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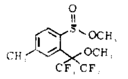
(49) At probe temperatures greater than the 75 °C melting point of **25**, sample decomposition occurred causing the M − OCH_3 to M+· ratio to decrease from 300 to 2.7. This large relative increase in the molecular ion could be due to a new type of sulfurane rearrangement to **46**. Sultine **7** and its fragmentation peaks were also very prominent at these high probe temperatures.



46

Reactions of Trialkoxysulfuranes (Orthosulfinates) with Trifluoromethanesulfonic Acid.[1] The First Isolation of a Dialkoxysulfonium Salt and the Mechanisms of Decomposition of Such Salts

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Abstract: Trialkoxysulfuranes **1a**, **1b**, and **1c** are synthesized. Their reactions with trifluoromethanesulfonic (triflic) acid give, respectively, triflate esters **2a** and **2b** and dialkoxysulfonium triflate **10c**, the first isolated dialkoxysulfonium salt. From oxygen-18 labeling studies and relative rates of reactions, a mechanism involving rate-determining formation of high energy fluorinated carbonium ions, in an ionization reaction involving a sultine leaving group, is proposed for the formation of triflate esters **2a** and **2b**. Comparisons with other sulfurane and alkoxysulfonium chemistry are advanced.

Interesting differences between the reactions of dialkoxy- and trialkoxysulfuranes with bifunctional reagents have recently been reported.[1] Here we describe the reactions of trifluoromethanesulfonic acid (triflic acid) with several trialkoxysulfuranes and constrast this to the alkoxysulfonium ion formation seen in the reactions of triflic acid with acyclic[2] and cyclic[3] dialkoxysulfuranes. While alkoxysulfonium salts can also easily be prepared by alkylation of sulfoxides,[4] dialkoxysulfonium ions have only recently been detected in solution[5] as thermally unstable fluorosulfonates or as triflates stable in the presence of a high concentration of methyl triflate. Here we report the first isolation of a dialkoxysulfonium salt and the mechanism of decomposition of other dialkoxysulfonium ions postulated to be intermediates in reactions of trialkoxysulfuranes with triflic acid.

Experimental Section

Fluorine chemical shifts are reported on the ϕ scale in parts per million upfield from fluorotrichloromethane and proton chemical shifts are reported on the δ scale in parts per million downfield from Me_4Si. Sulfuranes **1a–c**, sultene **9**, and sulfonium triflate **10c** were prepared and transferred in an inert atmosphere box under nitrogen. The reported elemental analyses are within 0.4% of theoretical values unless otherwise noted.

Reaction of 1a with Trifluoromethanesulfonic acid (TfOH). To a solution of sulfurane **1a**[1] in ether or $CDCl_3$ in an NMR tube at 41 °C was added 1 equiv of TfOH. The solution became homogeneous over 5-10 min as the TfOH singlet at ϕ 77.8 ($CDCl_3$) or 79.1 (ether) in the ^{19}F NMR spectrum diminished in intensity. The sulfurane peaks at ϕ 70.1, 71.4, and 72.7 also disappeared over this time interval being replaced by (in $CDCl_3$) a quartet of triplets at ϕ 71.0 (6.1 F) and a septet at 74.4 (2.9 F) of hexafluorocumyl triflate **2a** ($PhC(CF_3)_2OSO_2CF_3$, R_FOTf), quartets at 74.9 (3.4 F) and 75.9 ($J = 8$ Hz) due to sulfinate **3**, and an overlapping singlet at 75.8 due to hexafluorocumyl alcohol (R_FOH) (10.9 F total).

The reaction was repeated on a larger scale to isolate the R_FOTf. To a suspension of 0.98 g (1.27 mmol) of sulfurane **1a** in CCl_4 was added 0.198 mL (2.23 mmol) of TfOH. After being stirred for 15 min, the homogeneous solution was extracted with aqueous KOH to remove excess acid and sulfinate **3**. Solvent was removed at 0.05 Torr leaving

0.281 g (59%) of **2a**, a colorless liquid which upon cooling gave a white solid (mp −11 to −7.5 °C): ^{1}H NMR (CCl_4) δ 7.3–7.9 (m); ^{19}F NMR ϕ 71.2 (quartet of triplets, J_{FF} = 2.1, J_{HF} = 1.0 Hz, 6.0 F), 74.8 (septet, J_{FF} = 2.1 Hz, 3.0 F); mass spectrum (10 eV) *m/e* (rel intensity) 376 (100, $M^{+}\cdot$), 357 (0.5, M − F), 356 (1.0, M − HF), 307 (5.83, M − CF_3), 243 (39.8, $PhC(CF_3)_2O$), 227 (4.55, $PhC(CF_3)_2$), 223 (10.0), 105 (14.5, PhCO), 69 (1.17, CF_3). Anal. ($C_{10}H_5F_9O_3S$) C, H.

This material was identical with an authentic sample of **2a** (R_FOTf) prepared by the reaction of R_FOK[6] with triflic anhydride[7] in CCl_4.

Reactions of Triflate 2a. A. With Aqueous Base. To triflate **2a** dissolved in diglyme in an NMR tube was added aqueous KOH. When the tube was shaken, it immediately became warm and gave a ^{19}F NMR spectrum showing that the peaks for **2a** had been replaced by singlets at ϕ 74.4 (area 2.1) and 78.0 (area 1.0) due to KOR_F and KOTf, respectively.

B. With Methanol. Triflate **2a** was dissolved in CH_3OH and heated to 60 °C for 55 min. Analysis of the mixture by ^{19}F NMR showed that 25% of the triflate was left but the rest had reacted to give 75% conversion to TfOH (singlet at ϕ 78.4), a 27% conversion (36% yield) to hexafluorocumyl methyl ether (**5**) (broad singlet at 70.5, lit. 71.3[1] or 70.5[8]), a 47.5% conversion (64% yield) to ether (**6b**) (doublet at 65.4, J_{HF} = 9 Hz), and a trace of R_FOH (singlet at 74.7).

C. With H_2O. A two-phase mixture of 30 μL of triflate **2a** and 15 μL of H_2O was heated in an NMR tube for 16 h at 73 °C. Tetrahydrofuran was added and a ^{19}F NMR spectrum of the resulting solution showed TfOH (singlet, ϕ 78.4) and a 1:1 mixture of R_FOH (singlet, ϕ 74.8) and phenol **6a** (doublet, 63.2, J = 8 Hz).

1,1-Bis[1-(*p-tert*-butylphenyl)-1-trifluoromethyl-2,2,2-trifluoroethanolato]-5-methyl-3,3-bis(trifluoromethyl)-3*H*-2,1-benzoxathiole (1b). To a stirred solution of 2.40 g (8.0 mmol) of *p-tert*-butylhexafluorocumyl alcohol (*p-t*-BuR_FOH, **4b**)[3] in 50 mL of dry ether was added 0.55 g (14 mmol) of KH in small portions over a 15-min period. After an additional 15 min of stirring, the mixture was filtered. Solvent was evaporated from the filtrate under vacuum leaving *p-t*-BuR_FOK as a white, flaky powder. To this salt, sultene **9**[1] (1.13 g, 3.92 mmol), and 40 mL of dry CCl_4 was added 0.21 mL (4.1 mmol) of Br_2 with stirring over a 5-min period. After 1 h of stirring the mixture was filtered under dry N_2. Solvent was removed from the filtrate under vacuum (0.05 Torr) yielding sulfurane **1b** which was recrystallized from ether–pentane to give 1.94 g (56%) of white crystals: mp 143–148.5 °C; ^{1}H NMR (CCl_4) δ 1.33 (s, 18.3, $(CH_3)_3C$), 2.62 (s, 2.7, $ArCH_3$), 7.32 (broad s, 7.7, aromatic protons on the alkoxy group), 7.67 (broad s, 3.3, aromatic protons on the trisubstituted ring); ^{19}F NMR (CCl_4) ϕ 72.0 and 73.0 (2 broad quartets, J = 9 Hz, 6 F each, *p-t*-BuR_FO), 72.4 (broad s, 6 F, ring CF_3).

Reaction of Sulfurane 1b with TfOH. To a solution of sulfurane **1b** in CCl_4 in an NMR tube was added a little less than 1 equiv of TfOH. By the time the TfOH region could be scanned (ca. 30 s after the addition), no TfOH peak could be seen in the ^{19}F NMR spectrum. The sulfurane peaks at ϕ 72.0, 72.4, and 73.0 had decreased and new peaks at 71.6 and 75.2 (triflate **2b**) had appeared along with a singlet at 76.2 (alcohol **4b**) and quartets at 76.1 and 75.5 (sultine **3**). The addition of another drop of TfOH caused the sulfurane peaks to disappear before another ^{19}F NMR spectrum could be taken. Now a TfOH peak of constant intensity was present at ϕ 78.6. Extraction with cold aqueous KOH removed sultine **3** and most of alcohol **4b** from the reaction mixture (^{19}F NMR). Removal of solvent gave crude triflate **2b** as a colorless liquid which turned dark upon storage at room temperature for several days. It could be stored for at least several weeks at −20 °C without noticeable decomposition. The material was identical with authentic **2b** prepared by the reaction of *p-t*-BuR_FOK[3] with triflic anhydride[7] in CCl_4 (^{19}F NMR, ^{1}H NMR).

1-(*p-tert*-Butylphenyl)-1-trifluoromethyl-2,2,2-trifluoroethanol-^{18}O (4b-^{18}O). A two-phase mixture of triflate **2b** (1.721 g, 3.66 mmol if assumed to be 92% pure) was heated with 0.16 g (8.0 mmol) of H_2O (1.58% ^{16}O, 1.92% ^{17}O, and 96.5% ^{18}O) in an NMR tube with occasional shaking at 74 °C for 15 min. Analysis by ^{19}F NMR showed that triflate **2b** had been replaced by compounds showing singlets at ϕ 75.7 (alcohol **4b**) and 79.2 (TfOH) plus a few minor peaks. The mixture was poured into CH_2Cl_2 and extracted with saturated aqueous $NaHCO_3$. Solvent was removed from the organic layer under vacuum giving a dark oil which was sublimed twice (25 °C, 0.1 Torr) to give 0.578 g (52%) of a white solid, mp 37–47.5 °C (lit.[3] unlabeled **4b** 49.5–51.5 °C): mass spectrum (10 eV) *m/e* (average rel intensity of three scans) 305 (0.05), 304 (1.05), 303 (14.5), 302 (100), 301 (3.79), 300 (16.1, $M^{+}\cdot$ for unlabeled **4b**), 289 (0.16), 288 (3.13), 287 (22.8), 286 (0.81), 285 (3.68, M − CH_3 of unlabeled **4b**), 284 (4.37), 41 (2.7, C_3H_5); calculated[9] isotope ratio for molecular ion assuming natural abundance carbon and hydrogen isotopes and 85.2% ^{18}O, 1.0% ^{17}O, and 13.8% ^{16}O, 302 (100), 301 (3.77), 300 (16.2).

1,1-Bis[2-(*p-tert*-butylphenyl)-1-trifluoromethyl-2,2,2-trifluoroethanolato-^{18}O]-5-methyl-3,3-bis(trifluoromethyl)-3*H*-2,1-benzoxathiole (1b-^{18}O). To a solution of 0.578 g (1.91 mmol) of labeled alcohol **4b** in 10 mL of dry ether was added 0.13 g (3.2 mmol) of KH in small portions with stirring. After an additional 30 min of stirring, the mixture was filtered. Solvent was evaporated from the filtrate under a stream of dry N_2. To the remaining salt were added 10 mL of CCl_4 and 0.30 g (1.0 mmol) of sultene **9**.[1] Bromine was added to the clear yellow solution over a 5-min period until the red color remained (47 μL, 0.92 mmol). After stirring for 30 min, the mixture was filtered and solvent was removed from the filtrate under vacuum (0.1 Torr). Recrystallization from ether–pentane gave 0.47 g (53%) of white crystals, mp 140–147.5 °C.

Reaction of Labeled Sulfurane 1b with TfOH. To a solution of 75 mg (0.085 mmol) of **1b**-^{18}O in CCl_4 was added 7.3 μL (0.083 mmol) of TfOH. Extraction with aqueous KOH followed by evaporation of the solvent under a nitrogen stream yielded 18.4 mg (51%) of a colorless, thick liquid, triflate **2b**: ^{19}F NMR (CCl_4) ϕ 71.4 (m), 75.0 (septet); mass spectrum (10 eV) *m/e* (average rel intensity of five scans) 435 (0.28), 434 (2.07), 433 (5.15), 432 (30.1, $M^{+}\cdot$ for unlabeled **2b**), 420 (0.66), 419 (6.01), 418 (14.8), 417 (100, M − CH_3 for unlabeled **2b**), 283 (4.3, M − CF_3SO_3); calculated[9] isotope ratio for molecular ion assuming natural abundance carbon, oxygen, sulfur, and hydrogen isotopes, 434 (1.87), 433 (4.88), 432 (30.1); calculated[9] isotope ratio for molecular ion assuming natural abundance carbon, hydrogen, and sulfur isotopes and 0.37% ^{18}O, 0.33% ^{17}O, and 99.3% ^{16}O, 434 (2.07), 433 (5.15), 432 (30.1).

Potassium Perfluoro-*tert*-butyl Alkoxide. To perfluoro-*tert*-butyl alcohol (PCR, Inc., 3.42 g, 14.5 mmol) stirred in 30 mL of dry ether was added 1.15 g (28.7 mmol) of KH over a 10-min period. After 30 min of additional stirring, filtration of the mixture and evaporation of the solvent yielded 3.96 g (99.7%) of the alkoxide as a white powder.

1,1-Bis[1,1-bis(trifluoromethyl)-2,2,2-trifluoroethanolato]-5-methyl-3,3-bis(trifluoromethyl)-3*H*-2,1-benzoxathiole (1c). To potassium perfluoro-*tert*-butoxide (3.96 g, 14.4 mmol), CCl_4 (100 mL), ether (5 mL), and sultene **9** (2.12 g, 7.36 mmol) was added 0.383 mL (7.48 mmol) of bromine over a 20-min period. After 1 h of stirring, the orange mixture was filtered and solvent was removed from the filtrate at 0.2 Torr. Recrystallization from ether–pentane yielded 4.01 g (72%) of sulfurane **1c** as white crystals: mp 106–107.5 °C; ^{1}H NMR, (CCl_4) δ 2.63 (s, 3.0, $ArCH_3$), 7.63 (s, 3.0, aromatic protons); ^{19}F NMR (CCl_4) ϕ 72.8 (large sharp singlet, $-C(CF_3)_3$ groups), 72.9 (smaller overlapping broad singlet, ring CF_3 groups); mass spectrum (70 eV) *m/e* (rel intensity) 739 (0.4, M − F), 738 (1.6, M − HF), 523 (100, M − $OC(CF_3)_3$), 288 (50, M − $2OC(CF_3)_3$), 219 (87.5), 166 (6.3), 150 (13.8), 69 (14.1, CF_3).

Reactions of Sulfurane 1c. A. *tert*-Amyl Alcohol. To a solution of sulfurane **1c** in CCl_4 in an NMR tube was added *tert*-amyl alcohol. An immediate reaction occurred yielding 2-methyl-1-butene and 2-methyl-2-butene in a 65:35 ratio by NMR integration. The expected ^{1}H and ^{19}F NMR peaks for sultine **3** were also seen along with a ^{19}F NMR singlet at ϕ 74.8 due to perfluoro-*tert*-butyl alcohol.

B. Trifluoromethanesulfonic Acid (TFOH). To a soluton of 0.90 g (1.2 mmol) of sulfurane **1c** in 10 mL of dry ether was added 98 μL (1.24 mmol) of TfOH. The fine white precipitate that immediately formed was filtered and dried under nitrogen to give 0.73 g (91%) of sulfonium triflate **10c**, mp 132–133 °C (with rapid decomposition to a dark red liquid): ^{19}F NMR ($CDCl_3$) ϕ 70.3 (q, J_{FF} = 2 Hz, 9.3, $OC(CF_3)_3$), 72.5 (q, 3.0, J_{FF} = 9 Hz, ring CF_3 trans to $OC(CF_3)_3$), 73.4 (broad m, 3.0, ring CF_3 cis to $OC(CF_3)_3$), 79.5 (s, 2.6, O_3SCF_3); ^{1}H NMR ($CDCl_3$) δ 2.69 (s, 3, CH_3), 7.77 (broad s, 1, proton ortho to fluoroalkyl group), 7.95 (d, 1, J = 8.5 Hz, proton para to fluoroalkyl group), 8.57 (d, 1, J = 8.5 Hz, proton ortho to sulfur).

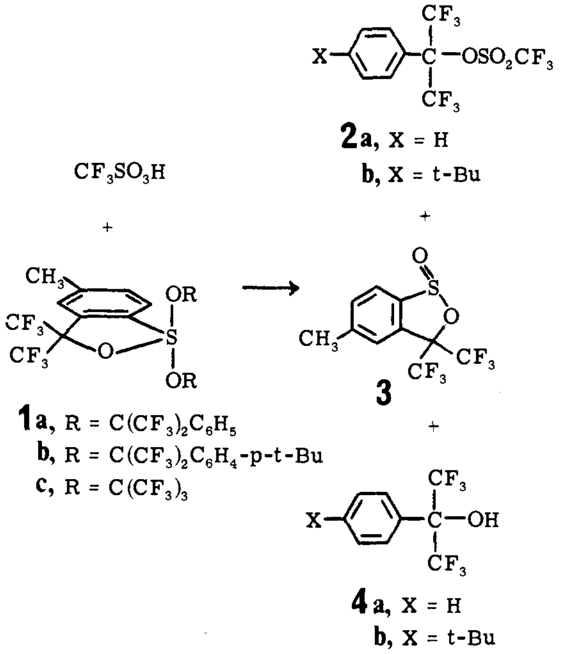
Decomposition of Sulfonium Triflate 10c. Upon storage at room temperature for several weeks, **10c** changed from a white powder to a bright orange powder to a dark red mass. In $CDCl_3$ at 70 °C, complete decomposition of **10c** to a red precipitate took 6 h, followed by ^{19}F NMR spectroscopy. The soluble products gave a large singlet at ϕ 74.7 [$(CF_3)_3COH$], a smaller singlet at 75.6, and a singlet at 78.4 (TfOH). No trace of perfluoro-*tert*-butyl triflate was seen.

Reaction of Sulfonium Triflate 10c with Hexafluorocumyl Alcohol. To a solution of sulfurane **1c** in ether was added a slight excess of triflic acid forming a suspension of sulfonium triflate **10c** in ether to which was added 2 equiv of hexafluorocumyl alcohol.[10] As the mixture reacted over a 4-day period at 25 °C, the precipitate (**10c**) gradually dissolved and the ^{19}F NMR signal for the hexafluorocumyl alcohol at ϕ 75.2 diminished in intensity while peaks for sultine **3** and hexafluorocumyl triflate (**2a**) appeared and the peak for perfluoro-*tert*-butyl alcohol grew in intensity.

Perfluoro-*tert*-butyl Triflate. A solution containing perfluoro-*tert*-butyl triflate was obtained by treating an ether solution of perfluoro-*tert*-butyl alcohol with excess KH, filtering, evaporating, and adding CCl_4 and trifluoromethanesulfonic anhydride.[7] Extraction with aqueous KOH left a solution containing perfluoro-*tert*-butyl triflate identified by its ^{19}F NMR peaks at ϕ 70.3 (q, J = 1.3 Hz, 9 F) and 73.7 (10 peaks, J = 1.3 Hz, 3 F) and a singlet at 75.8 (18% of total signal) due to an unknown by-product.

Results

Formation of Triflate Esters. Since the treatment of solutions of certain acyclic[2] and cyclic[3] dialkoxysulfuranes with triflic acid has been reported to give rapid precipitation of alkoxysulfonium triflates, the analogous reaction was tried with trialkoxysulfurane **1a**.[1] Instead of rapid precipitation of a dialkoxysulfonium triflate, the slow formation of products more soluble than **1a** was seen by ^1H and ^{19}F NMR. Two of these were identified as hexafluorocumyl alcohol[10] (**4a**) and sultine **3**.[1] The third product, isolated in 59% yield, was identified as hexafluorocumyl triflate (**2a**) on the basis of its ^1H and ^{19}F NMR spectra, mass spectrum, elemental analysis, and comparison with an authentic sample of **2a**, prepared by treatment of the potassium salt of alcohol **4a** with triflic anhydride. During the 5-10 min it took sulfurane **1a** to react with triflic acid, no intermediates were detected by ^{19}F NMR spectroscopy.



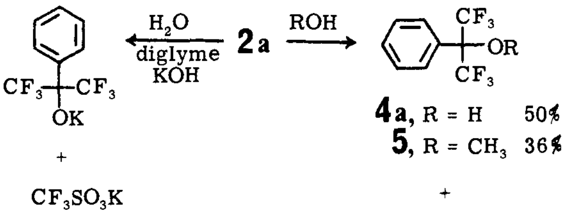
2a, X = H
b, X = t-Bu

1a, $R = C(CF_3)_2C_6H_5$
b, $R = C(CF_3)_2C_6H_4\text{-p-t-Bu}$
c, $R = C(CF_3)_3$

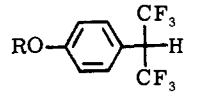
3

4a, X = H
b, X = t-Bu

To probe the mechanism of this reaction, it was desired to prepare sulfurane **1a** with its apical alkoxy groups labeled with oxygen-18. This could easily be done[1] if alcohol **4a**-^{18}O could be prepared. The hydrolysis of triflate **2a** was investigated to see if this would be a practical route to the labeled alcohol. In the presence of diglyme as a cosolvent, aqueous KOH rapidly reacts with **2a** at room temperature to give the potassium salts of **4a** and triflic acid as the only products detectable by ^{19}F NMR spectroscopy. In contrast when **2a** is heated in the absence of base with methanol or water, a third type of product in addition to **4a** or **5** is also formed in a much slower reaction. These products are thought to be ether **6b** and phenol **6a** on the basis of their ^{19}F NMR spectra which show hexafluoroisopropyl doublets at ϕ 65.4 (J = 9 Hz) and 63.2 (J = 8 Hz), respectively, close to the values (ϕ 65.8, J = 9 Hz) reported[3] for phenol ether **7**. These different products are explained if the reaction goes by nucleophilic attack of hydroxide ion at sulfur in the presence of base and cosolvent and by a S_N1 mechanism in their absence. Carbonium ion **8a** could be attacked by water or methanol at the benzilic or para carbon to give the observed products. Although this evidence for a possible S_N1 mechanism indicates that labeled alcohol **4a** could be made from water-^{18}O by this method, because of the possible problems involved in separating **4a** from phenol **6a**, it was decided to study the analogous reactions of alcohol **4b**, with a *tert*-butyl group blocking the para position of the aromatic ring.



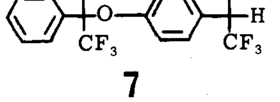
4a, R = H 50%
5, R = CH_3 36%



6a, R = H 50%
b, R = CH_3 64%

+

CF_3SO_3H



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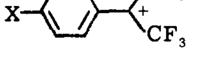
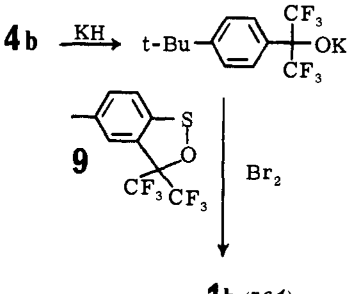


8a, X = H
b, X = t-Bu

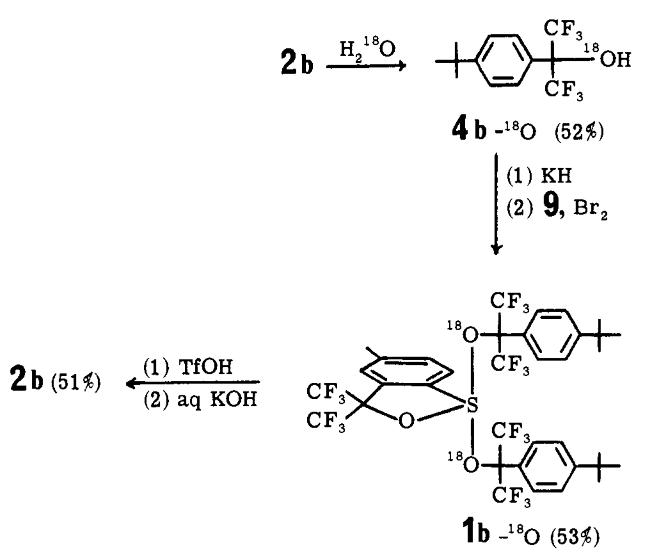
Sulfurane **1b**, prepared in the usual way,[1] showed strong similarities in its ^1H and ^{19}F NMR spectra to those of **1a**, including the absence of a low-field doublet for the proton ortho to sulfur and similar fluorine chemical shifts, suggesting that these two sulfuranes have the same diequatorially bridged structure.[1]



1b (56%)

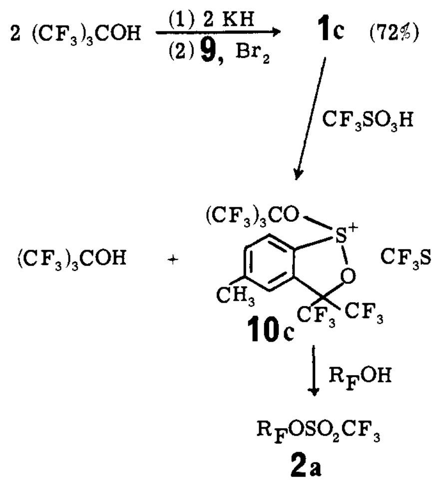
As expected for a reaction generating the *p-tert*-butyl-substituted benzylic cation (**8b**), **1b** reacts with triflic acid to give sultine **3**, alcohol **4b**, and triflate **2b** at a much faster rate (by a factor of more than 10) than the analogous reaction of **1a**. Crude triflate **2b**, which was isolated as a colorless oil by extraction of the reaction mixture with aqueous base, was identified by its ^{19}F NMR and mass spectra, which are very similar to those of **2a**. However, **2b** is less thermally stable than **2a** and must be stored below 0 °C.

Oxygen-18 Labeling Studies. Triflate **2b** containing about 4 mol % of alcohol **4b** as an impurity was heated with excess water-^{18}O (96.5 atom % ^{18}O) to give alcohol **4b** containing 85.2



atom % ^{18}O by mass spectrometric analysis. This was converted, by the pictured route, to **1b**-^{18}O. When this labeled sulfurane was treated with triflic acid, the resulting triflate **2b** was shown by mass spectrometry to contain no more than 0.4% of the ^{18}O label, an amount indistinguishable from natural abundance levels within the estimated experimental error.

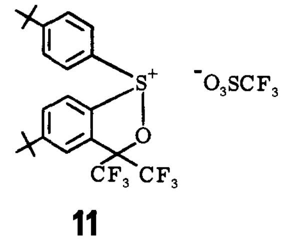
Isolation of a Dialkoxysulfonium Triflate. Sulfurane **1c**, prepared as shown, gave a relatively simple NMR spectrum



with proton singlets at δ 2.63 and 7.63 for the methyl and the aromatic protons, respectively, and with large and small overlapping fluorine singlets at ϕ 72.8 and 72.9 for the perfluoro-*tert*-butyl and ring trifluoromethyl groups, respectively. The lack of a downfield ^1H NMR doublet for the aromatic proton ortho to sulfur and the low chemical shift for the ring trifluoromethyl groups indicate that sulfurane **1c**, like **1a** and **1b**, has a structure containing a diequatorially linked ring.[1]

Sulfurane **1c** is also similar to **1a**[1] and **1b** in many of its chemical properties including rapid hydrolysis to sultine **3** and perfluoro-*tert*-butyl alcohol by wet air or solvents and rapid dehydration of tertiary alcohols such as *tert*-amyl alcohol to olefins, but with triflic acid it reacts differently. The addition of triflic acid to an ether solution of **1c** results in the immediate formation of a precipitate, sulfonium salt **10c**, isolated in 91% yield as a white powder, mp 132–133 °C. This material decomposes rapidly to a dark red liquid upon melting by a process that appears to be autocatalytic, with the first appearing red spots quickly spreading over the whole sample. In $CDCl_3$ at 70 °C decomposition to a red precipitate takes 6 h yielding large amounts of $(CF_3)_3COH$ and some triflic acid by ^{19}F NMR. No sultine **3** or perfluoro-*tert*-butyl triflate, expected by analogy to the reaction of sulfuranes **1a** and **1b** with triflic acid, could be detected in this product mixture by ^{19}F NMR. Triflate ester **2a**, however, was formed over a 4-day period when excess alcohol **4a** was added to the ether suspension of **10c**.

Sulfonium triflate **10c** was slightly soluble in $CDCl_3$, showing a ^1H NMR doublet at δ 8.57 for the proton ortho to sulfur similar to that seen at δ 8.46 for an analogous alkoxysulfonium triflate (**11**).[3] The ^{19}F NMR spectrum of **10c** showed two resonances for the ring trifluoromethyl groups at ϕ 72.5 and 73.4. The 73.4-ppm multiplet is assigned to the CF_3 group cis to the perfluoroalkoxy group on the basis of coupling (J_{FF} = 2 Hz) between the two groups.

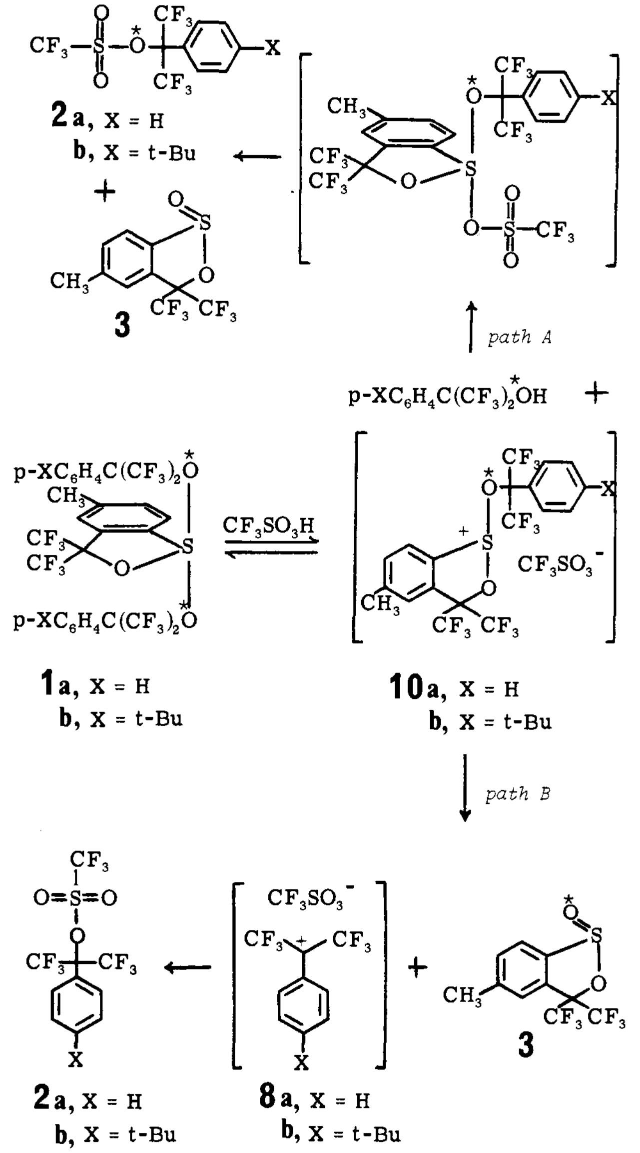


11

Discussion

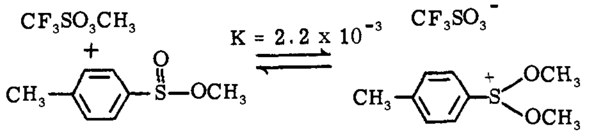
Scheme I shows two possible mechanisms for the reaction of sulfuranes **1a** and **1b** with triflic acid. The first step in both

Scheme I



mechanisms involves reversible ionization to dialkoxysulfonium ion **10** which is not present in large enough concentrations to be detectible by NMR at intermediate stages of the reaction when **1a** is the reactant.

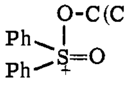
The reactions of triflic acid with sulfurane **1c** and with several diaryldialkoxysulfranes,[2,3] which provide crystalline isolable sulfonium triflates, provide precedents for this step. Reactions between substrates less reactive than triflic acid and a variety of sulfuranes[1,2,6a,8,11] have been postulated to involve a similar ionization as the first step. Dimethoxysulfonium ions have been demonstrated[5] as high energy species present in small equilibrium concentrations when certain methyl sulfinates are treated with high concentrations of methyl triflate. This facile alkylation of triflate ion by dimethoxysulfonium ions to give triflate esters and sulfinates also serves as a precedent for the remaining steps of the reaction.



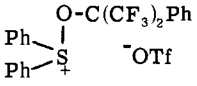
The high reactivity of these aryldialkoxysulfonium ions, compared to that of the diarylalkoxysulfonium[2,3,4] ions, can be rationalized to result from the inductive destabilization provided by the second electronegative alkoxy ligand to sulfur. Clearly sulfinate **3** is an extraordinarily good leaving group in the ionization reactions studied here.

Whether sulfonium triflate **10** reacts further by path a or path b was determined by the use of a sulfurane containing apical alkoxy ligands labeled with oxygen-18 as shown in Scheme **I**. Path a, which predicts that labeled triflate **2b** would be formed from labeled **1b**, cannot be correct since only unlabeled **2b** was produced. On the other hand, path b not only correctly predicts the formation of unlabeled **2b**, but is also consistent with many other data. The faster reaction of **1b** than **1a** can be interpreted as evidence for a transition state resembling carbonium ion **8** in the rate-determining step. The rough estimate that **1b** reacts at least ten times more rapidly than **1a** leads to a calculated ρ for this reaction using $\sigma^+ \leq -4$, near the value seen in similar ionizations such as those of cumyl chloride.[12] This also explains the lack of reaction of **10c** by this pathway since ionization to the perfluoro-*tert*-butyl cation should be an extremely high energy process.

Carbonium ion **8a** has been reported[13] to be too reactive to be produced in NMR detectable concentrations when alcohol **4a** is dissolved in SO_2-SbF_5-FSO_3H. Even with a triflate leaving group, solvolysis to **8a** is slow (in CH_3OH at 60 °C triflate **2a** has a half-life of ca. 30 min). However, **1a** reacts to completion with triflic acid at 40 °C in roughly 5 min in ether or $CDCl_3$ in a reaction involving small concentrations of sulfonium ion **10a**. Sultine **3** is clearly an excellent leaving group, possibly comparable to nitrogen, which is expelled from 2,2,2-trifluoroethyldiazonium ions at −20 °C.[14] Carbonium ion **8a** has also been postulated[3] to be formed from O-alkylated sulfone cation **12**, but it does not form at a rapid rate at room temperature from isolable sulfonium triflate **13**.[2,3] The overall leaving group ability in these reactions appears to be in the order $N_2 \approx$ sultine **3** $\approx Ph_2SO_2 > {}^-O_3SCF_3 \geq Ph_2SO$.



12



13

The fact that sulfonium ion **10c** reacts slowly with added hexafluorocumyl alcohol (**4a**) to give triflate ester **2a** can be explained if **10c** undergoes slow ligand exchange with **4a**, possibly through a sulfurane intermediate, to produce sulfonium ion **10a** which fragments to the observed products, as it does when generated from **1a** and triflic acid.

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