

On reactions of carbon disulphide induced by ‘naked’ fluoride Part 2: Reactions with 2-*H*-heptafluoropropane, hexafluoropropene, and bis(2,2,2-trifluoroethyl)amine¹

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Abstract

The reaction of CS₂ and tetramethylammonium fluoride (TMAF) with 2-*H*-heptafluoropropane (R227) leads to 2,4-bis(hexafluoroisopropylidene)-1,3-dithietane as well as to the tetramethylammonium salt of heptafluorodithioisobutyric acid. The latter anion resulted also from the reaction of CS₂ and CsF with hexafluoropropene (HFP), whereas CS₂, TMAF and HFP reacted to compounds derived from HFP dimerization. *N,N*-bis(2,2,2-trifluoroethyl)dithiocarbamic acid anion was obtained from bis(trifluoroethyl)amine reacted with CS₂ and TMAF. © 1997 Elsevier Science S.A. All rights reserved.

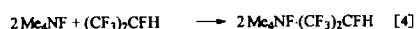
Keywords: Carbon disulphide

1. Introduction

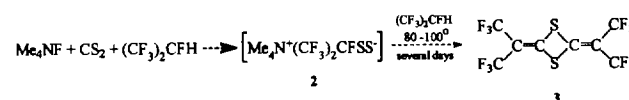
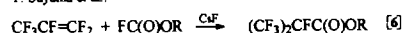
The hypothetical ‘naked’ fluoride, which should exhibit both a very high basicity and a high nucleophilicity, can be well approximated by tetramethylammonium fluoride (TMAF) [1]. Expectedly, the strong nucleophile reacts with CS₂, yielding FCS₂⁻ [2]. Formation of the latter is a necessary assumption to explain nucleophilic substitution reactions with fluoroaromatics [3], whereas other reactions with CS₂/F⁻ could be induced by F⁻ acting as a strong base too. Some examples of the latter type of reaction are given in the following.

2. Results and discussion

TMAF can be dissolved in 2-*H*-heptafluoropropane (R227) from which it may be obtained as 2:1 solvate [4] (Scheme 1). Because of this solubility, the reaction of TMAF with CO₂, which is known to yield (CH₃)₄N⁺ FCO₂⁻ [5], was repeated in R227 aiming at single crystals of the fluoroformate. Expectedly, TMAF reacts immediately with CO₂ in R227 to give solvated tetramethylammonium fluoroformate.



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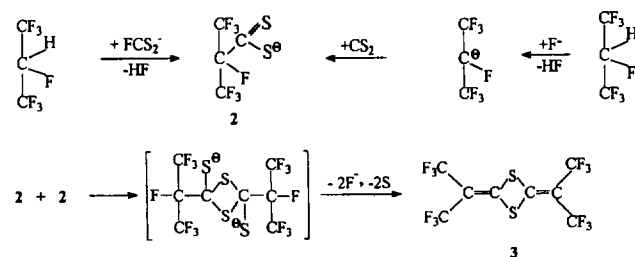
Scheme 1.

Prolonged heating of the reaction mixture at about 80 °C over several days did not yield the single crystals but the tetramethylammonium salt of heptafluoroisobutyric acid (1) (Scheme 1). This reaction corresponds with those reported by Suyama et al. [6], who obtained esters of heptafluoroisobutyric acid by reacting hexafluoropropene (HFP) with esters of fluoroformic acid in the presence of caesium fluoride (Scheme 1).

Similar experiments with CS₂ instead of CO₂ came to unexpected results. CS₂ reacts with TMAF in R227 smoothly too, yielding immediately a solid reddish product insoluble in R227, presumably the FCS₂⁻ salt. When the reaction mixture was held at 70–75 °C for about 6 days, the solid became dark, deep red. After removal of unreacted R227 and CS₂ in vacuo, the residual solid was extracted with ether or acetone, and the extracts analysed. It was found that 2,4-bis(hexafluoroisobutyryl)-1,3-dithietane (3) was the main product.

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propylidene)-1,3-dithietane (3) had been formed (Scheme 1) together with other products not identified. The analytical data of 3 are in agreement with those reported by Raasch [7].

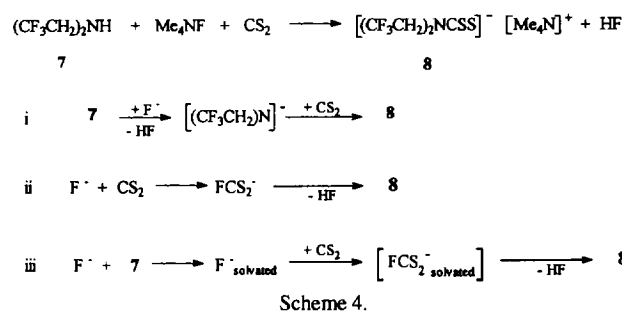
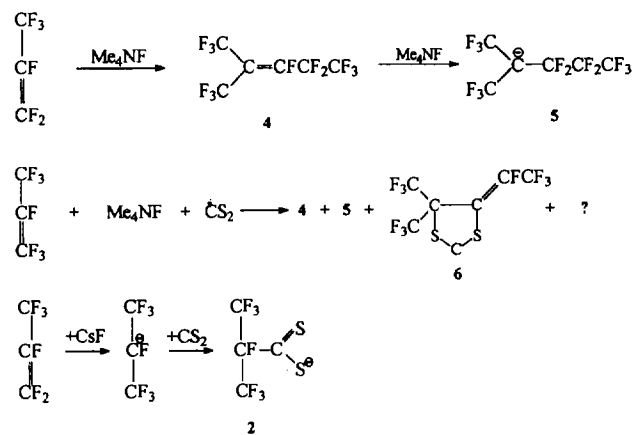
In Scheme 2, a mechanism of the formation of dithietane is proposed, which implies intermediate formation of the anion of heptafluorodithioisobutyric acid (2). The involvement of this is supported by its detection in separate experiments. As in the case of the reaction with CO₂, 2 (or 1 respectively) could be formed in two ways (Scheme 2). The path via dithiofluoromate (or fluoromate respectively) is more likely not only because of the similarity to the reaction of Suyama et al. [6], but also because it does not need the formation of substantial amounts of heptafluoropropane carbanion, which should cause HFP dimers or HFP oligomers as by-products. The latter were not detected in the reactions discussed but were always detected when TMAF was allowed to react with R227 in the presence of a polar solvent.

The situation changes with HFP being used instead of R227. TMAF reacts with HFP exothermically by dimerization of the latter, yielding nearly exclusively perfluoro(2-methyl-pentene-2) (4) [8] as well as its carbanion (5) [9] (Scheme 3). If TMAF is reacted with HFP in the presence of CS₂, the same products are predominant, however, at least two additional products are formed. One of them was tentatively assigned, based primarily on MS data, to 1,3-dithia-2-thion-4,4-bis(trifluoromethyl)-5-tetrafluoroethylidene-cyclopentane (6) (Scheme 3).

The same reaction was tried with CsF. On heating a mixture of HFP, CS₂ and CsF at about 80 °C for several days, the CsF became a rather voluminous pale yellow powder, which proved to be the caesium salt of heptafluorodithioisobutyric acid (Scheme 3), whilst excessive HFP and CS₂ remained unchanged.

These results show that in HFP the 'naked' fluoride ion of TMAF, the reactivity of which is much higher than that of CsF, forces the reaction primarily towards the formation of HFP carbanion and its reaction products 4, 5, and 6, whereas in R227 the reactivity of TMAF is distinctly reduced to about that of CsF in HFP, obviously by solvation.

Reactions of CS₂ with secondary amines are used to prepare *N,N*-dialkyl-dithiocarbamic acid. Thus, diethylamine can be reacted under mild conditions, for example in the presence of aqueous NaOH; under similar conditions, bis(2,2,2-trifluoroethyl)amine (7) does not react. However, under the action of TMAF, 7 reacts smoothly with CS₂,



yielding the expected tetramethylammonium salt of *N,N*-bis(2,2,2-trifluoroethyl)dithiocarbamic acid (8) (Scheme 4), which could be characterized by its ¹⁹F NMR, ¹H NMR, ¹³C NMR, IR, Raman and FAB-MS spectra. The reaction could proceed basically in two ways (Scheme 4), which differ in their respective primary attack of the 'naked' fluoride, which could be either on the amine (path (i)) or on the CS₂ (path (ii)). TMAF reacts slightly exothermically with 7, but this is obviously solvation rather than amide formation. Thus it is likely that despite its reduced reactivity, the solvated fluoride reacts with CS₂ (path (iii)), and the dithiofluoromate formed this way reacts immediately with the solvate 7 yielding the observed anion of *N,N*-bis(2,2,2-trifluoroethyl)dithiocarbamic acid (8).

3. Experimental details

¹⁹F NMR spectra were recorded with a Jeol FX90Q spectrometer at 84.25 MHz using CFC1₃ as external standard with upfield values designated negative. ¹H NMR spectra were recorded with a Jeol FX90Q spectrometer at 89.55 MHz using TMS as external standard. ¹³C NMR spectra were recorded with a Bruker AC250 spectrometer at 62.896 MHz using TMS as external standard. IR spectra were recorded with a Perkin-Elmer 983 instrument either in KBr or in a 10 cm gas cuvette with KBr windows. Raman spectra were recorded

with a Ramalog (Spex) instrument using an argon laser (488 and 514 nm). FAB-MS spectra were obtained with a Varian-Mat CH₂DF instrument using xenon, only negative ions were recorded. GC/MS was carried out with a Varian Saturn II instrument using a 50 m Norion capillary coated with NB 54 phase.

TMAF was prepared according to Christe et al. [1]. Solvents were dried applying standard procedures. Bis(2,2,2-trifluoroethyl)amine (Fluorochem Ltd.) as well as hexafluoropropene and 2-*H*-heptafluoropropane were used as supplied.

3.1. General procedure

All reactions were carried out in thoroughly dried glass tubes of ca. 8 mm external diameter, fused at one end. Whereas solid compounds were handled in a dry-box, liquid and gaseous compounds were distilled at or below room temperature against $-196\text{ }^{\circ}\text{C}$ using a vacuum system. After all the reaction mixture components had been condensed in, the glass tubes were fused at the open end, and kept in an air oven under the conditions indicated. Then the tubes were cooled below the boiling points of the respective reactants, opened under exclusion of air, and volatiles were distilled off.

3.2. Reactions with R227

Synthesis of **1**. 90 mg (0.97 mmol) TMAF, 130 mg (2.9 mmol) CO₂ and excess R227 were reacted for several weeks at room temperature with repeated warming to $80\text{ }^{\circ}\text{C}$ followed by slow cooling down. The reaction mixture consisted of a white solid and a liquid phase. The solid was freed from all volatiles at room temperature in oil vacuum, one part of it was dissolved in H₂O, another in diluted sulphuric acid which was subsequently extracted with ether. ¹⁹F NMR spectra of the ethereal solution showed signals at -75 ppm (d, $J_{\text{FF}}=7.3\text{ Hz}$) and at -181 ppm (m, $J_{\text{FF}}=7.3\text{ Hz}$), and of the aqueous solution at -73 ppm (d, $J_{\text{FF}}=7.5\text{ Hz}$) and at -172 ppm (m, $J_{\text{FF}}=7.5\text{ Hz}$) (besides signals of F⁻, and SiF₆⁻), corresponding to those of heptafluoroisobutyric acid and its anion (**1**) respectively. From GC/MS of the ethereal solution, the MS data are in agreement with (CF₃)₂CF₂COOH: 214 (M⁺), 150 (C₃F₆⁺), 69 (base peak), 45 (COOH⁺).

Synthesis of **2**. 80 mg (0.86 mmol) TMAF, 450 mg (5.9 mmol) CS₂ and excess R227 were kept at $80\text{ }^{\circ}\text{C}$ for 48 h. After that time the reaction tube was opened, volatiles distilled off (unreacted CS₂ and R227 only), and the brownish residue dissolved in water. In the ¹⁹F NMR spectrum of the aqueous solution were signals at -73 ppm and at -173 ppm , identical with those of heptafluorodithioisobutyric acid anion (**2**) obtained on reaction of CS₂ with HFP and CsF (see later).

Synthesis of **3**. In a similar experiment, 90 mg (0.97 mmol) TMAF, excess CS₂ and excess R227 were reacted at $70\text{--}75\text{ }^{\circ}\text{C}$ for 9 days. After that time, gas phase IR spectra of the

volatiles distilled off showed at the end of the distillation the presence of an absorption band at 1618 cm^{-1} , besides the characteristic bands of CS₂ and R227. Extraction of the residual deep brown solid with ether gave a deep red solution which had in its ¹⁹F NMR spectrum a strong signal at -59 ppm , besides some smaller signals. Successive extraction with acetone yielded a brownish red solution, the ¹⁹F NMR spectrum of which consisted of a strong peak at -59.3 ppm and a much smaller peak at -54.5 ppm . According to GC/MS, the ether solution contained basically one compound. MS: 388 (C₈F₁₂S₂⁺, M⁺, 73%), 369 (M-F⁺), 194 (C₄F₆S⁺, M/2⁺, 47%), 175 (C₄F₅S⁺, 53%), 106 (C₃F₂S⁺, 35%), 69 (base peak). IR, ¹⁹F NMR, and MS data are in accordance with those of 2,4-bis(hexafluoroisopropylidene)-1,3-dithietane (**3**) [7].

3.3. Reactions with HFP

Synthesis of **4** and **5**. Excess HFP (about 3–4 mmol) was condensed on about 1 mmol TMAF. With rising temperature, a slightly exothermic reaction started at room temperature, which was completed by keeping the mixture at about $60\text{ }^{\circ}\text{C}$ over 24 h. The liquid phase consisted now nearly exclusively of a HFP dimer, i.e. perfluoro(2-methyl-pentene-2) (**4**), identified by its ¹⁹F NMR spectrum [8], whereas TMAF was transformed into a yellow, sticky product, soluble in acetonitrile, which proved [9] to be perfluoro-2-methylpentan-2-yl(tetramethylammonium) (**5**).

Synthesis of **4**, **5** and probably **6**. 130 mg (1.4 mmol) TMAF was reacted with 144 mg (1.9 mmol) CS₂ and excess HFP at $70\text{--}80\text{ }^{\circ}\text{C}$ for 7 days. After that time, the liquid phase consisted according to its ¹⁹F NMR spectrum mainly of **4**, whereas the ¹⁹F NMR spectrum of the MeCN solution of the residue was that of a rather complex mixture. Again, the major constituent was the carbanion **5**, and by fractional extraction of the solid with MeCN, two sets of ¹⁹F NMR peaks were found to be likely to belong to individual compounds, i.e. at -52 , -58 , -76 and -100 ppm , and at -48 , -54 , -80 and -116 ppm respectively. GC/MS of the MeCN solution showed also several compounds present, among them were small amounts of HFP-dimer and also HFP-trimer. A major constituent had MS (m/e)⁺ 370, 294, 275, 225, 175, 144, 87, 76, 69 (base peak), 63, and 44. These data can be tentatively assigned to 1,3-dithia-2-thio-4,4-bis(trifluoromethyl)-5-tetrafluoroethylidene-cyclopentane (**6**), MW 370, which could fit the first set of ¹⁹F NMR peaks mentioned above.

Synthesis of **2** from CsF. 160 mg (1.05 mmol) CsF, 200 mg (2.6 mmol) CS₂ and excess HFP were reacted at about $80\text{ }^{\circ}\text{C}$ for 10 days. After evaporation of the volatiles (unreacted CS₂ and HFP), one part of the pale yellow solid residue was dissolved in MeCN, another in diluted hydrochloric acid which was subsequently extracted with ether. The ¹⁹F NMR spectra of the solutions showed two signals each, in MeCN an intense signal at -73 ppm (d, $J=8.5\text{ Hz}$) and a small signal at -172 ppm (m, $J=8.6\text{ Hz}$), and in ether solution an intense signal at -73 ppm and a small signal at

– 180 ppm, which can be attributed to the anion of heptafluorodithioisobutyric acid (**2**) and the free acid respectively.

3.4. Reaction with bis(2,2,2-trifluoroethyl)amine (**7**)

Synthesis of **8**. 95 mg (1 mmol) TMAF and excessive CS₂ and **7** were warmed from –196 °C to room temperature in the course of about 3 h under repeated shaking, and then for another 1 h kept at about 60 °C. From the reaction mixture the volatiles were distilled off (CS₂ and **7** only), and the residual solid was dissolved in CD₃CN, D₆-DMSO, or in MeCN from which crystals could be obtained too. The following NMR spectra were recorded. ¹⁹F NMR in MeCN: –67 ppm (t, ³J_{FH} = 9.8 Hz). ¹H NMR in CD₃CN: 5.5 ppm (quart, ³J_{FH} = 9.3 Hz), 3.3 ppm (s, Me₄N⁺). ¹³C NMR in D₆-DMSO: 222 ppm (s, CSS[–]), 125 ppm (quart, ¹J_{CF} = 283.1 Hz, CF₃), 54 ppm (t, ¹J_{CN} = 3.6 Hz, [CH₃]₄N⁺), 51 ppm (quart, ²J_{CF} = 32.5 Hz, CH₂). FAB-MS from DMSO/glycerol: 256 (100%, [CF₃CH₂]₂NCSS[–]), 586 (13%, [(CH₃)₄N]⁺ · 2-[(CF₃CH₂)₂NCSS][–]). All these data are consistent with a tetramethylammonium salt of *N,N*-bis(2,2,2-trifluoroethyl)dithiocarbamic acid (**8**) as formulated. Crystals of **8** from MeCN solution were used to take IR and Raman spectra. IR (cm^{–1}): 3009 m, 2955 m, 1486 s, 1426 m, 1414 m, 1399 m, 1368 s, 1316 vs, 1263 vs, 1232 s, 1163 vs, 1148 vs, 1102

vs, 1016 vs, 956 m, 943 s, 828 m, 685 s, 583 m. Raman (cm^{–1}): 3008 m, 2953 s, 1459 m, 1415 m, 1372 s, 1285 m, 1238 m, 942 m, 824 m, 752 s, 673 m, 609 vs, 528 s, 443 vs, 379 vs, 286 m.

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