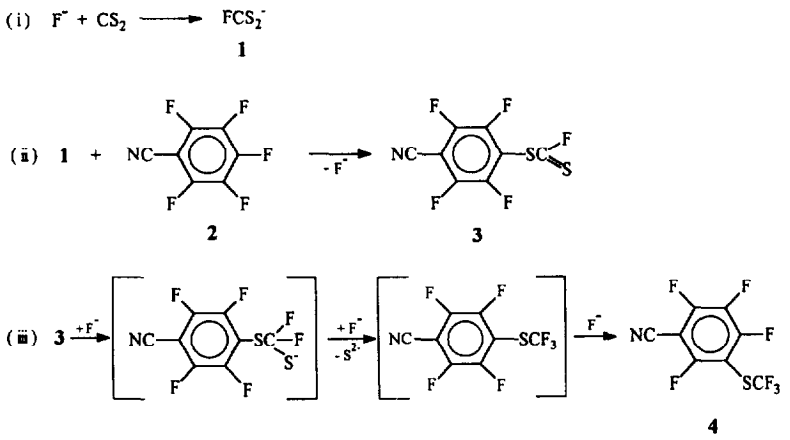
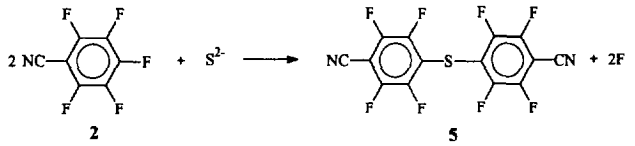


Scheme 1.



Scheme 2.

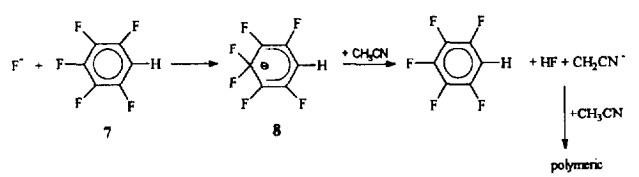
ably in two steps, and shifting of the trifluoromethylthio group or its precursor to the meta position yielding 3-(trifluoromethylthio)tetrafluorobenzonitrile (**4**). Such shifting was postulated [3] to explain observed meta substitution products from the reaction of pentafluoropyridine with the trifluoromethylthiolate anion.

For each trifluoromethylthio group introduced, two fluoride ions were needed in addition to the ion substituted (Scheme 1). However, in the experiment, all F_5PhCN could be reacted by using as little as one fifth the molar amount of TMAF. Since F_5PhCN is the only additional fluoride source in the system, and the sulphide ion is a nucleophile in itself, reactions of the type as given in Scheme 2 have to occur with the consequence that TMAF is needed as a catalyst only.

Orienting reactions of 2,4-dinitrofluorobenzene (2,4-$(NO_2)_2PhF$, **6**) with TMAF and CS_2 in DMF as well as in MeCN yielded complex mixtures from which only limited information could be gained. Again, the formation of trifluoromethylthio substituent could be observed, as indicated by its characteristic ^{19}F NMR signal at about -41 ppm, and it was accompanied by partial substitution of NO_2 by F, in accordance with a report given in [4]. Thus, difluoro(trifluoromethylthio)benzene could be detected by GC/MS. In addition, ^{19}F NMR of the reaction mixtures indicated the formation of the fluorosulphate anion, attributed to a comparatively strong signal at about $+38.5$ ppm which was stable for more than 24 h, even in aqueous solution. The formation of SO_3F^- can be rationalized by assuming oxidation of S^{2-} anions formed in a reaction sequence similar to that given in Scheme 1 by NO_3^- in the presence of very reactive 'naked' F^-.

Pentafluorobenzene (F_5PhH, **7**) could be reacted with TMAF and CS_2 too. On reaction with TMAF in an inert solvent such as pentafluoroethane (R125), an ochre-coloured insoluble solid was formed, possibly the Meisenheimer σ-complex **8** (Scheme 3) [5], from which we could not yet obtain a crystal for structural analysis. The isolated product reacts rapidly with MeCN with the formation of large amounts of HF_2^- yielding a brown turbid mixture. These observations can be described by a reaction sequence as given in Scheme 3. In accordance with Scheme 3, a few drops of F_5PhH added to an otherwise comparatively stable suspension of TMAF in MeCN starts the reaction between the latter.

When F_5PhH was reacted with TMAF and CS_2 without a solvent added, rather irregular and badly reproducible product mixtures were obtained. Thus, an experiment with about 1:1 molar ratio of TMAF to F_5PhH and excess CS_2 resulted probably in the formation of a CF_3S group, as indicated by a comparably strong ^{19}F NMR signal at -41 ppm both in the reaction mixture and in an ether extract of the sticky reddish brown product. However, the ^{19}F NMR spectrum of the ether extract of an acidified (H_2SO_4) aqueous solution of the brownish black solid products from an experiment with a large excess of F_5PhH gave some evidence for the possible formation of pentafluorodithiobenzoic acid. Similarly, from a reaction with F_5PhH, TMAF and CO_2, worked up the same way, the formation of pentafluorobenzoic acid was probable, according to the ^{19}F NMR spectrum which corresponds well with literature data. The two spectra, of the reaction with CS_2 as well as with CO_2, are within error identical. Therefore, and because of the lack of further analytical data, we cannot be sure that pentafluorodithiobenzoic acid was present in our NMR sample, but pentafluorobenzoic acid formed by hydrolysis. The probable formation of the tetramethylammonium salts of these acids could be explained either by direct reaction of CS_2 or CO_2 respectively with a pentafluorophenyl anion formed intermediately by HF abstraction from the Meisen-



Scheme 3.

heimer complex **8**, or by reaction of preformed dithiofluoroformiate anion [2] or fluoroformiate anion [6] respectively with F_5PhH or its Meisenheimer complex with F^- (**8**).

3. Experimental details

^{19}F NMR spectra were recorded with a Jeol FX90Q spectrometer at 84.25 MHz using $CFCl_3$ as external standard with upfield values designated negative. ^{13}C NMR spectra were recorded with a Bruker AC 250 instrument at 62.896 MHz using TMS as external standard. GC/MS was done with a Varian Saturn II instrument using a Nordion 50 m capillary coated with a NB 54 phase.

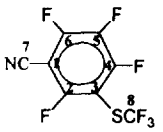
TMAF was prepared according to a procedure given in [7]. Solvents were dried applying standard procedures; the fluoroaromatics were used as supplied by Fluorochem Ltd.

3.1. Reactions with F_5PhCN (2)

To 10 ml DMF (dried over a molecular sieve) in a thoroughly dried 25 ml flask were added 0.2 g (2.15 mmol) anhydrous TMAF [7], 1.3 g (17.1 mmol) CS_2 (dried over P_4O_{10}), and 2 g (10.4 mmol) F_5PhCN; the mixture, which turned immediately cherry red, was stirred magnetically for 3 days at room temperature. After that time the mixture had become deeper coloured and slightly turbid, and the solid TMAF had nearly disappeared. ^{19}F NMR showed no more unreacted F_5PhCN but an intense new signal at -41.9 ppm and other new signals in the regions from -41.3 to -45.7 ppm as well as from -84.5 to -160 ppm. On distillation in a closed system at about 80 °C and 0.01 mmHg, and with the receiver cooled with liquid N_2, a liquid, mostly DMF, and a solid residue were obtained. The DMF solution was mixed with 100 ml H_2O, extracted with cyclopentane (5×), the combined extracts washed with H_2O (3×), dried (Na_2SO_4), and the solvent distilled off in vacuo, yielding about 0.5 g (1.8 mmol, 17.5%) of **4**, containing only small amounts of other unidentified compounds. The solid deep reddish brown residue of the distillation was extracted with Et_2O, yielding a fair yellow solution consisting according to GC/MS mainly of bis(trifluoromethylthio)trifluorobenzonitrile (MS 357 (M^+, base peak), 69), of additional **4** and of small amounts of tris(trifluoromethylthio)difluorobenzonitrile (MS 439 (M^+, 58%), 69 (base peak)). Following Et_2O, the residue was extracted with CH_3CN, yielding a deep brownish red solution of fluorine containing compounds, the composition of which is not yet clear. An aqueous solution of the small and now colourless residue contained F^- but not S^{2-}.

3.2. 3-(trifluoromethylthio)tetrafluorobenzonitrile (4)

Colourless liquid, b.p. 202–204 °C (uncorrected). MS: 275 (M^+), 206 ([M-CF_3]$^+$), 162 ($C_5F_4CN^+$), 69 (CF_3^+, base peak).



^{19}F NMR

-41.9 ppm (t, $3F^8$)	$^5J_{8,F2} = {}^5J_{F8,F4} = 5$ Hz
-97.4 ppm (dq, $1F^2$)	$^5J_{F2,F5} = 11$ Hz, $^5J_{F2,F8} = 5$ Hz
-110.7 ppm (m, $1F^4$)	$^3J_{F4,F5} = 22$ Hz, $^4J_{F4,F6} = 15$ Hz, $^5J_{F4,F8} = 5$ Hz
-117.6 ppm (dd, $1F^6$)	$^3J_{F6,F5} = 22$ Hz, $^4J_{F6,F4} = 15$ Hz
-158.2 ppm (td, $1F^5$)	$^3J_{F5,F4} = {}^3J_{F5,F6} = 22$ Hz, $^5J_{F5,F2} = 11$ Hz

^{13}C NMR

160.4 ppm (dq, C^2)	$^1J_{C,F} = 259.2$ Hz, $^3J_{C,F} \sim {}^4J_{C,F} = \sim 4$ Hz
155.9 ppm (dm, C^4)	$^1J_{C,F} = 269$ Hz, $^2J_{C,F} = 10.4$ Hz, $^3J_{C,F} = 5.4$ Hz, $^3J_{C,F} = 5$ Hz
154.1 ppm (dm, C^6)	$^1J_{C,F} = 268.8$ Hz, $^2J_{C,F} = 12.7$ Hz, $^3J_{C,F} = 6.5$ Hz, $^3J_{C,F} = 6.2$ Hz
137.5 ppm (dm, C^5)	$^1J_{C,F} = 257.3$ Hz, $^2J_{C,F} = 17$ Hz, $^2J_{C,F} = 13.8$ Hz, $^4J_{C,F} = 5.2$ Hz
127.1 ppm (q, C^8)	$^1J_{C,F} = 311.4$ Hz
105.8 ppm (s, C^7)	
100.5 ppm (m, C^3)	$^2J_{C,F} = 23$ Hz, $^2J_{C,F} = 20.6$ Hz, $J_{C,F} = 5.5$ Hz
90.8 ppm (m, C^1)	$^2J_{C,F} = 23$ Hz, $J_{C,F} = 16.6$ Hz, $J_{C,F} = 5.5$ Hz

3.3. Reactions with 2,4-$(NO_2)_2$PhF (6)

To 120 mg (1.29 mmol) TMAF, in a thoroughly dried glass tube, were added 230 mg (1.24 mmol) **6**, 128 mg (1.68 mmol) CS_2 and ca. 5 ml DMF. The mixture turned red immediately. After 10 days at 50 °C the sealed tube was opened, whereby some nitrous gases were liberated, and the deep red solution as well as the reddish black solid formed were investigated by ^{19}F NMR and GC/MS. ^{19}F NMR of the solution showed new peaks at about $-41/-42$ ppm and at -101 to -115 ppm and a very small peak at $+38$ ppm. The latter was much more intense in $MeCN^-$ and especially in aqueous solutions of the solid product; it can probably be assigned to SO_3F^-. One component of the DMF solution could be identified by GC/MS as difluoro(trifluoromethylthio)benzene in agreement with the ^{19}F NMR data. MS: 214 (M^+, 54%), 195 (M-F^+), 145 (M-CF_3^+), 101 (SCF_3^+, base peak), 69 (CF_3^+).

3.4. Reactions with F_5PhH (7)

To 90 mg (0.97 mmol) TMAF in a dried glass tube, 140 mg (0.83 mmol) **7** and about 6 ml C_2F_5H (R125) were distilled. The sealed tube was shaken repeatedly at room

temperature over a period of 3 days, with the white TMAF changing to a yellow solid. ^{19}F NMR of the sealed tube showed the signals of R125 and of **7** only. The isolated product reacts with MeCN yielding a brown slurry consisting mainly of fluorine-free polymeric organic material; ^{19}F NMR shows HF_2^- as well as **7**. The same results were obtained when the reaction was carried out directly in MeCN.

150 mg (0.89 mmol) F_5PhH were added to 90 mg (0.97 mmol) TMAF in a dried glass tube. After 5 h at room temperature, excess CS_2 was added, and the mixture kept at 75 °C for 30 days. Then the sealed tube containing a liquid and a reddish brown product sticking to the glass was opened, volatiles distilled off (CS_2 only), and the residue extracted. ^{19}F NMR of the ether extract showed intense signals at −41.6, −41.9, and −108.7 ppm, and some more rather small signals.

To 90 mg (0.97 mmol) TMAF in a dried glass tube were added 127 mg (1.67 mmol) CS_2 and excess F_5PhH. The sealed tube was kept at 75 °C for 40 days without any change in its ^{19}F NMR spectrum despite the formation of large amounts of brownish black solid. After that time all volatiles were distilled off and the solid residue was washed with ether (^{19}F NMR showed F_5PhH only). To the washed residue was added diluted sulphuric acid (ca. 50% w/w) and the mixture was extracted with ether. The ^{19}F NMR spectrum of the extract showed signals at −140, −153, and −163 ppm (in addition to very small amounts of F_5PhH), identical with those of pentafluorobenzoic acid [8].

To 105 mg (1.13 mmol) TMAF in a dried glass tube were added F_5PhH in excess and about 2.5 mmol CO_2 (about 8 atm at room temperature). The sealed tube was kept at 80 °C for 2 weeks during which the white TMAF became pale reddish. The tube was cooled to −78 °C, opened and all volatiles distilled off (CO_2 and F_5PhH). The residual solid was dissolved in diluted sulphuric acid (under development of more CO_2), and extracted with ether. The ^{19}F NMR spectrum of the extract showed (in addition to small amounts of F_5PhH) signals at −140, −153, and −163 ppm, which can be attributed to pentafluorobenzoic acid [8].

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