Synthesis of CF_3-Containing Sulfur Heterocycles. The First Stable 2-Thietanol Derivative

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The reaction of α,β-unsaturated CF_3-containing ketones $R^1R^2C{=}CHCOCF_3$ **1**−**4** with ammonium hydrosulfide was investigated. The structure of the enones was shown to influence the reaction path, and the corresponding six-membered sulfur heterocycles bearing trifluoromethyl groups, **5**−**8**, or mercaptan, **9**, were obtained. The reaction of 3-adamantylidene-1,1,1-trifluoropropan-2-one, **3**, results in the corresponding four-membered heterocycle **8**, which has a stable 2-thietanol fragment. The oxidation of sulfides **5**−**8** by hydrogen peroxide yields sulfones **10**−**12** or 1,3-sultine **13** (in the case of **8**). Product stereochemistry and reaction mechanism are discussed.

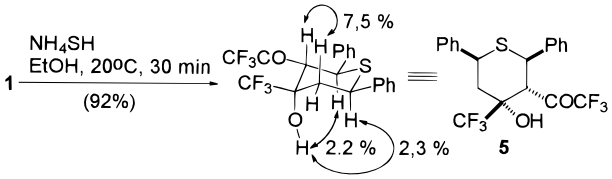
Introduction

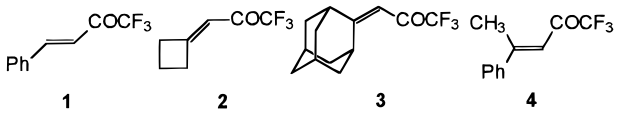
Recently we proposed a novel method for direct electrophilic trifluoroacylation of unsaturated hydrocarbons which is based on the use of trifluoroacetic anhydride in the presence of dimethyl sulfide−boron trifluoride complex.[1−3] This method leads to the preparation of unsaturated ketones containing trifluoroacetyl groups. Direct trifluoroacylation is known only in the cases of electron rich alkenes such as enamines,[4] vinyl thioethers[5] and vinyl ethers,[6] or organometallics.[7,8] Little is known about the reactivity of enones containing a trifluoromethyl group.

We have investigated the reactions of these ketones with different bifunctional nucleophiles including hydrazines, urea derivatives, and 1,2-diamines. The reactions open the possibility of a one-step synthesis of CF_3-containing pyrazolidines, pyrazolines,[9] thiazines,[10] pyrimidines,[11] and benzodiazepines.[12] We have found that α,β-enones bearing trifluoromethyl groups have some specificity in the reaction with nucleophiles. The particular features of these ketones include very high reactivity at both the double bond and the carbonyl group, the formation of stable fragments $CF_3C(OH)N$− or $CF_3C(OH)O$−, and the stereoselectivity of addition of some nucleophiles.[9−12]

The first investigation of the reaction of unsaturated ketones and aldehydes with hydrogen sulfide and sodium sulfide dates back to the very beginning of the 20th century.[13,14] Nevertheless, the stereochemistry of the reaction products was not investigated in detail. Recently the reaction of α,β-enones with hydrogen sulfide was used by Corey for a two-step reduction of unsaturated ketones.[15] In this paper we report on the results of the reaction of ammonium hydrosulfide with unsaturated ketones bearing trifluoromethyl groups **1**−**4**

Scheme 1





Results and Discussion

We have found that the reaction of enones **1**−**4** with NH_4SH takes place under very mild conditions. The reaction of ketone **1** proceeds stereospecifically, giving only one diastereomer out of eight possible. The configuration of tetrahydrothiopyran **5** was established by 2D $^1H{-}^1H$ NOESY experiments (Scheme 1). This compound has equatorially arranged Ph, Ph, CF_3, and $COCF_3$ groups and an axial OH group.

Formally the course of this reaction is the Michael addition of hydrosulfide anion to the double bonds of two molecules of **1** with subsequent aldol condensation (Scheme 2). We believe that the transition state for cyclization of the precursor to **5** has a chair conformation with all bulky groups (Ph, Ph, $COCF_3$, and CF_3) equatorial. Thus, effective 1,3-induction of the chiral center formed after the first addition of the nucleophile to the

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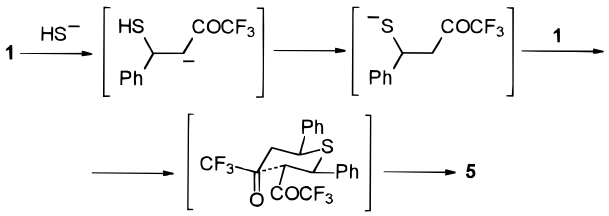
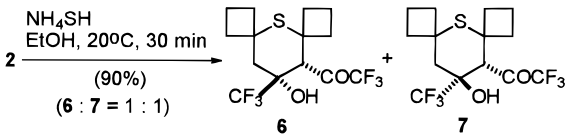
Scheme 2



Scheme 3

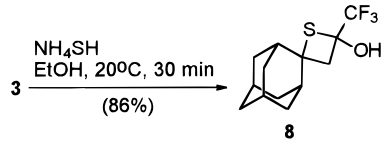


double bond in enone **1** takes place (examples of similar induction are known[16,17]). Earlier, we found that the reaction of ketone **1** with urea derivatives also proceeds stereoselectively, resulting in diastereomers with *trans* phenyl and hydroxyl groups.[11]

Reaction of NH_4SH with ketone **2** leads to a 1/1 mixture of *cis*- and *trans*-diastereomers **6** and **7**, respectively (Scheme 3). Compounds **6** and **7** have significant differences in melting points (45 and 136 °C, respectively), solubility, and chromatographic characteristics (compound **6** is more soluble and has higher chromatographic mobility). IR spectral analysis and molecular models show the presence of an intramolecular H-bond in *cis*-tetrahydrothiopyran **6**. The *trans*-diastereomer **7** has a larger distance between the OH proton and the carbonyl group. We believe that in sulfide **7** intermolecular H-bonding takes place. Compound **6** has a 2.80 Hz coupling constant between the equatorial methine proton H-3 and the equatorial proton H-5 due to the periplanar "W" conformation of this fragment, which is probably stabilized by the intramolecular H-bond. No coupling constant to the proton H-3 was observed for **7**.

Formation of two diastereomers in the case of ketone **2**, as compared to one diastereomer with **1**, is likely due to steric differences in the substituents in **1** (H and Ph) compared with **2** (cyclobutane ring).

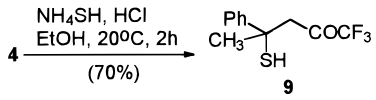
A very unusual result was obtained in the reaction of ammonium hydrosulfide with ketone **3**. The only product was the corresponding four-membered trifluoromethyl-containing heterocycle (eq 1). The formation of thietanes occurs through $2\pi + 2\pi$ photoreaction or thermal reaction of thiones with alkenes. Thietanes having a spiro adamantane fragment were obtained by this method.[18] 2-Thietanols have not been described previously, apparently because the semithioacetal fragment is unstable in the four-membered cycles. Although a patent reports the synthesis of some 2-thietanol derivatives,[19] subsequent investigation did not confirm these results.[20] 2-Alkoxy- and 2-acyloxy-substituted thietanes were obtained by cycloaddition of bis(trifluoromethyl)thioketene with vinyl ethers or esters, respectively,[21] while 2-acetoxy derivatives were synthesized by acetoxylation of some thietanes with lead tetraacetate.[22] Attempts to obtain substituted 2-thietanols by deacetylation of the initially formed acetates led only to their polymerization.[23] We assume that compound **8** is stable due to both the trifluoromethyl group stabilizing the geminal HO-C-S fragments[24] and the adamantane structure, which stabilizes spiro-attached small rings.[25] Formation of the corresponding tetrahydrothiopyrans as in the cases of ketones **1** and **2** does not take place for ketone **3**, apparently due to steric reasons.



(1)

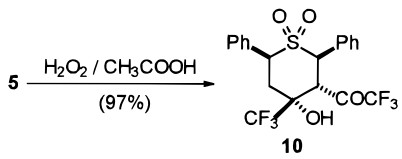
An attempt to make the analogous thietanols from ketones **1** and **2** at low temperature with a 20-fold excess of ammonium hydrosulfide was unsuccessful, and only the corresponding tetrahydrothiopyrans **5**, **6**, and **7** were isolated.

The reaction of ketone **4** with ammonium hydrosulfide under the same conditions results in oligomerization, but in the presence of HCl the corresponding mercaptan **9** is obtained (eq 2).[26] It seems likely that under the usual basic conditions, condensation of mercaptan **9** takes place. In spite of the similar structures of ketones **1** and **4**, enone **4** is much less reactive. We think that the formation of the corresponding tetrahydrothiopyran does not take place due to 1,3 diaxial repulsions of the methyl groups. Apparently one of the reasons for cyclization in the case of ketone **3** is stabilization of thietanol **7** by adamantane. In the case of ketone **4**, this type of reaction does not occur.



(2)

We have also investigated the oxidation of sulfides **5**, **6**, **7**, and **8** by hydrogen peroxide in acetic acid. Oxidation of sulfide **5** gave the corresponding sulfone **10** having the same configuration as the precursor sulfide **5** (eq 3).



(3)

We found that oxidation of sulfide **6** results in the corresponding sulfone **11** with *cis*-arranged OH and CF_3-CO groups like in the original sulfide (Scheme 4). Oxidation of sulfide **7** initially leads to a mixture of the sulfones **11** and **12** in the ratio 5.5/1. Reflux of this mixture of diastereomers **11** and **12** in 70% acetic acid results in isomerization to sulfone **11**. Sulfone **11** is the thermodynamically controlled product, and sulfone **12** isomerizes into **11** under acidic conditions (CH_3COOH).

Oxidation of sulfide **8** which has a 2-thietanol fragment proceeds unusually. The corresponding sultine **13** as a mixture of diastereomers (2.7/1) is formed[27] (eq 4). The

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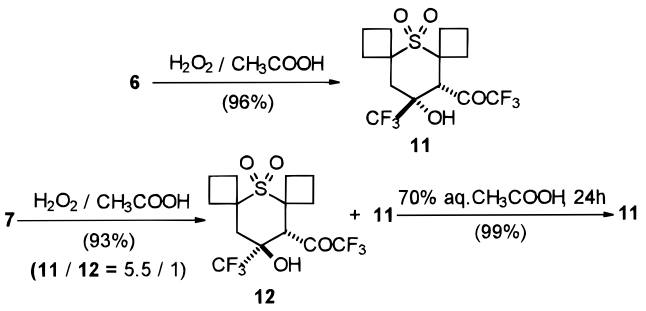
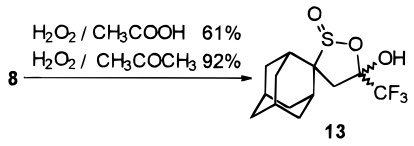
(26) **CAUTION!** Mercaptan **9** has a strong stench and is very likely poisonous.
(27) The yield of the sultine was higher when acetic acid was changed to acetone as the solvent.

Scheme 4

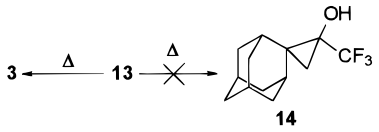


formation of 1,3-sultines was found to proceed by thermal-[28] or base-initiated[29] cleavage of 1,1-thietane dioxides. We believe that the labile semi-thioacetal fragment in sultine **13** facilitates the cleavage of the thietane ring. The structure of the *trans*-diastereomer of **13** (**13a**) was confirmed by X-ray crystallography.



(4)

We have also attempted thermal extrusion of sulfur dioxide from sultine **13** to make the corresponding cyclopropane **14**, but only the starting ketone **3** was obtained (eq 5).



(5)

Conclusion

Thus reaction of trifluoromethyl-bearing enones with ammonium hydrosulfide gives rise to tetrahydrothiopyrans, mercaptan, or 2-thietanol derivatives depending upon the structure of original ketones. In spite of the possibility of conjugated double bond formation by water elimination in the products, in all cases the compounds with a stable CF_3−C−OH fragment were obtained. Reaction of ketone **1** proceeds diastereoselectively. Oxidation of sulfides by hydrogen peroxide results in the corresponding sulfones. In the case of thietanol **8**, the 1,3-sultine **13** was formed.

Experimental Section

Melting points were determined in sealed capillarie, and are uncorrected. Hydrogen peroxide (30% aqueous solution) was used without purification. α,β-Unsaturated ketones **1**−**4** were prepared as described previously.[3] Ammonium hydrosulfide was prepared by the literature method[30] and was used as a 25% aqueous solution.

***rel*-(2*S*,3*R*,4*S*,6*R*)-3,4,5,6-Tetrahydro-2,6-diphenyl-3-(trifluoroacetyl)-4-(trifluoromethyl)-2*H*-thiopyran-4-ol (5).** NH_4SH (1.5 mL of a 25% aqueous solution, 7.4 mmol) was added to a solution of 2.0 g (10 mmol) of ketone **1** in EtOH (20 mL). After 30 min, water (30 mL) was added, the resulting suspension was filtered, and the precipitate was washed with water (2 × 20 mL). The crude product was recrystallized from 80% aqueous EtOH: yield 2.0 g (92%), mp 106 °C; IR (Nujol) 3490, 1740 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.25 (t, 1H, *J* = 13.0 Hz), 2.55 (dd, 1H, *J* = 13.9, 2.5 Hz), 3.83 (s, 1H), 3.96 (d, 1H, *J* = 11.0 Hz), 4.57 (dd, 1H, *J* = 2.4, 12.2 Hz), 4.59 (d, 1H, *J* = 11.0 Hz), 7.25−7.42 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 37.5, 41.9, 48.4, 51.8, 113.8 (q, *J* = 291.7 Hz), 125.0 (q, *J* = 286.5 Hz), 127.9, 128.2, 128.5, 128.9, 129.1, 129.3, 135.2, 138.9, 196.9 (q, *J* = 37.8 Hz). Anal. Calcd for $C_{20}H_{16}F_6O_2S$: C, 55.30; H, 3.71. Found: C, 55.47; H, 3.74.

Reaction of NH_4SH with Ketone 2. NH_4SH (1.5 mL of a 25% aqueous solution, 7.4 mmol) was added to a solution of 1.6 g (10 mmol) of ketone **2** in EtOH (20 mL). After 30 min, water (30 mL) was added, and the precipitate—a mixture of isomers **6** and **7**—was filtered and dried in *vacuo*. Cold (0 °C) hexane (20 mL) was added to the precipitate, and the mixture was filtered. The solution contained the more soluble *cis*-isomer **6** with traces of *trans*-isomer **7**, and the precipitate was almost pure **7**. The *cis*- and *trans*-isomers were purified by recrystallization from 80% aqueous EtOH and hexane, respectively. The yield of the mixture of isomers without separation was 1.6 g (90%).

***cis*-2,2;6,6-Bis(trimethylene)-3,4,5,6-tetrahydro-3-(trifluoroacetyl)-4-(trifluoromethyl)-2*H*-thiopyran-4-ol (6):** yield 0.56 g (31%), mp 45 °C; IR (Nujol) 3340, 1750 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.72−1.90 (m, 3H), 2.00−2.20 (m, 5H), 2.32−2.40 (m, 2H), 2.50−2.58 (m, 1H), 2.64−2.78 (m, 3H), 3.46 (d, 1H, *J* = 2.8 Hz), 3.68 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 17.2, 18.5, 31.3, 33.5, 36.0, 36.7, 40.8, 44.3, 49.7, 51.3, 78.8 (q, *J* = 26.3 Hz), 114.4 (q, *J* = 290.0 Hz), 124.6 (q, *J* = 286.0 Hz), 195.8 (q, *J* = 36.0 Hz). Anal. Calcd for $C_{14}H_{16}F_6O_2S$: C, 46.41; H, 4.45. Found: C, 46.75; H, 4.68.

***trans*-2,2;6,6-Bis(trimethylene)-3,4,5,6-tetrahydro-3-(trifluoroacetyl)-4-(trifluoromethyl)-2*H*-thiopyran-4-ol (7):** yield 0.65 g (36%), mp 136 °C; IR (Nujol) 3480, 1750 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.64−1.75 (m, 1H), 1.90−2.04 (m, 3H), 2.12−2.29 (m, 4H), 2.34−2.48 (m, 4H), 2.51−2.60 (m, 3H), 3.81 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 17.3, 18.7, 33.3, 36.3, 37.2, 38.6, 40.7, 44.6, 50.0, 51.3, 78.3 (q, *J* = 26.5 Hz), 124.5 (q, *J* = 284.0 Hz), 186.7 (q, *J* = 38.8 Hz). Anal. Calcd for $C_{14}H_{16}F_6O_2S$: C, 46.41; H, 4.45. Found: C, 46.42; H, 4.48.

4′-(Trifluoromethyl)spiro[adamantane-2,2′-thietan]-4′-ol (8). NH_4SH (2 mL of a 25% aqueous solution, 10 mmol) was added to a solution of 1.2 g (5 mmol) of ketone **3** in EtOH (15 mL). After 30 min, water (20 mL) was added, and the product was extracted into hexane. The solution was dried with $CaCl_2$, the solvent was removed *in vacuo*, and the product was crystallized over 5 h at 0 °C. The product was suspended in cold (−30 °C) hexane (15 mL) and filtered: yield 1.2 g (86%), mp 60 °C; IR (Nujol) 3300, 1460 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.60−2.30 (m, 14H), 2.76 (dq, 1H, *J* = 14.2, 1.2 Hz), 2.98 (q, 1H, *J* = 1.5 Hz), 3.12 (d, 1H, *J* = 14.2 Hz); ^{13}C NMR ($CDCl_3$) δ 25.9, 26.4, 32.5, 32.8, 33.1, 33.8, 36.5, 39.6, 41.8, 46.7, 52.3, 73.9 (q, *J* = 34.8 Hz), 124.0 (q, *J* = 280.3 Hz). Anal. Calcd for $C_{13}H_{17}F_3OS$: C, 56.10; H, 6.16. Found: C, 56.39; H, 6.17.

1-Methyl-3-oxo-1-phenyl-4,4,4-trifluorobutane-1-thiol (9). NH_4SH (2 mL of a 25% aqueous solution, 10 mmol) was added to a mixture of 1.2 g (5 mmol) of ketone **4** and aqueous HCl (35%, 3 mL) in EtOH (15 mL). After 2 h, water (20 mL) was added, and the product was extracted into $CHCl_3$ (3515 mL). The solution was dried with $CaCl_2$, the solvent was removed *in vacuo*, and the residue was purified by column chromatography on silica gel using hexane as an eluent. The product was a viscous oil, yield 0.90 g (70%): ^1H NMR ($CDCl_3$) δ 1.93 (s, 3H), 2.75 (s, 1H), 3.58 (s, 2H), 7.20−7.60 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 31.2, 45.9, 50.9, 115.0 (q, *J* = 292.3 Hz), 125.3, 126.7, 128.5, 144.8, 188.2 (q, *J* = 35.2 Hz); MS (80 eV) *m*/*z* (relative intensity) 258 (M^+, 36), 214 (32), 145 (36), 117 (32), 116 (19), 115 (100), 105 (19), 91 (19), 77 (23).

General Procedure for Oxidation of Sulfides to Sulfones. A mixture of 2.5 mmol of corresponding sulfide, 5 mL of 30% aqueous H_2O_2, and 25 mL of CH_3COOH was refluxed for 5 h. Water (20 mL) was added, and the solution was cooled to 0 °C. The crystalline product, sulfones **10**−**12,** was filtered, washed with water (3 × 30 mL), and dried *in vacuo*.

***rel*-(2*S*,3*R*,4*S*,6*R*)-3,4,5,6-Tetrahydro-2,6-diphenyl-3-(trifluoroacetyl)-4-(trifluoromethyl)-2*H*-thiopyran-4-ol 1,1-dioxide (10):** yield 1.1 g (97%), mp 206−207 °C dec; IR (Nujol) 3420, 1765, 1300, 1150 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.72 (dd, 1H,

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Table 1. Summary of Data Collections, Structure Solution, and Refinement Details for 13a

(a) Crystal Data

empirical formula	$C_{13}H_{17}F_3SO_3$	c, Å	19.617(10)
fw	310.33	V, Å^3	2696(3)
color, habit	colorless, block	space group	*Pbca*
crystal cize, mm	0.22 × 0.28 × 0.15	Z	8
crystal system	orthorhombic	F(000)	1152
a, Å	11.896(8)	d_{calc}, g cm^{-3}	1.53
b, Å	11.553(6)	μ, cm^{-1}	0.026

(b) Data Acquisition[a]

radiation (λ,Åè)	graphite-monochromatize Mo Kα (0.71069)	*hkl* range of reflections	0 16, 0 16, 0 27
		total reflections	2995
temp, °C	25	total unique reflections	2752
scan mode	$\omega/2\theta$	obsd reflections with $I > 1\sigma(I)$	913
2θ range	$2 < 2\theta < 60$		

(c) Structure Solution and Refinement[b]

solution method	Patterson (SHELX86)
H-atom treatment	riding model, except OH hydrogen
no. of refined parameters	181
R, R_w, gof	0.0462, 0.0462, 2.52
density range in final Δ-map, e Å^{-3}	min, −0.24; max, 0.25
weighting scheme	$1/\sigma^2(F_o)$

[a] Diffraction measurements were carried out on an Enraf-Nonius CAD4 diffractometer. [b] All calculations were done on an IBM PC 486 computer.

J = 14.8, 2.4 Hz), 3.26 (t, 1H, J = 14.0 Hz), 4.72 (d, 1H, J = 12.1 Hz), 5.01 (dd, 1H, J = 13.1, 2.4 Hz), 5.15 (d, 1H, J = 11.8 Hz), 6.61 (s, 1H), 7.25−7.70 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 36.9, 50.8, 60.7, 64.2, 78.2 (q, J = 28.0 Hz), 114.5 (q, J = 269.5 Hz), 115.0 (q, J = 292.4 Hz), 128.8, 129.5, 129.7, 130.1, 130.3, 130.8, 131.1, 134.4, 188.2 (q, J = 38.2 Hz). Anal. Calcd for $C_{20}H_{16}F_6O_4S$: C, 51.62; H, 3.25. Found: C, 51.34; H, 3.20.

***trans*-2,2;6,6-Bis(trimethylene)-3,4,5,6-tetrahydro-3-(trifluoroacetyl)-4-(trifluoromethyl)-2*H*-thiopyran-4-ol 1,1-dioxide (11);** yield 0.81 g (96%), mp 142−143 °C dec; IR (Nujol) 3380, 1780, 1300, 1150 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.70−2.32 (m, 6H), 2.38 (d, 1H, J = 14.7 Hz), 2.58−2.67 (m, 1H), 2.73 (d, 1H, J = 14.7 Hz), 2.96−3.10 (m, 5H), 3.68 (s, 1H), 4.18 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 16.0, 16.8, 25.3, 26.1, 27.6, 29.5, 37.9, 47.1, 57.1, 60.5, 76.9 (q, J = 27.1 Hz), 114.3 (q, J = 291.0 Hz), 124.0 (q, J = 286.0 Hz), 192.3 (q, J = 37.0 Hz). Anal. Calcd for $C_{14}H_{16}F_3O_4S$: C, 42.75; H, 3,84. Found: C, 42.50; H, 4.07.

2,2;6,6-Bis(trimethylene)-3,4,5,6-tetrahydro-3-(trifluoroacetyl)-4-(trifluoromethyl)-2*H*-thiopyran-4-ol 1,1-dioxide, mixture of *cis*/*trans* **12**/**11** = 1/5.5, yield 0.78 g (93%), mp 140−141 °C dec; IR (Nujol) 3380, 1780, 1300, 1150 cm^{-1}; ^{1}H NMR ($CDCl_3$) signals for major *trans*-isomer are identical those listed above; signals for minor *cis*-isomer δ 1.70−2.35 (m, 6H), 2.53 (dd, 1H, J = 14.9 Hz, J = 2.0 Hz), 2.55−3.50 (m, 1H), 3.62 (s, 1H), 4.31 (d, 1H, J = 2.0 Hz); ^{13}C NMR ($CDCl_3$) signals for major *trans*-isomer are identical those listed above; signals for minor *cis*-isomer δ 16.3, 17.0, 25.6, 28.6, 31.4, 34.6, 36.7, 53.3, 59.4, 60.7, 74.9 (q, J = 29.1 Hz), 121.1 (q, J = 285.4 Hz), 194.9 (q, J = 37.0 Hz). Anal. Calcd for $C_{14}H_{16}F_3O_4S$: C, 42.75; H, 3,84. Found: C, 42.45; H, 4.10.

Isomerization of a Mixture of Isomers 11 and 12 to Sulfone 11. A solution of 1.0 g (2.96 mmol) of a mixture of isomeric sulfones **11** and **12** obtained by oxidation of sulfide **6** in 20 mL of 70% aqueous CH_3COOH was refluxed for 24 h. Water was added, and the mixture was cooled to 0 °C. The crystalline product was filtered, washed with water (3 × 30 mL), and dried *in vacuo*. The product had spectral data and a melting point identical with those of sulfone **11**, yield 0.99 g (99%).

3′-(Trifluoromethyl)spiro[adamantane-2,1′-propane-1′,3′-sultin]-3′-ol (13), 2.7/1 mixture of *cis*- and *trans*-isomers. **Method A.** A mixture of 1.0 g (3.6 mmol) of **8**, 5 mL of 30% aqueous H_2O_2, and 25 mL of CH_3COOH was heated to boiling. After the mixture cooled to rt, water (30 mL) was added, and the product was extracted into $CHCl_3$ (3 × 15 mL). The extract was dried with $CaCl_2$, and the solvent was removed *in vacuo*. Hexane (15 mL) was added into the residue, and the crystalline product was filtered and washed with hexane (2 × 15 mL). The product was dissolved in small amounts of Et_2O (∼3 mL), precipitated by cold (5 °C) hexane, and filtered: yield 0.68 g (61%), mp 150−152 °C dec. **Method B.** A mixture of 1 g (3.2 mmol) of **8**, 8 mL of 30% aqueous hydrogen peroxide, and 30 mL of acetone was refluxed for 24 h. Water (40 mL) was added, and the subsequent treatment was identical to method A: yield 1.0 g (92%), mp 150−151 °C dec; IR (Nujol) 3300, 1130 cm^{-1}; ^{1}H NMR ($CDCl_3$) signals of major isomer δ 1.70−2.45 (m, 14H), 2.50 (d, 1H, J = 14.1 Hz), 2.78 (d, 1H, J = 14.1 Hz), 4.58 (broad s, 1H); signals of minor isomer δ 1.70−2.45 (m, 14H), 3.03 (d, 1H, J = 15.0 Hz), 5.12 (broad s, 1H); ^{13}C NMR ($CDCl_3$) signals of major isomer δ 26.7, 26.8, 32.5, 33.5, 34.9, 35.0, 35.6, 37.4, 37.7, 80.4, 110.1 (q, J = 35.0 Hz), 121.2 (q, J = 283.0 Hz); signals of minor isomer δ 26.4, 30.2, 30.3, 33.3, 33.4, 34.7, 35.5, 37.2, 42.2, 82.2, 112.4 (q, J = 35.0 Hz), 121.0 (q, J = 282.0 Hz). Anal. Calcd for $C_{13}H_{17}F_3SO_3$: C, 50.31; H, 5.52. Found: C, 50.53; H, 5.78.

Structural Analysis of Sultine 13a. Crystal data, data collections, and refinement parameters for **13a** are summarized in Table 1. The data were corrected for Lorentz and polarization effects. The structure was solved by the Patterson method and refined anisotropically by full-matrix least squares for all non-hydrogen atoms. The hydroxyl hydrogen atom was located from difference Fourier synthesis and refined with isotropic thermal parameters. Other hydrogen atoms were included in geometrically idealized position ($d_{C,H}$ = 0.96 Å) with fixed isotropic thermal parameters. The authors have deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, U.K.

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Supporting Information Available: ORTEP drawing of **13a**, details of data acquisition, and ^{1}H and ^{13}C spectra of **5** and **8** (6 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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