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Novel reactions of perfluoro-2-(trifluoromethyl)-propene

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Abstract

Unlike its hydrocarbon counterpart, perfluoro-2-(trifluoromethyl)propene is a highly reactive compound. It participates in both heterolytic and homolytic reactions. It readily reacts with nucleophiles and sluggishly with electrophiles. It reacts as well with common organic solvents, such as dimethylformamide, ethanol and others. In this communication, we describe its reactions with trifluoromethylthiocopper, sulfur trioxide and tributyltin cyanide, the mechanism of formation of the various products and their mass spectral data.

Introduction

Perfluoro-2-(trifluoromethyl)-propene (**1**), also known as perfluoroisobutylene, is a uniquely reactive molecule. It participates in both heterolytic and homolytic reactions. Arylmagnesium halides react with **1** to furnish only trisubstituted 'inner' olefins via the migration of the double bond [1]. However, alkyl Grignard reagents yield both allyl- and vinyl-substituted products on reacting with **1** [2]. The aryllithium reagents react with **1** to give mono- and di-substituted vinylic derivatives [3]. In the presence of moist charcoal, **1** gives hexafluoroisobutyric acid (**2**), 1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)-propene (**3**), 1,1,3,3,3- pentafluoropropylene (**4**), 1,1,1,3,3,3-hexafluoropropane (**5**) and HF [4]. Its interesting chemistry has been the subject of an excellent, exhaustive review [5].

Perfluoro-olefins have been reported to form polymeric products when heated with bis(trifluoromethylthio)mercury at 225 °C under 300 atm pressure for 14 h [6]. Free-radical catalyzed addition of Br_2 to **1** has been described [7a]. Contrary to the results of the reaction of **1** with elemental sulfur in

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the presence of SbF_5, the reaction of perfluoro-olefins with elemental sulfur has been reported to proceed via free-radical intermediates [7b].

In continuation of our interest in the chemistry of the trifluoromethylthio group [8a–d], it has now been observed that **1** reacts with trifluoromethylthiocopper (**6**) under extremely mild conditions (−78 °C) to give a mixture of compounds containing both vinyl- and allyl-substituted products via free-radical intermediates. It was also found that 1,1-dibromohexafluoroisobutylene (**7**) reacts with **6** to furnish both mono- and di-substituted trifluoromethyl sulfides. Treatment of the allylic sulfide **10** prepared from **6** and the allylic iodo derivative **8** with KI gives a mixture of compounds carrying the trifluoromethylthio moiety. With tributyltin cyanide, the fluorosulfonate derivative **9** prepared by the insertion of SO_3, gave three compounds containing the cyano group. This paper describes these unusual results along with the mass spectral fragmentation of the various products formed during the course of these reactions.

Experimental

General procedure

Warning!! Because of the high inhalation toxicity of 1 [9], all reactions should be carried out in an efficient hood. Mass spectra were recorded on a Finnigan model 5100 GC–MS spectrometer equipped with a silica 25 m×0.31 mm (i.d.) capillary column (J & W Scientific, Rancho Cordova, CA). Routine GC analyses were carried out using a Hewlett Packard 5890A gas chromatograph equipped with a DB-5 30 m×0.31 mm (i.d.) capillary column (J & W Scientific, Folsom, CA). NMR spectra (^{13}C and ^{19}F) were recorded in $CDCl_3$ on a Varian VXR-400S spectrometer at 100 MHz and 376 MHz, respectively. The external reference for ^{19}F data was CCl_3F and, for ^{13}C NMR, tetramethylsilane (TMS) was used as an internal standard. The reactions were carried out in a flame-dried, argon-purged 10 or 25 ml capacity flask equipped with a magnetic stirrer, gas inlet pressure equalizing dropping funnel and a reflux condenser with the coolant maintained at −20 °C by a Lauda RC56 refrigerated circulating bath and a Dry Ice/acetone trap. Perfluoro-2-(trifluoromethyl) propene (>99% pure by GC methods) (**1**) was used as received from Armageddon Chemical Company (Durham, NC). Trifluoromethylthiocopper was prepared as described elsewhere [10]. Acetonitrile was dried over calcium hydride and freshly distilled as needed. All reactions were carried out using stoichiometric quantities of reagents. Reaction mixtures were allowed to come to ambient temperature prior to flash distillation under reduced pressure and products collected at −78 °C.

Synthesis of 2-(trifluoromethylthiodifluoromethyl)-pentafluoropropene (10)

(a) Perfluoroalkenylfluorosulfonate (9)

A 300 ml capacity Hastalloy stirring autoclave reactor was charged with sulfur trioxide (30 g, 0.38 mol) and trimethyl borate (1.5 g, 0.0125 mol) in an argon-filled glove bag and quickly sealed. The reactor was cooled to −78 °C and **1** (100 g, 0.5 mol) was slowly sparged into the reactor over the course of 1 h. The reaction mixture was stirred at −78 °C for 0.5 h and allowed to slowly warm up to 20–25 °C with stirring. Carefully maintaining the reaction temperature at 30–35 °C, the reaction mixture was stirred for 2 h, then stirred overnight at ambient temperature. A Dry Ice/acetone trap, with a mineral oil bubbler attached to prevent the entrance of moisture, was connected to the reactor and the latter slowly opened to relieve pressure until no further bubbling was observed. The reaction mixture was transferred from the reactor to a round-bottom flask and flash-distilled (90 mmHg) without heating to remove volatile byproducts. The flask was slowly heated to 90 °C (oil bath temperature) to yield 37.8 g of product (86% pure by GLC, 31% yield). ^{13}C NMR δ: 160.3 (J=313 Hz, C=CF$_2$); 5.4 (CF$_3$–C=); 120.0 (J=276 Hz, CF$_3$–C=); 119.3 (J=279 Hz, CF$_2$OSO$_2$) ppm. ^{19}F NMR δ: −64.9 (=CF$_2$); −60.7 (CF$_3$); −61.0 (CF$_2$O)–); and 46.1 [J=9.3 (t), FSO$_2$–] ppm. MS (m/z): 280.

(b) 2-(Difluoroiodomethyl)-pentafluoropropene (8)

A mixture of the above fluorosulfonate (8.3 g, 0.03 mol) and dry potassium iodide (7.5 g, 0.045 mol) in dry sulfolane (10 ml) was heated at 90–95 °C in the absence of light (the iodo derivative is light-sensitive) for 1 h. The reaction mixture was cooled to ambient temperature, then flash-distilled under reduced pressure into a receiver cooled to −78 °C. Refractionation of the distillate gave an 82% pure sample (GC). ^{13}C NMR δ: 156.9 (J=308 Hz, C=CF$_2$); 95.7 (CF$_3$$C$=); 120.5 ($J$=271 Hz, CF$_3$C=); and 80.3 (J=314 Hz, CF$_2$I) ppm. ^{19}F NMR δ: −62.0; −67.3 (=CF$_2$); −58.3 (CF$_3$); and −38.2 (CF$_2$I) ppm. MS (m/z): 258.

(c) 2-(Trifluoromethylthiodifluoromethyl)-pentafluoropropene (10)

A mixture of the allylic iodo derivative **8** (1.3 g, 4.22 mmol) and trifluoromethylthiocopper (**6**) (1.08 g, 6.54 mmol) in dry freshly distilled acetonitrile (2 ml) was stirred whilst being protected from light under an argon atmosphere at ambient temperature. Within 1 min, a white precipitate was formed. The reaction mixture was further heated at 80 °C for 1 h. After cooling to ambient temperature, the reaction mixture was flash-distilled under reduced pressure into a receiver cooled to −78 °C. Redistillation of the sample gave a 97.5% pure sample, b.p. 68–70 °C. ^{19}F NMR δ: −38.1(t) (J=9.4 Hz, SCF$_3$); −67.3 (m) (SCF$_2$); −58.3 (J=27.1 Hz, J=9.2 Hz, C–CF$_3$); −59.7 (m) and −60.9 (m) (=CF$_2$) ppm. MS (m/z): 282 [see eqn. (1)].

Reaction of 1,1-dibromo-2,2-bis(trifluoromethyl)-ethylene (7) with trifluoromethylthiocopper (6)

A solution consisting of stoichiometric amounts of **7** (3.12 g, 0.01 mol) and **6** (2.05 g, 0.01 mol) in dry freshly distilled acetonitrile (3 ml) was heated at 85–95 °C (oil bath temperature) for 5 h. After cooling to ambient temperature, the reaction mixture was flash-distilled under reduced pressure into a receiver cooled to −78 °C. GC–MS analysis of the distillate showed the presence of the following three compounds: 1-bromo-1-trifluoromethylthio-2,2-bis(trifluoromethyl)-ethylene (**11**), 51%; 1,1-bis(trifluoromethylthio)-2,2-bis(trifluoromethyl)-ethylene (**12**), 15% and bis(trifluoromethyl)disulfide (**19**), 0.3% (Table 1). The rest was starting material [see eqn. (2)]. ^{13}C NMR δ: Compound **11**: 127.0 (J=312 Hz, SCF$_3$); 125.4 [J=3 Hz (m), =C–Br]; 131.1 [J=32.8 Hz (hep), =C(CF$_3$)]; 119.6 [J=278 Hz (q), CF$_3$]; and 119.8 [J=278 Hz (q), CF$_3$] ppm. ^{19}F NMR δ: −38.7 [J=2.3 Hz (q), SCF$_3$]; −57.0 [J=2.3 Hz (q of q), J=10.4 Hz, CF$_3$]; and −59.7 [J=10.4 Hz (q), CF$_3$] ppm. ^{13}C NMR δ: compound **12**: 126.6 (J=312 Hz, SCF$_3$); 137.0 [J=3.0 Hz (m), =C(SCF$_3$]; 135.8 [J=32.8 (hep), C=C(SCF$_3$)$_2$]; and 119.2 [J=280 Hz (q), CF$_3$] ppm. ^{19}F NMR δ −35.8 [J=1.6 Hz (hep), SCF$_3$]; −57.9 [J=1.6 Hz (hep), CF$_3$] ppm [see eqn. (2)].

Reaction of perfluoro-2-(trifluoromethyl)-propene (1) with trifluoromethylthiocopper (6)

To a slurry of **6** (2.05 g, 0.01 mol) contained in 5 ml of freshly distilled acetonitrile cooled to −78 °C, was sparged an equimolar amount of **1** (2.0 g, 0.001 mol) and the reaction stirred at −78 °C for 2 h, allowed to come to ambient temperature and heated at 55–60 °C for 4 h. After cooling to ambient temperature, the reaction mixture was flash-distilled under reduced pressure into a receiver cooled to −78 °C. The GC–MS analysis of the distillate showed the presence of **1**, 1-(trifluoromethylthio)-perfluoro-2-(trifluoromethyl)-propene (**13**), 1-(trifluoromethylthio)-2*H*, 2-(trifluoromethylthiodifluoromethyl)-perfluoropropane (**14**), 3,3,3-trifluoropropionic acid (**15**), hexafluoroisobutyric acid (**2**), 1,1,1,3,3,3-hexafluoro-2-(trifluoromethyl)-propane (**3**) and 2,2,3,3-tetra(trifluoromethyl)-perfluorobutane (**16**) [see eqn. (3)].

Reaction of allylic fluorosulfonate (9) with trifluoromethylthiocopper (6)

To a slurry of **6** (1.44 g, 7.0 mmol) in freshly distilled acetonitrile (5 ml), **9** (1.71 g, 6.12 mmol) was added dropwise with stirring. An immediate mild exothermic reaction ensued. The reaction mixture was stirred for 0.5 h at ambient temperature and then at 90 °C for 2 h, then flash-distilled under reduced pressure into a receiver cooled to −78 °C. The distillate was analyzed by GC and GC–MS methods and was found to contain the desired compound, namely **10**, as one of the major products. The GC–MS analysis of **10** was similar to that obtained earlier [cf. eqn. (1)]. Eight additional compounds were characterized as byproducts of the reaction [see eqn. (4)].

Reaction of allylic fluorosulfonate (9) with tributyltin cyanide

To **9** (5.0 g, 17.9 mmol) in dry sulfolane (10 ml) was added with stirring tributyltin cyanide (5.64 g, 17.9 mmol) in small portions via a solid addition funnel. The reaction was exothermic. The mixture was stirred for 1 h and flash-distilled under reduced pressure into a receiver cooled to −78 °C. The

TABLE 1

Mass spectral fragmentation of compounds in order of increasing molecular weight. The number below the compound refers to the number in the text

$CF_3CH_2CO_2H$ **(15)**	$M^+=128$; 111 (M−OH); 109 (M−F); 91 ($CF_2{=}CH{-}C{=}O$); 89 (109−HF); 83 (CF_3CH_2); 64 ($CF_2{=}CH_2$, 100%); 59 (M−CF_3); 51 (CHF_2); 47 (COF); 45 ($CF{=}CH_2$, 100%); and 42 ($CH_2{=}C{=}O$)
$CF_3CH_2C(O)F$ **(21)**	$M^+=130$; 111 (M−F); 91 (C_3HF_2O); 83 (CF_3CH_2); 69 (CF_3, 100%); 64 ($CF_2{=}CH_2$); 51 (CHF_2); 47 [C(O)F]; and 42 (111−CF_3)
$(CF_3)_2CHCO_2H$ **(2)**	$M^+=196$; 179 (M−OH); 132 ($CF_3CH{=}CF_2$); 113 (132 −F); 91 (C_3HF_2O); 82 (132−CF_2); 75 ($CF_2{=}C{=}CH$); 69 (CF_3, 100%); 63 (82−F); 51 (CHF_2); and 45 ($CF{=}CH_2$)
$(CF_3)_2C{=}CF_2$ **(1)**	$M^+=200$; 181 (M−F); 162 (181−F); 150 (M−CF_2); 131 (M−CF_3); 112 (131−F); 93 (C_3F_3, 100%); 81 (150−CF_3); 74 (93−F); 69 (CF_3); 63 (CSF); and 50 (CF_2)
CF_3SSCF_3 **(19)**	$M^+=202$; 133 (M−CF_3); 114 (133−F); 82 (CSF_2); 69 (CF_3, 100%); 63 (CSF); 51 (SF); and 44 (CS)
$CF_3(CNCF_2)C{=}CF_2$ **(17)**	$M^+=207$; 188 (M−F); 181 (M−CN); 162 (181−F); 143 (162−F); 138 (M−CF_3); 131 (181−CF_2); 119 (138−F); 112 (138−CN); 100 ($CF_2{=}CF_2$); 93 ($CF_2{=}C{=}CF$); 76 (CF_2CN); and 69 (CF_3, 100%)
$CF_3(CNCF_2)C{=}C(F)(CN)$ **(18)**	$M^+=214$; 200 (M−N); 195 (M−F); 188 (M−CN); 181 (200−F); 162 (188−CN, 100%); 145 (M−CF_3); 138 (188−CF_2); 119 ($CNCCCF_3$); 107 (CF_3CCCN); 100 ($CNCCCF_2$); 93 (119−CN); 76 (CF_2CN); 69 (CF_3); and 50 (CF_2)
$(CF_3S)_2CH_2$ **(20)**	$M^+=216$; 147 (M−CF_3); 115 (M−SCF_3); 101 (SCF_3); 82 (CSF_2); 69 (CF_3, 100%); 63 (CSF); 50 (CF_2); and 45 (CSH)
$(CF_3)_3CH$ **(3)**	$M^+=220$ (not seen); 201 (M−F); 181 (201−HF); 150 [$C(CF_3)_2$]; 132 (201−CF_3); 113 (132−F); 93 (C_3F_3); 82 (132−CF_2); 75 (113−2F); 69 (CF_3, 100%); 63 (82−F); 50 (CF_2); 44 (63−F); and 32 (CHF)
$CF_3(CNCF_2)C{=}C(CN)_2$ **(25)**	$M^+=221$; 202 (M−F); 195 (M−CN); 145 (M−CF_2CN); 138 (CF_3CCFCN); 119 (CF_3CCCN); 100 (CF_2CCCN); 81 (100−F); 76 (CH_2CN, 100%); 69 (CF_3); 64 [$C(CN)_2$]; and 50 (CF_2)
$CF_3(FSO_3CF_2)C{=}CF_2$ **(9)**	$M^+=280$; 261 (M−F); 211 (M−CF_3); 181 (M−SO_3F, 100%); 159 [$CF_2{=}C(CO)CF_3$]; 131 (159−CO); 112 ($CF_2{=}C{=}CF_2$); 100 ($CF_2{=}CF_2$); 83 (112−F); and 69 (CF_3)
$CF_3(CF_3SCF_2)C{=}CF_2$ **(10)**	$M^+=282$; 263 (M−F); 213 (263−CF_2); 194 (213−F); 181 (M−SCF_3); 93 (C_3F_3); 82 (CSF_2); 69 (CF_3, 100%); 63 (CSF); and 44 (CS)
$(CF_3)_2C{=}CF(SCF_3)$ **(13)**	$M^+=282$; 263 (M−F); 194 (M−CF_3); 175 (194−F); 163 (194−CF); 144 (175−CF); 125 (194−CF_3); 106 (175−CF_3); 101 (SCF_3); 87 (106−F); 75 (C_2FS); 69 (CF_3, 100%); 63 (CSF); and 50 (CF_2)
$(CF_3)_2CH{-}CF_2SCF_3$ **(22)**	$M^+=302$; 283 (M−F); 200 (M−CF_3SH); 151 (CF_3SCF_2); 132 (201−CF_3); 113 (132−F, 100%); 107 (M−195); 101 (SCF_3); 82 (CSF_2); 69 (CF_3, 100%); and 63 (CSF)

(*continued*)

TABLE 1 (*continued*)

$(CF_3)_2C{=}C(Br)(SCF_3)$ (**11**)	$M^+ = 342$; 323 (M − 19); 263 (M − Br); 194 ($M - CF_3Br$); 175 (194 − F); 144 (175 − CF); 125 (144 − F); 106 (125 − F); 101 (SCF_3); 93 (C_3F_3); 87 (106 − F); 69 (CF_3, 100%); 63 (CSF); 50 (CF_2); and 44 (CS)
$(CF_3)_2C{=}C(SCF_3)_2$ (**23**) or (**28**)	$M^+ = 364$ (not seen); 345 (M − F); 263 ($M - SCF_3$); 207 ($CF_3SCF_2C{=}C{=}S$); 194 ($263 - CF_3$); 175 ($CF_3SCF{=}C{=}CF$); 151 (CF_3SCF_2); 125 (CF_3SC_2); 106 (125 − F); 101 (SCF_3); 93 ($CF_2{=}C{=}CF$); 69 (CF_3, 100%); 63 (SCF); and 51 (SF)
$(CF_3)_2C{=}C(SCF_3)_2$ (**12**)	$M^+ = 364$; 345 (M − F); 295 ($M - CF_3$); 257 (295 − 2F); 226 [$C_2(SCF_3)_2$]; 213 (C_4F_7S); 207 (226 − F); 194 ($295 - SCF_3$); 175 (294 − F); 157 (M − 207); 113 (C_2F_3S); 106 ($175 - CF_3$); 101 (SCF_3); 93 (C_3F_3); 82 (CSF_2); 69 (CF_3, 100%); 63 (CSF); 50 (CF_2); and 44 (CS)
$(CF_3SCF_2)_2C{=}CF_2$ (**29**) or (**30**)	$M^+ = 364$ (not seen); 345 (M − F); 263 ($M - SCF_3$); 207 ($CF_3SCF_2{-}C{=}C{=}S$); 194 ($263 - CF_3$); 175 ($CF_3SCF{=}C{=}CF$); 125 ($194 - CF_3$); 69 (CF_3, 100%); and 63 (CSF)
$CF_3(CF_3SCF_2)CHCF_2SCF_3$ (**14**)	$M^+ = 384$ (not seen); 315 ($M - CF_3$); 283 ($M - SCF_3$); 213 ($CF_3SCF_2{-}C{=}CF_2$); 151 (CF_3SCF_2); 113 ($CF_2{=}CH{-}CF_2$); 82 (CSF_2); 69 (CF_3, 100%); and 63 (CSF)
$(CF_3)_3CC(CF_3)_3$ (**16**)	$M^+ = 438$; 419 (M − F); 93 (C_3H_3); 69 (CF_3, 100%); and 50 (CF_2)

distillate, as analyzed by GC methods, showed the presence of three major components identified from their mass spectral fragmentation pattern as 1-cyano-2-(trifluoromethyl)-perfluoropropene (**17**), (37.5%); perfluoro-2-(trifluoromethyl)-propene (**1**), (16%); and 1-cyano-2-(cyanodifluoromethyl)-perfluoropropene (**18**), (15.1%). Trace amounts of 2-(cyanodifluoromethyl)-2-(trifluoromethyl)-1,1-dicyano-ethylene (**25**) and starting material **9** were also detected. Two additional compounds remain unidentified [see eqn. (5)].

Reaction of 2-(trifluoromethylthiodifluoromethyl)-pentafluoropropene (10) with potassium fluoride

Treatment of **10** (0.01 mol) with an equivalent amount of potassium fluoride under an argon atmosphere at −78 °C for 1 h, followed by stirring for an additional 1 h at ambient temperature, gave a slightly yellow colored solution. GC analysis of the reaction mixture showed the reaction mixture to be complex. However, GC–MS analysis permitted the identification of the prominent components (Table 1). Three trace impurities from the reaction mixture have as yet not been characterized [see eqn. (6)].

Bis-(trifluoromethylthio)methane (20)

A mixture containing **6** (2.0 g, 0.01 mol) and dry, freshly distilled diiodomethane (1.33 g, 0.005 mol) in 5 ml of dry sulfolane, was heated at 85–90 °C (oil bath temperature) under an argon atmosphere for 8 h. The reaction mixture was cooled, then flash-distilled under reduced pressure into a Dry Ice/acetone-cooled receiver. The distillate was redistilled through a Vigreaux column to yield a pure sample of the desired product (96.5% by GLC). ^1H NMR δ: 4.28 (s) ($-CH_2-$) ppm. ^{13}C NMR δ: 129.9 (SCF_3); and 28.6 ($-CH_2-$) ppm.

Results and discussion

The fluorosulfonate derivative **9** was prepared by the allylic insertion of SO_3 into **1**, essentially according to the procedure applied to the synthesis of perfluoropropenefluorosulfonate [11] [eqn. (1)].

$$\underset{\mathbf{(1)}}{(CF_3)_2C{=}CF_2} \xrightarrow{SO_3/B(OCH_3)_3} \underset{\mathbf{(9)}}{(CF_3)(FSO_3CF_2)C{=}CF_2} \xrightarrow{KI} \underset{\mathbf{(8)}}{(CF_3)(ICF_2)C{=}CF_2} \xrightarrow{6} \underset{\mathbf{(10)}}{(CF_3)(CF_3SCF_2)C{=}CF_2} \qquad (1)$$

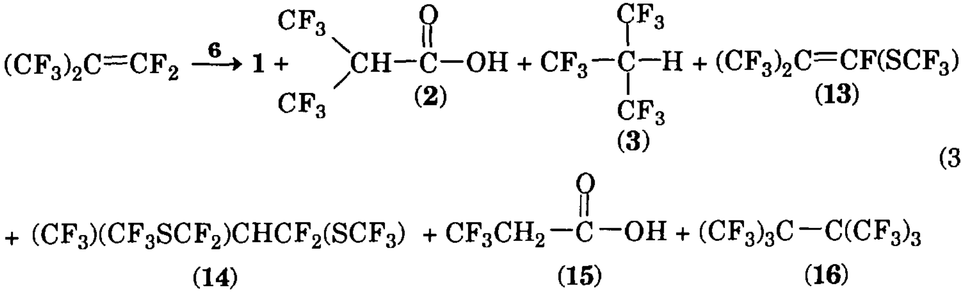
It appears that the lability of the allylic fluorine is the primary reason for the incorporation of SO_3. The transformation of **9** into its corresponding iodo derivative, namely 2-(difluoroiodomethyl)-perfluoropropene (**8**), was carried out as described earlier [11]. Since **8** is light-sensitive, its reactions were carried out in the dark. The reaction of **6** with **8** furnished 2-(trifluoromethylthiodifluoromethyl)-pentafluoropropene (**10**).

The reaction of **6** with **7** is straightforward [eqn. (2)].

$$\underset{\mathbf{(7)}}{(CF_3)_2C{=}CBr_2} \xrightarrow{6} 7 + \underset{\mathbf{(11)}}{(CF_3)_2C{=}CBr(SCF_3)} + \underset{\mathbf{(12)}}{(CF_3)_2C{=}C(SCF_3)_2} + \underset{\mathbf{(19)}}{CF_3SSCF_3} \qquad (2)$$

One or both of the vinylic bromines are replaced by the trifluoromethylthio group. The formation of **19** via its free-radical precursor, **24**, has already been mentioned and rationalized [8, 12a].

With a view to directly introducing the trifluoromethylthio functionality into **1**, it was treated with **6** under mild conditions. Contrary to an earlier report [6], we have identified **13** as a major product of this reaction [eqn. (3)].



$$\mathrm{(CF_3)_2C{=}CF_2 \xrightarrow{6} 1 + \underset{(2)}{(CF_3)_2CH{-}\overset{O}{\overset{\|}{C}}{-}OH} + \underset{(3)}{CF_3{-}\overset{CF_3}{\underset{CF_3}{C}}{-}H} + \underset{(13)}{(CF_3)_2C{=}CF(SCF_3)}} \qquad (3)$$

$$\mathrm{+ \underset{(14)}{(CF_3)(CF_3SCF_2)CHCF_2(SCF_3)} + \underset{(15)}{CF_3CH_2{-}\overset{O}{\overset{\|}{C}}{-}OH} + \underset{(16)}{(CF_3)_3C{-}C(CF_3)_3}}$$

Of the remaining products of this reaction, **2**, **3**, **14** and **15** have been characterized by GC–MS data (Table 1). The one explanation for the formation of **2** and **15** is that they are probably formed as a result of the reaction of **1** with moisture. Such a possibility has been reported [4]. Finally, another compound with a molecular weight of 438 has tentatively been identified as **16**.

An attempt was made to prepare **10** directly by treating **6** with **9** [eqn. (4)].

$$\mathrm{\underset{(9)}{(CF_3)(FSO_3CF_2)C{=}CF_2} \xrightarrow{6} \underset{(1)}{(CF_3)_2C{=}CF_2} + \underset{(10)}{(CF_3)(CF_3SCF_2)C{=}CF_2}}$$

$$\mathrm{+ \underset{(13)}{(CF_3)_2C{=}CF(SCF_3)} + \underset{(14)}{(CF_3)(CF_3SCF_2)CH{-}CF_2(SCF_3)}}$$

$$\mathrm{+ \underset{(19)}{CF_3S{-}SCF_3} + \underset{(20)}{CF_3SCH_2SCF_3}}$$

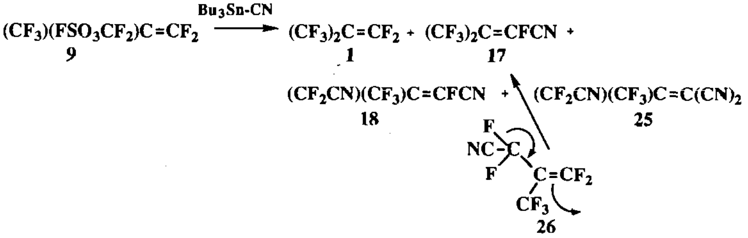
$$\mathrm{+ \underset{(21)}{CF_3CH_2C(O)F} + \underset{(22)}{CF_3SCF_2CH(CF_3)_2}}$$

$$\mathrm{+ \underset{(23)}{(CF_3)(CF_3SCF_2)C{=}CF(SCF_3)}} \qquad (4)$$

This apparently simple reaction turned out to be a complex process. Eight compounds were characterized as products of this reaction; three others, which have not been identified, appear to be polymeric compounds. Included in this list of eight compounds are: bis(trifluoromethyl)disulfide (**19**), bis-(trifluoromethylthio)methane (**20**), 3,3,3-trifluoropropionyl fluoride (**21**), **1**, **10**, **13**, **14**, 2-(trifluoromethylthiodifluoromethyl)-2*H*-perfluoropropane (**22**) and 2-(trifluoromethylthiodifluoromethyl)-1-(trifluoromethylthio)-perfluoropropene (**23**). For comparison purposes, an authentic sample of **20** was prepared by treating **6** with diiodomethane [10a] whose mass spectrum was identical with that of **20**.

Recently, it has been reported that **6** reacts with a variety of organic substrates via the trifluoromethylthiyl radical (**24**) [10b]. The formation of **19** and its higher homologs from **24** has been rationalized [8, 12a]. The free-radical catalyzed reactions of trifluoromethylsulfenyl chloride have also been described [12b]. Further, it was reported that **19** is capable of "quantitatively liberating fluoride" [12c]. The fluorine thus liberated reacts with **9** to generate **1**. The formation of **20** was initially somewhat puzzling. Its formation can be rationalized on the basis of the reaction of **24** with acetonitrile. Acetonitrile is the only source of the methylene moiety in the reaction mixture. Similarly, when reactions are carried out using the trifluoromethylthiocopper acetonitrile adduct, the formation of **20** is also observed. There are precedents for the involvement of solvents in chemical reactions [12d–f]. This inference is further substantiated by the identification of two products, **14** and **22**, formed by the addition of HF to the double bond of their olefinic precursors, namely, **23** and **10**, respectively. The HF required for the addition reaction could have come from the dissociation of CF_3SH into $C(S)F_2 + HF$ as suggested earlier by Haszeldine and Kidd [13]. The probable origin of CF_3SH can be traced to hydrogen abstraction by the thiyl radical **24** from acetonitrile. Another possibility is that the HF could have originated via hydrogen abstraction from acetonitrile by the fluoride radical generated *in situ* from the thiyl radical **24**. While **10** is the result of allylic substitution, **23** is formed from both allylic and vinylic replacement of fluorine. The formation of **21** has not, as of yet, been rationalized. The only source from which **21** could have originated is **1**, itself formed from the attack by fluoride on **9**. The identification of **1** as a product of this reaction supports the above contention [eqn. (6)]. The reaction of **1** with moisture in the presence of carbon has been reported to give **21** [4].

The reaction of **9** with tributyltin cyanide is not as simple as was first considered [eqn. (5)].



(5)

This reaction furnishes **1**, 1-cyano-2-(trifluoromethyl)-perfluoropropene (**17**), 1-cyano-2-(cyanodifluoromethyl)-perfluoropropene (**18**) and 1,1-dicyano-2-(cyanodifluoromethyl)-perfluoropropene (**25**). It is known that nucleophiles readily add to **1**. The formation of **17** can be rationalized as arising from the elimination of fluoride from the allyl-substituted intermediate (**26**) and the concomitant migration of the double bond. The identification of **17**, **18** and **25** illustrates the fact that both allyl- and vinyl-substituted products of **1** are capable of further reactions with nucleophiles [5]. What is interesting in the case of **25** is that both vinylic fluorines are replaced, in addition to the substitution of the allylic fluorine. In contrast, the reaction of **1** with sodium cyanide furnished only a geminally substituted product and no allyl-substituted product was detected [14].

Two structures are possible for the tricyano derivative: **25** and 1-cyano-2,3-bis(cyanodifluoromethyl)-perfluoropropene (**27**). On the basis of the presence of a dicyanocarbene ion in the GC–MS spectrum of the compound, structure **25** was assigned to this compound. It has been suggested that allyl-substituted intermediates are capable of eliminating allylic fluorine to give rearranged products [5]. The formation and detection of **17** serve as a direct proof of this suggestion.

When **10** is treated with KF, a host of compounds are formed [eqn. (6)].

$$\underset{(\mathbf{10})}{(\mathrm{CF_3})(\mathrm{CF_3SCF_2})\mathrm{C{=}CF_2}} \xrightarrow{\mathrm{KF}} \underset{(\mathbf{1})}{(\mathrm{CF_3})_2\mathrm{C{=}CF_2}} + \underset{(\mathbf{13})}{(\mathrm{CF_3})_2\mathrm{C{=}CF(SCF_3)}}$$

$$+\, \underset{(\mathbf{14})}{(\mathrm{CF_3})(\mathrm{CF_3SCF_2})\mathrm{CH{-}CF_2(SCF_3)}} + \underset{(\mathbf{21})}{\mathrm{CF_3CH_2C(O)F}}$$

$$+\, \underset{(\mathbf{23})}{\mathrm{CF_3}(\mathrm{CF_3SCF_2})\mathrm{C{=}CF(SCF_3)}} \text{ or } \underset{(\mathbf{28})}{(\mathrm{CF_3SCF_2})_2\mathrm{C{=}CF_2}}$$

$$+\, \underset{(\mathbf{29})}{\mathrm{CF_3}(\mathrm{CF_3SCF_2})\mathrm{C{=}C(SCF_3)_2}} \text{ or } \underset{(\mathbf{30})}{(\mathrm{CF_3SCF_2})_2\mathrm{C{=}CF(SCF_3)}}$$

$$+\, \underset{(\mathbf{31})}{(\mathrm{CF_3SCF_2})_2\mathrm{CHCF(CF_3)_2}} \text{ or } \underset{(\mathbf{32})}{(\mathrm{CF_3})_2\mathrm{CHCF(SCF_3)_2}}$$

$$+\, \underset{(\mathbf{22})}{(\mathrm{CF_3S})\mathrm{CF_2CH(CF_3)_2}} \qquad (6)$$

The majority of these compounds have been identified from their GC–MS spectra (Table 1). In addition to the starting material **10**, **1**, **13**, **14**, **21**, **23** or bis-2,2-(trifluoromethylthiodifluoromethyl)-perfluoroethylene (**28**), bis-1,1-(trifluoromethylthio)-2-(trifluoromethylthiodifluoromethyl)-perfluoropropene (**29**) or 1-(trifluoromethylthio)-2,2-bis-(trifluoromethylthiodifluoromethyl)-fluoroethylene (**30**), bis-1,1-(trifluoromethylthiodifluoromethyl)-1*H*-bis-2,2-(trifluoromethyl)-fluoroethane (**31**), or bis-1,1-(trifluoromethyl)-1*H*-bis-2,2-(trifluoromethylthio)-perfluoropropane (**32**) and 1-(trifluoromethyl)-1*H*-2-(trifluoromethylthio)-perfluoropropane (**22**) have been identified as products of this reaction [eqn. (6)]. The formation of **1** is simply a case of the replacement of the trifluoromethylthio moiety by fluoride. The origin of **21** has been previously discussed. The trifluoromethylthiyl group liberated, as mentioned above, replaces the vinylic fluorine to give **13**. Three structures are possible for the bis(trifluoromethylthio) derivative: **12**, **23** and **28**. Since the mass spectrum of an authentic sample of **12** is different from that of this compound, only structures **23** and **28** remain to be considered as possible structures. However, a choice between these two structures was not possible. Of the two structures, **29** and **30**, we favor **29** based on the presence of the ion ($m/z = 207$) found in its mass spectrum. The formation of the saturated compounds containing hydrogen can be rationalized, as already mentioned, on the basis of the addition of HF to the double bond.

The parent molecular ions are observed for all but three compounds; in the latter case, the fragmentation pattern is consistent with the assigned structures (Table 1). The splitting off of CF_3 ($m/z = 69$); CF_2 ($m/z = 50$) and (M − F) appear to be a common characteristic. The ion CF_2 ($m/z = 50$) is due to the difluorocarbene coming from the CF_3 group. Often the ion ($m/z = 100$) representing C_2F_4 is seen. In the majority of cases, the CF_3 ion ($m/z = 69$) is the most prominent peak. The low energy mass spectral fragmentation of **1** has recently been reported [15].

While compounds containing the trifluoromethylthio function usually lose SCF_3 ($m/z = 101$), ions corresponding to CSF_2 ($m/z = 82$), CSF ($m/z = 63$) and CS ($m/z = 44$) are also found in the mass spectral fragmentation pattern of these compounds. Mass spectral fragmentation data of a large number of compounds containing the SCF_3 group have been recently discussed in a series of papers [16].

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