**Table VII.** Solution and Refinement for **55**

| | |
|---|---|
| system used | Siemens SHELXTL PLUS (PC Version) |
| solution | direct methods |
| refinement method | full-matrix least-squares |
| quantity minimized | $\sum w(F_o - F_c)^2$ |
| absolute structure | N/A |
| extinction correction | N/A |
| hydrogen atoms | riding model, fixed isotropic $U$ |
| weighting scheme | $w^{-1} = \sigma^2(F) + 0.0008F^2$ |
| number of parameters refined | 228 |
| final $R$ indices (obs data) | $R = 5.43\%$, $R_w = 6.07\%$ |
| $R$ indices (all data) | $R = 7.90\%$, $R_w = 6.59\%$ |
| goodness-of-fit | 1.45 |
| largest and mean $\Delta/\sigma$ | 0.002, 0.000 |
| data-to-parameter ratio | 5.8:1 |
| largest difference peak | 0.26 eÅ$^{-3}$ |
| largest difference hole | −0.20 eÅ$^{-3}$ |

**57**: $^1$H NMR (CDCl$_3$) $\delta$ 0.34 (s, 9 H), 7.34–7.42 (m, 11 H); $^{13}$C NMR (CDCl$_3$) $\delta$ −1.0, 128.5, 128.7, 129.1, 130.0, 130.1, 141.4, 149.7, 150.2, 152.0, 190.4, 192.4; IR (film) 3061 w, 2954 m, 1728 m, 1690 vs, 1631 w, 1486 w, 1443 w, 1352 m, 1246 m, 1122 s, 845 s, 692 s; mass spectrum, $m/e$ (% relative intensity) 332 M$^+$ (90), 317 (100), 303 (10), 289 (20), 273 (8), 259 (10), 245 (12), 229 (15), 215 (45); calcd for C$_{21}$H$_{20}$O$_2$Si $m/e$ 332.1233, found $m/e$ 332.1263. Spectral data for quinone **56**: $^1$H NMR (CDCl$_3$) $\delta$ 6.93 (s, 2 H), 6.98 (dd, 4 H, $J$ = 7.7, 1.7 Hz), 7.19–7.22 (m, 6 H); $^{13}$C NMR (CDCl$_3$) $\delta$ 127.7, 128.4, 130.4, 132.4, 136.4, 143.4, 187.0; IR (film) 3060 w, 2926 w, 1654 vs, 1443 w, 1326 w, 1296 m, 1090 m, 1010 m, 843 w, 744 m, 696 s; mass spectrum, $m/e$ (% relative intensity) 260 M$^+$ (100), 231 (20), 215 (8), 202 (10), 178 (30), 152 (10); calcd for C$_{18}$H$_{12}$O$_2$ $m/e$ 260.0837, found $m/e$ 260.0858.

When the reaction was repeated but the oxidative workup was deleted, the cyclopentadienone **55** could be isolated from this reaction mixture and purified by chromatography on silica gel to give **55** as a dark-purple solid (mp 118–120 °C, $R_f$ = 0.49, 1:1:4): $^1$H NMR (CDCl$_3$) $\delta$ 0.15 (s, 9 H), 1.95 (s, 2 H), 4.10 (s, 3 H), 7.2–7.3 (m, 5 H), 7.34 (m, 5 H); $^{13}$C NMR (CDCl$_3$) $\delta$ −0.35 (s, CH$_3$), 12.75 (t, CH$_2$), 59.61 (q, OCH$_3$), 126.55 (s), 127.99 (s), 128.67 (d), 128.77 (d), 129.24 (s), 130.32 (d), 130.50 (d),

131.44 (s), 132.39 (s), 148.32 (s, C-2), 168.53 (s, C-3), 200.48 (s, C-1); IR (CCl$_4$) 3084 w, 3059 m, 3022 w, 1730 m, 1708 s, 1693 s, 1648 s, 1617 m, 1485 w, 1447 w, 1406 w, 1349 m, 1314 m, 1293 s, 1179 w, 1163 w, 1144 w, 1123 w, 1078 w, 1047 w, 1029 w, 959 w, 904 w, 881 w cm$^{-1}$; mass spectrum, $m/e$ (% relative intensity) 349 M$^+$ + 1 (4), 348 M$^+$ (19), 334 (11), 333 (46), 318 (6), 317 (21), 215 (6), 178 (3), 73 (100); calcd for C$_{22}$H$_{24}$O$_2$Si $m/e$ 348.1615, measured $m/e$ 348.1550.

**Crystal Structure of the ((Trimethylsilyl)methyl)cyclopentadienone 55.** A single crystal of **55** suitable for X-ray analysis was grown from ethyl acetate/hexane. The approximate size of the crystal used for data collection measured 0.15 × 0.15 × 0.3 mm. The crystal was mounted on a Nicholet P2$_1$ automatic diffractometer equipped with an incident beam graphite crystal monochromator. All measurements were made at 25 °C using Mo K$\alpha$ radiation. The unit-cell constants and the orientation matrix to be used in data collection were obtained from a least square refinement of 15 centered general reflections. Crystal data are listed in Table V. Table VI summarizes the data collection. No decay was noted for the three standard reflections. The solution and refinement is summarized in Table VII.

**Supplementary Material Available:** X-ray crystallographic data for compound **55** including a figure showing the molecular structure and numbering scheme and tables of fractional coordinates, isotropic and anisotropic thermal parameters, bond distances, and bond angles (6 pages); a listing of observed and calculated structure factors for **55** (5 pages). Ordering information is given on any current masthead page.

# Trifluoromethanesulfonyl Hypofluorite, a Hitherto Unknown Fluoroxy Compound

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**Abstract:** Trifluoromethanesulfonyl hypofluorite (CF$_3$SO$_2$OF) has been synthesized by the reaction of fluorosulfuryl hypofluorite (FSO$_2$OF) with cesium trifluoromethanesulfonate. It is the first compound in which a sulfur atom is bonded both to carbon and to an O–F moiety. The compound has a melting point of −87 ± 2 °C and an extrapolated boiling point of 0 ± 1 °C. The $^{19}$F NMR spectrum of the compound in CFCl$_3$ at −80 °C shows a CF$_3$ doublet at −71 ppm and a broad OF singlet at +238 ppm. From the latter can be deduced an O–F bond energy of about 145 kJ/mol, comparable to that of FSO$_2$OF. The compound hydrolyses in base to give a mixture of O$_2$ and CF$_4$, along with (presumably) sulfate and trifluoromethanesulfonate. It decomposes thermally in the presence of CsF to yield principally CF$_3$SO$_2$F and OF$_2$ along with (presumably) cesium trifluoromethanesulfonate.

The successful synthesis in recent years of a variety of unexpected hypofluorites or fluoroxy compounds, i.e., compounds containing the O–F moiety, has effectively undermined most preconceptions as to which of these compounds might be synthesized. Nevertheless, a few islands of "nonexistence" have persisted, among which are compounds containing an S–O–F linkage and in which the sulfur is also bonded to carbon. We would expect formation of such a compound to be favored if the carbon were also surrounded by highly electronegative substituents.

Nevertheless, the simplest compound that meets this criterion, trifluoromethanesulfonyl hypofluorite ("triflyl" hypofluorite, CF$_3$SO$_2$OF) has until now remained unknown. The conventional rationalization for its nonexistence has been the weakness of the carbon–sulfur bond, which would be readily susceptible to oxidative cleavage by the hypofluorite fluorine.

The two most general methods of synthesizing hypofluorites are the metal-fluoride-catalyzed addition of molecular fluorine across an M=O or M≡O multiple bond, as in the formation of

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CF$_3$OF from CO or COF$_2$[1] and of FSO$_2$OF from SO$_3$,[2] and the reaction of fluorine with oxyacids and their salts, as in the formation of NO$_2$OF from HNO$_3$[3] and CH$_3$C(O)OF from NaOC-(O)CH$_3$.[4,5] The first of these approaches does not appear readily applicable to the synthesis of triflyl hypofluorite, while preliminary experiments that we have undertaken using the second approach (fluorination of trifluoromethanesulfonic acid or its salts) have failed to yield any interesting products.

Several more exotic synthetic approaches, however, have in the past succeeded where conventional techniques have failed. One of these is the use of fluorosulfuryl hypofluorite (FSO$_2$OF) as a fluorinating agent for the preparation of other fluoroxy compounds. Its first application for this purpose was by Ruff and Lustig,[6] who reacted it with CsOSF$_5$ in an alternative synthesis of SF$_5$OF. Subsequently, Christe and his colleagues[7] used the analogous reaction with CsOTeF$_5$ to prepare TeF$_5$OF, which had resisted more conventional preparative efforts so stubbornly that it had been thought to be too unstable to be synthesized.[8]

In this paper, we describe the successful synthesis of trifluoromethanesulfonyl hypofluorite by the reaction of FSO$_2$OF with cesium trifluoromethanesulfonate.

## Experimental Section

*CAUTION*: The synthesis described here entails the use of elemental fluorine under pressure and at elevated temperature. Fluorine is a toxic, highly reactive, and extremely corrosive gas, and anyone undertaking to repeat this work should be thoroughly familiar with the proper procedures for its safe handling. (See, for example, ref 9.) In particular, adequate ventilation should be assured at all times, and all contact with readily oxidizable materials should be avoided. In addition, the synthetic procedure requires the intermediate production and isolation of FSO$_2$OF, a compound that has been reported under at least some circumstances to undergo explosive decomposition and/or reaction. The final product, trifluoromethanesulfonyl hypofluorite, is a new compound, the hazards of which must still be considered unknown. It is only prudent to prepare these substances in no greater quantities than are absolutely required and to use face shields, gloves, and explosion barriers when working with them.

**Reagents.** Fluorosulfuryl hypofluorite was prepared by the overnight reaction of sulfur trioxide with an excess of molecular fluorine in a passivated Monel pressure vessel at 200 °C and 2–3 atm total initial pressure. The excess fluorine was pumped away at liquid nitrogen temperature, after which the product was distilled from a bath at –79 °C in a Monel, Teflon, and Kel-F vacuum line. The purity of the product was verified by mass and IR spectrometry. Cesium trifluoromethanesulfonate was prepared by neutralizing a cesium hydroxide solution potentiometrically with trifluoromethanesulfonic acid, followed by drying the neutral solution first under a heat lamp and then in a vacuum oven at 100 °C. Fluorine was used as a ca. 97% commercial product (Matheson), trifluoromethanesulfonic acid was obtained from Aldrich Chemical Co., anhydrous CsF from Cerac, Inc., and sulfur trioxide and cesium hydroxide from Alpha Inorganic Chemicals.

**Vapor Pressure and Melting Point Measurements.** The vapor pressure of CF$_3$SO$_2$OF was measured in a small vacuum line equipped with an MKS Baratron pressure gauge. During these measurements the liquid was contained in a Kel-F tube, while the vapor came in contact with stainless steel, Monel, nickel, and Kel-F. The melting point of CF$_3$S-O$_2$OF was measured on a sample contained in a Kel-F tube immersed in an alcohol bath in an unsilvered Dewar flask. Temperatures for melting point and vapor pressure measurements were determined to ±0.1 °C with a copper–constantan thermocouple calibrated against a platinum resistance thermometer. Pressure measurements for quantitation of gaseous reagents and products at ambient temperature were also made

**Table I.** Vapor Pressure of Trifluoromethanesulfonyl Hypofluorite

| | vapor pressure, Torr | |
|---|---|---|
| $t$, °C | obsd | calcd[a] |
| –87.1 | 2.87 | 2.83 |
| –83.6 | 4.02 | 3.91 |
| –78.3 | 5.92 | 6.25 |
| –69.9 | 12.6$_5$ | 12.5 |
| –64.1 | 20.0 | 19.5 |
| –53.4 | 43.2 | 41.7 |
| –46.0 | 67.6 | 67.6 |
| –34.7 | 133 | 134 |
| –23.2 | 247 | 251 |

[a] From the equation $\ln p$ (Torr) $= 18.58 - 3263/T$ (K)

with the Baratron gauge in calibrated volumes. The resulting quantities are expressed in units of Torr·liters.

**Mass, Infrared, and NMR Spectrometry.** The 70-eV electron-impact mass spectra of CF$_3$SO$_2$OF and its decomposition and reaction products were determined with a Finnigan 400 quadrupole mass spectrometer equipped with a Kel-F inlet tube and using a data system provided by Shrader Analytical Labs. Chemiionization mass spectra were obtained with a Hewlett-Packard 5989 spectrometer, into which the sample was introduced through a rather long stainless steel capillary inlet. Sample decomposition in this inlet appears to have been substantial. The infrared spectrum of CF$_3$SO$_2$OF vapor at ambient temperature was measured at 1 cm$^{-1}$ resolution with a Nicolet 510P FTIR spectrometer. Samples were contained in a Kel-F cell of 10-cm path length, fitted with AgCl windows. Some attack on the windows was occasionally observed. Fluorine-19 NMR spectra were measured unlocked at 282.4 MHz on a Bruker AM300 spectrometer. The sample probe was cooled to –80 °C. Samples were distilled in vacuum into thin-walled Kel-F tubes of 3–4-mm o.d., along with CFCl$_3$ solvent, which also served as reference. These tubes were heat-sealed and inserted into 5-mm o.d. glass NMR tubes.

**Preparation and Purification of Trifluoromethanesulfonyl Hypofluorite.** In a typical preparation, 1.8 mmol of cesium trifluoromethanesulfonate was placed in the bottom of a heavy-walled 25-cm$^3$ Kel-F tube that was closed with a Kel-F valve. The tube was evacuated, and 1.2 mmol of FSO$_2$OF was condensed onto it at liquid nitrogen temperature. The tube was warmed to –79 °C and allowed to remain for several hours, after which it was warmed to –18 °C and held at this temperature for 3–4 weeks. The reaction vessel was then cooled to about –100 °C in an alcohol bath, and the unreacted FSO$_2$OF was pumped off, along with small amounts of O$_2$ and CF$_4$ that had been formed. The pump-off of volatiles was monitored by mass spectrometry; nearly complete removal of the FSO$_2$OF was indicated when the mass peak at $m/e$ = 69 was more than 10 times the intensity of that at $m/e$ = 83. The remaining product (0.7 mmol) was distilled from a chloroform slush bath at about –64 °C.

**Identification of Reaction and Decomposition Products.** Oxygen, oxygen difluoride, and carbon tetrafluoride were identified by their mass spectra and by their volatility at very low temperatures. Carbon tetrafluoride was also identified by its characteristic infrared band at 1283 cm$^{-1}$. Trifluoromethanesulfonyl fluoride (CF$_3$SO$_2$F) was identified by its IR and $^{19}$F NMR spectra, which agreed with those reported in the literature.[10]

## Results

At low temperature, trifluoromethanesulfonyl hypofluorite is a white solid, melting at –87 ± 2 °C to a colorless liquid. The vapor pressure of the compound as a function of temperature is presented in Table I. The results indicate an enthalpy of vaporization of 27.2 ± 0.2$_3$ kJ/mol and yield an extrapolated normal boiling point of 0.0 ± 0.8 °C, where uncertainties are given at the 2$\sigma$ level. The corresponding Trouton constant of 99.6 ± 0.9 J/mol·K is a little larger than that of FSO$_2$OF (92.6 J/mol·K).[2]

The principal peaks in the mass spectrum of triflyl hypofluorite are at $m/e$ (assignment, relative intensity) 69 (CF$_3$$^+$, 100), 64 (SO$_2$$^+$, 8), 50 (CF$_2$$^+$, 6), 48 (SO$^+$, 9.$_5$), and 31 (CF$^+$, 4.$_6$). Chemiionization mass spectrometry showed a small peak at $m/e$ 169 (M + 1), along with a very large peak at 151 (presumably M + 1 of CF$_3$SO$_2$OH formed by hydrolytic decomposition of the hypofluorite in the metal capillary inlet system).

The principal bands in the mid-infrared spectrum of triflyl hypofluorite (2–3 Torr, AgCl) are seen at cm$^{-1}$ (intensity): 1475

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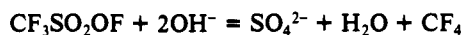
(s), 1247/1241/1235.$_6$ (vs), 1208 (sh), 1140.$_6$ (s), 794 ($\nu_{O-F}$ (?), m), 744 (m), 592 (m), 501 (w), 428 (vw). The $^{19}$F NMR spectrum of the compound (−80 °C in CFCl$_3$) shows a broadened singlet at very low field (+238 ppm, 1 F (bonded to O), $\Delta\nu_{1/2}$ = 14 Hz) and a doublet at moderately high field (−71 ppm, 3 F (bonded to C), $^4J_{FF}$ = 3.6 Hz). One of the NMR samples contained an impurity of FSO$_2$OF (doublets at +243 and +37 ppm).[11]

Trifluoromethanesulfonyl hypofluorite decomposes only rather slowly; even at room temperature a sample can survive for many hours. The thermal decomposition appears complex, and the products have not been completely characterized. Carbon tetrafluoride is formed, as is trifluoromethanesulfonyl fluoride (CF$_3$SO$_2$F). For analytical characterization, two reactions were utilized: alkaline hydrolysis and CsF-mediated thermal decomposition, the latter suggested by the work of Ruff and Lustig.[6]

Reaction of 5.5 Torr·L of CF$_3$SO$_2$OF with 4 cm$^3$ of aqueous 1 M NaOH produced 2.09 Torr·L of CF$_4$ and 1.68 Torr·L of O$_2$. This is consistent with the two parallel hydrolysis reactions

$$CF_3SO_2OF + 2OH^- = CF_3SO_3^- + F^- + H_2O + \tfrac{1}{2}O_2$$

and

$$CF_3SO_2OF + 2OH^- = SO_4^{2-} + H_2O + CF_4$$

proceeding in the ratio 1.61:1.

For the CsF-mediated reaction, 2.58 Torr·L of CF$_3$SO$_2$OF was heated for 5 h at 80 °C in a 25-cm$^3$ Kel-F reaction vessel in the presence of 0.44 g of CsF. Analysis of the gaseous products found 1.20 Torr·L of CF$_3$SO$_2$F, along with 1.26 Torr·L of an extremely volatile fraction that consisted mostly of OF$_2$, along with a small amount of O$_2$. This was reasonably consistent with the predominant reaction

$$2CF_3SO_2OF + CsF = CF_3SO_2F + CsOSO_2CF_3 + OF_2$$
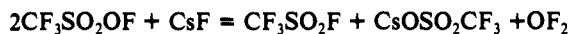
similar to the analogous reaction of FSO$_2$OF observed by Ruff and Lustig.[6]

## Discussion

Our results, particularly the $^{19}$F NMR spectrum, the chemiionization mass spectrum, and the decomposition and hydrolysis reactions, indicate rather conclusively that we have, in fact, prepared the hitherto unknown hypofluorite CF$_3$SO$_2$OF. The compound appears to be more stable than we might have expected, although the fact that CF$_4$ is formed during both thermal decomposition and alkaline hydrolysis lends some support to the prevalent notion that the C–S bond should be a weak point in such a molecule.

The O–F fluorine in trifluoromethanesulfonyl hypofluorite has a $^{19}$F chemical shift that is extremely far downfield, even for a fluoroxy compound.[12] Of known fluorine compounds, only

FSO$_2$OF, the fluorine oxides OF$_2$ and O$_2$F$_2$, and F$_2$ itself have more positive shifts. A negative correlation has recently been established between $^{19}$F chemical shift and O–F bond energy in fluoroxy compounds.[13] On the basis of this correlation, we may estimate the O–F bond in CF$_3$SO$_2$OF to be quite weak, with a bond energy of about 145 kJ/mol, comparable to that of FSO$_2$OF. This is consistent with the fact that CF$_3$SO$_2$OF can be made by fluorination of cesium triflate with FSO$_2$OF, and it may explain why the compound has not been prepared by more conventional techniques.

The infrared band that we have tentatively assigned to the O–F vibration of triflyl hypofluorite is considerably lower in frequency that those assigned to other hypofluorites.[12] We have no immediate explanation for this; we saw no significant absorptions in the region around 880–890 cm$^{-1}$ where most other O–F vibrations are found. It is barely conceivable that the compound decomposes rapidly in the infrared cell, though we have no evidence for such rapid decomposition.

The CsF-mediated decomposition of triflyl hypofluorite is a curious reaction. It is strictly analogous to the corresponding reaction of FSO$_2$OF, for which Ruff and Lustig have postulated a mechanism involving the intermediate formation of CsOF.[6] Such an intermediate strikes us as inherently implausible, however, and we prefer to postulate an intermediate complex anion, similar to those proposed for other CsF-mediated reactions, such as the fluorination of COF$_2$ to CF$_3$OF.[14] We may then formulate the CsF-mediated triflyl hypofluorite decomposition
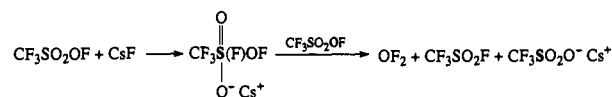


Past attempts to use FSO$_2$OF as a synthetic reagent have not been notably successful. It has developed a reputation for being somewhat unpredictable and difficult to handle and control, under some conditions even dangerously explosive.[12] In our small-scale experiments we have encountered no difficulties in handling CF$_3$SO$_2$OF. It remains to be seen, however, whether practical synthetic applications for this compound will develop.

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