Trifluoromethyldisulfane. A Reactive Nucleophile toward Fluorinated Acid Halides

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Abstract: Introduction of the -SS- linkage into fluorinated compounds is enhanced by the nucleophilic behavior of trifluoromethyldisulfane toward fluorinated acid halides. In the presence of potassium fluoride at −25 °C, CF_3SSH was allowed to react with $CF_3C(O)F$, $CF_3C(O)SCl$, COF_2, $FC(O)(CF_2)_3C(O)F$, and $FC(O)C(O)F$ to form $CF_3C(O)SSCF_3$, $CF_3C(O)SSSCF_3$ and $CF_3C(O)SSCF_3$, $CF_3SSC(O)F$ and $CF_3SSC(O)SSCF_3$, $CF_3SSC(O)(CF_2)_3C(O)F$ and $CF_3SSC(O)(CF_2)_3C(O)SSCF_3$, and $CF_3SSC(O)C(O)F$ and $CF_3SSC(O)C(O)SSCF_3$, respectively. These new mono- and bis(trifluoromethyldisulfanes) are colorless, moderately stable liquids which are separated only with difficulty from the bis(trifluoromethyl)sulfanes which are formed concomitantly.

Although trifluoromethanethiol, CF_3SH, was synthesized many years ago,[1] its role as a synthetic reagent has been largely overshadowed by that of the mercurial $(CF_3S)_2Hg$.[2,3] The preparations of the higher members of the family trifluoromethyldisulfane, CF_3SSH,[4] and trifluoromethyltrisulfane, CF_3SSSH,[5] have been reported only recently and we find that the preparation of the mercurial derivatives of these compounds, analogous to that of CF_3SH, is not practical due to concomitant compound degradation and formation of mercury sulfide.

Earlier we showed that chlorotrifluoromethyldisulfane underwent metathetical reactions with thiols, thioacids, amines, and metal salts to form a wide variety of substituted trifluoromethyldi- and -trisulfanes.[6] Under photolytic conditions, chlorotrifluoromethyldisulfane adds the fragments Cl· and CF_3SS· to olefins to form new trifluoromethyl(chlorofluoroalkyl)disulfanes.

The acidic nature of the sulfanes, CF_3S_xH ($x = 1, 2, 3$), suggested that they also could be useful precursors to other interesting substituted trifluoromethylsulfanes if allowed to react with compounds which undergo attack at electrophilic centers. Thus, we report the preparation of new substituted mono- and bis(trifluoromethyldisulfanes) by reaction of fluorinated acid halides with trifluoromethyldisulfane in the presence of an alkali metal fluoride at 0 °C or below.

Results

Trifluoromethyldisulfane, prepared by reaction of trifluoromethanesulfenyl chloride with hydrogen sulfide as previously reported,[4] was allowed to react with a series of carbonyl halides. The resulting compounds were those to be expected from the nucleophilic displacement of the halide by CF_3SS^-.

$$CF_3SSH + R_fX \xrightarrow[-25\ °C]{MF} CF_3SSR_f + HX \cdot MF$$

where X = Cl, F; M = Cs, K; and $R_f = CF_3C(O)$, $FC(O)C(O)$, $CF_3C(O)S$, $FC(O)(CF_2)_3C(O)$, $FC(O)$. When the proper reactant ratios are used, disubstituted products are formed, e.g.,

$$2CF_3SSH + R_fF_2 \xrightarrow[-25\ °C]{MF} (CF_3SS)_2R_f + 2HF \cdot MF$$

where M = Cs, K and $R_f = C(O)(CF_2)_3C(O)$, $C(O)$, $C(O)C(O)$. These products were isolated in addition to the reaction by-products, $CF_3S_xCF_3$ ($x = 3, 4$), $CF_3SC(S)SCF_3$, CF_3SR_f, and $(CF_3S)_2R_f$. These substituted trifluoromethyldisulfanes are colorless, moderately volatile liquids which can be stored in Pyrex glass at 25 °C for short periods. However, at −78 °C they are stable indefinitely.

The infrared spectra of the compounds show characteristic absorptions for the CF_3SS- groups at approximately 1185 and 1110 cm^{-1} as well as a carbonyl stretch for $CF_3SSC(O)$- which is markedly lower in wavenumber than the carbonyl stretch in the corresponding fluorine and trifluoromethylperoxy analogues. Typically, while substitution of a fluorine by CF_3OO- lowers the absorption of the adjacent carbonyl by approximately 30 wavenumbers (e.g., $CF_3C(O)F$, 1890 (s, C=O) compared to $CF_3C(O)OOCF_3$, 1859 (s, C=O)),[7] substitution by CF_3SS- has a much larger effect (e.g., $CF_3C(O)SSCF_3$, 1768 (s, C=O)). The ^{19}F NMR spectra of the compounds show a resonance assignable to the CF_3SS- group(s) at approximately ϕ^* 45 in all of the compounds studied. The mass spectra contain appropriate fragmentation patterns and isotope ratios. All compounds studied give mass spectral peaks for CF_3SS^+ as well as recombination peaks for $CF_3S_xCF_3$ ($x = 3, 4$). The more stable compounds, $CF_3C(O)SSCF_3$ and $CF_3SSC(O)C(O)F$ also show intense molecular ions.

Discussion

The ^1H NMR data for sulfanes, HS_xH ($x = 1$-4), is seen to follow a definite trend with increasing chain length. The chemical shift values, as given in Table I, show a decreasing value of τ for the sulfanes with increasing sulfur chain length. This correlates with decreasing pK_1 values for the sulfanes indicating an increasingly acidic proton, e.g., $pK_1(H_2S) = 6.83$, $pK_1(H_2S_2) = 5.0$, $pK_1(H_2S_3) = 4.2$, $pK_1(H_2S_4) = 3.8$.[8] The chemical shift of the sulfanes is a function of the sulfur chain length over the range $x = 1, 2, 3$. At this point, there is a concomitant dimunition in the substituent effect of added sulfur atoms and in the difference in chemical shift.[9]

The chemical shift of the compounds in the series, CF_3S_xH ($x = 1, 2, 3$), does not change regularly as is the case for the sulfanes. For CF_3S_xH, as a result of the strong inductive effect of the CF_3 group, CF_3SH (compare CH_3SH at τ 8.8) has a chemical shift which is virtually identical to that of CF_3SSH where the lengthening of the sulfur chain essentially compensates for the decreasing influence of the CF_3- group. When $x = 3$, the sulfur chain length is the dominant factor, and the chemical shifts of the trifluoromethyltrisulfane and trisulfane are comparable.

Attempts have been made to generalize a correlation in the chemical shifts of protons with the electronegativities of substituent groups;[10] however, it has been shown that other factors often play a significant and, at times, dominant role in the chemical shift.[11,12] Therefore, it is not possible to draw a definite conclusion as to the acidities of the trifluoromethylsulfanes based on the chemical shift data and the available data for sulfanes other than to say that the proton is acidic in nature.

Table I. ^1H Nuclear Magnetic Resonance Data for Trifluoromethylsulfanes and Sulfanes

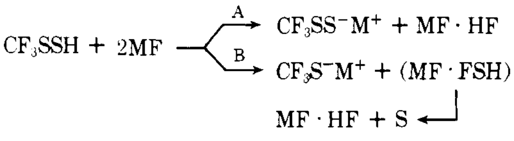
	τ (in $CFCl_3$)		τ^a (in CS_2)^b
CF_3SH	6.58	H_2S	9.15
CF_3SSH	6.59	H_2S_2	7.28
CF_3SSSH	5.81	H_2S_3	5.92
		H_2S_4	5.90

[a] Relative to Me_4Si. [b] M. Schmidt and W. Siebert in "Comprehensive Inorganic Chemistry", Vol. 2, A. F. Trotman-Dickenson, Ed., Pergamon Press, Oxford, 1973, p 835.

Although trifluoromethyldisulfane has an acidic proton, no reaction occurs with the halogen-containing compounds which were tried in the absence of metal fluoride. The metal fluoride enhances the formation of the strong nucleophile, CF_3SS^-, which then attacks the carbonyl carbon to form the observed products at low temperatures. If trifluoromethyldisulfane is allowed to warm to 25 °C in the presence of cesium fluoride or potassium fluoride, it is consumed rapidly according to

$$\mathrm{CF_3SSH + excess\ MF \xrightarrow{25\ ^\circ C} CF_3SS^-M^+ + CF_3S_{\it x}CF_3} \\ \mathrm{+ CF_3SC(S)SCF_3 + CF_3SH + S + MF\cdot HF} \quad (1)$$

where M = Cs, K and x = 2–4. These products may be formed by two competing reaction routes.



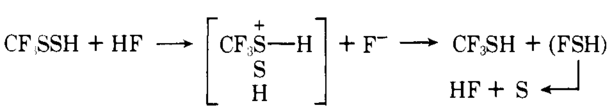
$$\mathrm{CF_3SSH + 2MF} \begin{cases} \xrightarrow{A} \mathrm{CF_3SS^-M^+ + MF\cdot HF} \\ \xrightarrow{B} \mathrm{CF_3S^-M^+ + (MF\cdot FSH)} \\ \qquad\qquad\qquad \mathrm{MF\cdot HF + S} \leftarrow \end{cases}$$

Mechanism A is a simple nucleophilic displacement resulting from attack by the fluoride ion and mechanism B is a nucleophilic cleavage of the S–S bond.[13,14] Based on these reaction routes, the products observed in reaction 1 can be explained. It has been shown that CF_3S^- will trimerize to form $CF_3SC(S)SCF_3$.[15] This anion, CF_3S^-, as well as CF_3SS^-, will attack S–S bonds to yield bis(trifluoromethyl)sulfanes, e.g.,

$$\mathrm{CF_3SSH + CF_3S_{\it x}^- \longrightarrow CF_3SS_{\it x}CF_3 + HS^-}$$

where x = 2, 3.

Trifluoromethanethiol is formed by a cation-assisted nucleophilic attack by the hydrogen fluoride which is formed in the overall reaction on trifluoromethyldisulfane,

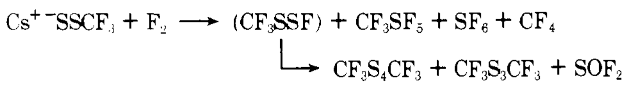


$$\mathrm{CF_3SSH + HF \longrightarrow \left[\begin{matrix} CF_3\overset{+}{S}{-}H \\ S \\ H \end{matrix}\right] + F^- \longrightarrow CF_3SH + (FSH)} \\ \mathrm{HF + S \leftarrow}$$

This is very similar to the instability of trifluoromethyl hydroperoxide, CF_3OOH, in the presence of HF and metal.[7]

$$\mathrm{CF_3OOH + HF \xrightarrow{metal} COF_2 + \tfrac{1}{2}O_2 + 2\,HF}$$

The formation of $Cs^{+-}SSCF_3$ is verified by allowing CF_3SSH to warm to 25 °C in the presence of CsF. After the volatile products ($CF_3S_xCF_3$, x = 2, 3) are removed, fluorine is added and reaction occurs.

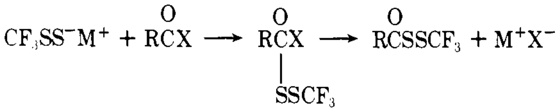


$$\mathrm{Cs^{+\,-}SSCF_3 + F_2 \longrightarrow (CF_3SSF) + CF_3SF_5 + SF_6 + CF_4} \\ \mathrm{\hookrightarrow CF_3S_4CF_3 + CF_3S_3CF_3 + SOF_2}$$

The decomposition products of CF_3SSF which were identified are consistent with previously reported results.[16]

Trifluoromethyldisulfane in the presence of cesium fluoride reacts much mmore rapidly and at lower temperatures than in the presence of potassium fluoride. This is due to the greater ability of cesium fluoride to act as a fluoride ion donor as well as a hydrogen fluoride acceptor. In order to reduce the amount of trifluoromethyldisulfane consumed by side reactions resulting from its interaction with the metal fluoride as described above and, concomitantly increase the yields of the desired products, potassium fluoride was used in the reactions with carbonyl compounds.

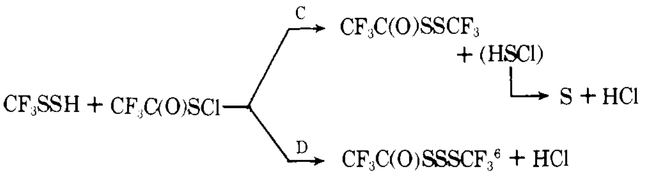
In the carbonyl compounds, the carbonyl carbon, due to the partial positive charge resulting from the polarization of the electrons in the carbonyl group towards the oxygen, is susceptible to nucleophilic attack by CF_3SS^-.



$$\mathrm{CF_3SS^-M^+ + R\overset{O}{C}X \longrightarrow R\overset{O}{\underset{SSCF_3}{C}}X \longrightarrow R\overset{O}{C}SSCF_3 + M^+X^-} \quad (2)$$

Higher yields are obtained when the reactant is the carbonyl fluoride, RC(O)F, rather than the carbonyl chloride, RC(O)Cl. In the fluoride, the carbonyl carbon is a better site for nucleophilic attack due to the greater relative positive charge resulting from the greater electronegativity of the fluorine relative to chlorine. Since a better site for nucleophilic attack is available, reaction 2 competes more successfully with the other possible reactions and yields are improved. Also, for an S_N2 reaction such as this, the carbon, which is initially in the trigonal configuration, tends, in the transition state, towards a tetrahedral configuration. As this occurs, the attached groups are brought closer together and a smalller atom, e.g., fluorine, will cause less steric hindrance than will a larger atom, e.g., chlorine, therefore facilitating the reaction.

The reaction of trifluoromethyldisulfane with trifluoroacetylsulfenyl chloride, $CF_3C(O)SCl$, differs from those discussed above because an additional reaction route is possible,



$$\mathrm{CF_3SSH + CF_3C(O)SCl} \begin{cases} \xrightarrow{C} \mathrm{CF_3C(O)SSCF_3 + (HSCl)} \\ \qquad\qquad\qquad \hookrightarrow \mathrm{S + HCl} \\ \xrightarrow{D} \mathrm{CF_3C(O)SSSCF_3{}^6 + HCl} \end{cases}$$

Mechanism C involving nucleophilic attack at the carbonyl carbon predominates, and only low yields of $CF_3C(O)SSSCF_3$ are obtained. This supports the carbonyl carbon as the more positive reaction site, as would be expected.

It is of interest to compare the reaction behavior of CF_3SSH with that of its oxygen analogue, CF_3OOH.[7] The products formed with fluorinated carbonyl compounds are strictly analogous although the yields obtained are much higher for the oxygen system. This difference in yields arises from the greater susceptibility of the S–S linkage to nucleophilic attack by both the fluoride ion of the alkali metal salt and the CF_3SS^- ion formed in the reaction. In order to decrease the extent of reaction 1 in favor of reaction 2, it is necessary to carry out the reactions at −25 °C. However, it was not possible to prevent reaction 1 completely by controlling the reaction temperature since at less than −25 °C, neither reaction occurs to any appreciable extent.

Experimental Section

Material. Trifluoromethyldisulfane[4] and trifluoroacetylsulfenyl chloride[17] were prepared via literature methods, purified using low temperature, vacuum distillation techniques, and identified by infrared spectroscopy. The metal fluorides were purchased from Baker and dried carefully before using. The following carbonyls were used as purchased: $CF_3C(O)F$ (PCR), FC(O)F (Matheson), FC(O)C(O)F (Hynes), and $FC(O)(CF_2)_3C(O)F$ (PCR).

Apparatus. All gases and volatile liquids were handled in a conventional glass vacuum apparatus using standard PVT techniques. Purification of products was by low temperature, vacuum distillation techniques. In some cases, final purification was obtained by gas chromatography using a column constructed of 0.25 in. copper tubing packed with 20% Kel F-3 polymer oil on Chromosorb P. Infrared spectra were recorded with a Perkin-Elmer Model 457 infrared spectrophotometer by using a 10-cm gas cell fitted with KBr windows. Varian HA-100 and EM-360 nuclear magnetic resonance spectrometers were used for ^{19}F and ^{1}H spectra with CCl_3F and $(CH_3)_4Si$, respectively, as internal standards. The mass spectra were determined on a Hitachi Perkin-Elmer RMU 6-E mass spectrometer. Vapor pressure studies were made by an isoteniscopic method. Elemental analysis were performed by Beller Laboratories in Göttingen, Germany.

General Procedure. Into a Pyrex reaction vessel containing an excess of potassium fluoride were condensed the proper ratio of trifluoromethyldisulfane and a carbonyl-containing compound. The reaction mixture was warmed slowly from −196 °C to the desired temperature and maintained at this temperature for 12 h. The resulting mixture was then separated via low temperature vacuum distillation techniques. The data characterizing the compounds are given below.

$CF_3SSC(O)F$: yield 55%; identified by NMR and ir.[18]

$CF_3SSC(O)SSCF_3$: yield 5%; ir 2290 (w), 1727 (vs), 1640 (w), 1305 (w), 1189 (vs), 1110 (vs), 832 (s), 761 (s), 491 (m), 454 (m); NMR ϕ^* 46.4, s. The compound decomposes slowly in glass at 25 °C.

$CF_3C(O)SSCF_3$: yield 60%; ir 1837 (w, br), 1768 (vs), 1282 (s), 1190 (vs), 1110 (vs), 928 (vs), 918 (m, sh), 760 (m), 738 (s); NMR ϕ^* 44.7 (s, CF_3S–), 73.1 (s, CF_3–C). The equation $\log P_{(mm)} = 7.29 - 1452.3/T$ describes the vapor pressure curve from which ΔH_v (6.64 kcal/mol), ΔS_v (20.2 eu), and the boiling point (56.2 °C) are obtained.

Anal. Calcd: C, 15.65; F, 49.6; S, 27.83. Found: C, 15.64; F, 49.7; S, 27.78.

$CF_3C(O)SSSCF_3$: yield 5%; identified by infrared spectrum.[6]

$CF_3SSC(O)C(O)F$: yield 30%; ir 1879 (m), 1836 (vs), 1753 (vs), 1232 (s), 1190 (vs), 1151 (s), 1115 (vs), 926 (vs), 760 (m), 725 (s); NMR ϕ^* 45.1 (s, CF_3S–), −16.3 (s, F–C). The equation $\log P_{(mm)} = 7.60 - 1820.2/T$ describes the vapor pressure curve from which ΔH_v (8.33 kcal/mol), ΔS_v (21.6 eu), and the boiling point (112.2 °C) are obtained.

Anal. Calcd: F, 36.5; S, 30.77. Found: F, 36.4; S, 30.71.

$[CF_3SSC(O)]_2$: yield 10%; ir 1739 (s), 1185 (vs), 1111 (vs), 895 (w), 760 (s); NMR ϕ^* 44.3, s. This compound decomposes in glass at 25 °C.

$CF_3SSC(O)(CF_2)_3C(O)F$: yield 10%; ir 1890 (vs), 1767 (m, sh), 1737 (vs), 1322 (m), 1180 (vs), 1110 (vs), 982 (s), 831 (m), 760 (m), 723 (m); NMR ($CF_3SSC(O)CF_2{}^ACF_2{}^BCF_2{}^CC(O)F^D$), ϕ^* 44.7 (s, CF_3–S), 114.7 (d, t, $CF_2{}^A$), 122.2 (d, $CF_2{}^B$), 117.3 (d, t, $CF_2{}^C$), −23.95 (t, t, t, $C(O)F^D$), $J_{AD} = 1.8$, $J_{AC} = 11.2$, $J_{BD} = 6.8$, $J_{CD} = 8.4$ Hz. Anal. Calcd: F, 53.1; S, 17.88. Found: F, 50.7; S, 17.60.

$[CF_3SSC(O)(CF_2)]_2CF_2$: yield 20%; ir 1740 (vs), 1328 (m), 1186 (vs), 1110 (vs), 988 (s), 837 (m), 759 (m), 571 (w), 493 (w); NMR ($CF_3SSC(O)CF_2{}^ACF_2{}^BCF_2{}^AC(O)SSCF_3$), ϕ^* 46.0 (s, CF_3S–), 119.2 (t, $CF_2{}^A$), 133.5 (p, $CF_2{}^B$), $J_{AB} = 10$ Hz. The equation $\log P_{(mm)} = 7.63 - 1758.0/T$ describes the vapor pressure curve from which ΔH_v (8.04 kcal/mol), ΔS_v (21.7 eu), and the boiling point (97.0 °C) are obtained.

Anal. Calcd: F, 48.3; S, 27.12. Found: F, 47.3; S, 29.68.

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Axial and Equatorial Phosphorus–Oxygen Basicity in a Six-Membered Ring Phosphate Anion: Effect of the Countercation

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Abstract: Reaction of the rigid six-membered ring phosphate anion **4** in methanol with diazomethane in 1,2-dimethoxyethane under mild conditions yields an order of magnitude more of methyl ester **2b** than its isomer **2a** with the noncomplexing countercations Na^+, Cs^+, and Me_4N^+. With Li^+, however, the ratio of **2a**/**2b** is close to 1, while with NH_4^+ and $C_6H_{11}NH_3^+$ it is 1.6. It is concluded that preferential association of Li^+ with the axial P–O oxygen via complexation and of NH_4^+ and $C_6H_{11}NH_3^+$ via hydrogen bonding accounts for the increased tendency toward methylation of the equatorial P–O oxygen. A possible indication of the in vivo behavior of cyclic nucleotide anions is pointed out.

Evidence from a variety of chemical and spectral sources has established the greater basicity of axially compared to equatorially directed phosphorus lone pairs and phosphoryl oxygens in six-membered ring phosphite and phosphate esters, respectively, such as **1** and **2**.[1] The axial and equatorial P=O linkages in the biologically important cyclic 3′,5′-AMP and GMP nucleotide anions **3** are very likely differentiated in their bonding characteristics by electronic effects similar to those