About 5–10 μL of a concentrated stock solution of **1**–**3** in acetonitrile was added to ca. 2.5 mL of the aqueous reaction medium by means of a microsyringe. Substrate concentrations were in the range 10^{-4}–10^{-5}M. The hydrolysis of **1** was followed at 255 nm, of **2** at 260 nm, and of **3** at 273 nm. The reactions were followed for at least three half-lives. Good first-order kinetics were observed and k_{obsd} values were reproducible to within 1–2%. Isobaric activation parameters were obtained from rate constants at four different temperatures in the range 25–45 °C. Excellent Eyring plots were found. The estimated error in $\Delta G^{\ddagger}$ is ±0.08 kJ·mol^{-1}, in $\Delta H^{\ddagger}$ ± 1.2 kJ·mol^{-1}, and in $\Delta S^{\ddagger}$ ± 4 J·mol^{-1}·K^{-1}.

Registry No. **1**, 15625-88-4; **2**, 60718-51-6; **3**, 79746-00-2; PMAA, 25087-26-7.

Synthesis and Structure of a New Stable Carbocation Stabilized by Two Neighboring Sulfur Atoms.
Dimethyl-9,9-bis(methylthio)-1-fluorenylcarbenium Ion

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9,9-Bis(methylthio)-1-isopropenylfluorene (**3**) and the corresponding alcohol **2** generate a carbocation **1** in trifluoroacetic acid solution at room temperature. This ion is sufficiently stable to be observed spectroscopically in this solution. A stable crystalline hexachloroantimonate of **1** was isolated. In trifluoroacetic acid-*d* at room temperature, the two C$^+$-methyl groups of **1** undergo H–D isotopic exchange to give the corresponding hexadeuterio cation. On the basis of electronic and ^{1}H NMR spectroscopic data at temperatures from 40 to −60 °C, it is concluded that ion **1** is not a sulfonium species but exists as a carbocation stabilized by electrons from the two neighboring sulfur atoms. Carbon-13 NMR data show that the positive charge is extensively delocalized over the neighboring sulfur atoms, with a small amount remaining on the carbon atom. The possibility is suggested that **1** is a pentacoordinated carbon species that resembles the transition states in S_N2 displacements.

Neighboring sulfur participation has long been known for its dramatic rate enhancement in solvolytic displacements. In order to shed some light on this phenomenon, attempts have been made in recent years to observe benzyl-,[1] trityl-,[2] and 9-anthracenylcarbenium[3a] ions stabilized by two neighboring sulfur atoms situated symmetrically around the cationic center. Another interest was possible observation of a hypervalent carbon species such as those proposed as metastable intermediates or transition states in S_N2 displacements. However, the species observed by NMR were sulfonium ions, not hypervalent carbon ions.

We have reported[4] that dimethyl-1-fluorenylcarbenium ion bearing two methylthio groups at the 9-position (**1**) is a very stable carbocation that can be observed directly in trifluoroacetic acid at room temperature and is possibly a hypervalent carbon species. Recently, Forbus and Martin[3b] reported the observation by ^{1}H NMR of a pentacoordinate carbon species of 9-anthracenylmethyl cation,[3a] but no electronic absorption spectrum was recorded.

In this paper we describe the synthesis and structure of stable carbocation **1** and the isolation of its crystalline hexachloroantimonate.

Preparation of Alcohol 2 and Olefin 3. Fluoranthene was oxidized with chromium trioxide to 9-fluorenone-1-carboxylic acid, which was converted to the methyl ester and then to the dimethyl dithioacetal. Reaction of this compound with methylmagnesium iodide afforded both 9,9-bis(methylthio)-α,α-dimethyl-1-fluorenemethanol (**2**) and 9,9-bis(methylthio)-1-isopropenylfluorene (**3**). Reaction of 9,9-bis(methylthio)-1-fluorenylmagnesium iodide or 9,9-bis(methylthio)-1-fluorenyllithium, which were derived from 9-fluorenone-1-carboxylic acid via the amide, amine, iodide, and thioacetalization, with $^{13}CO_2$ gave 9,9-bis(methylthio)fluorene-1-carboxylic acid enriched with ^{13}C (ca. 60%) at the carbonyl carbon. This compound was further converted into alcohol **2** and olefin **3**, both enriched with ^{13}C at the α-position.

Scheme I

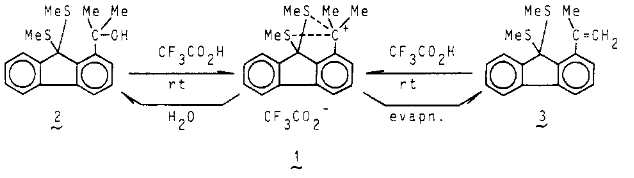

Table I. Electronic Absorption Spectral Data of Carbocation 1

counter-ion	solvent	temp, °C	λ_{max}, nm (ε)		
$CF_3CO_2^-$	CF_3CO_2H	+20	447 (5000)	387 (6500)	328 (5600)
		−20	447 (3600)	387 (4800)	328 (4300)
$SbCl_6^-$	CH_2Cl_2	+15	453 (4100)	394 (5600)	334 (4800)

Table II. ^{1}H NMR Spectral Data (60 MHz) of Carbocation 1 at 35 °C

		chemical shift, δ[a]		
counterion	solvent	$C^+–CH_3$	$C^+–CH_3$	$S–CH_3$
$CF_3CO_2^-$	CF_3CO_2H	2.70 (s)	1.95 (s)	2.31 (s)
$SbCl_6^-$	CD_3NO_2	2.69 (s)	2.02 (s)	2.48 (s)
	CD_2Cl_2	2.66 (s)	1.97 (s)	2.41 (s)

[a] Measured in ppm relative to internal Me_4Si.

Generation of Carbocation 1. Alcohol **2** was dissolved in trifluoroacetic acid (TFA) at room temperature and its

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[1] Hojo, M.; Ichi, T.; Yoshida, Z.; Tamaru, Y. *J. Am. Chem. Soc.* **1969**, *91*, 5170–5171.

[2] Breslow, R.; Kaplan, L.; LaFollete, D. *J. Am. Chem. Soc.* **1968**, *90*, 4056–4064.

[3] (a) Martin, J. C.; Basalay, R. J. *J. Am. Chem. Soc.* **1973**, *95*, 2572–2578. (b) Forbus, T. R., Jr.; Martin, J. C. *J. Am. Chem. Soc.* **1979**, *101*, 5057–5059.

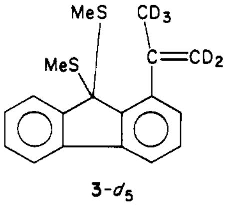
[4] Hojo, M.; Ichi, T.; Nakanishi, T.; Takaba, N. *Tetrahedron Lett.* **1977**, 2159–2162.

0022-3263/85/1950-1478$01.50/0

electronic absorption spectrum was recorded immediately. The spectrum, quite different from that taken in methanol, showed intense bands beyond 300 nm (Table I), implying formation of a carbenium ion.[5] The spectrum at −20 °C was the same. The ^1H NMR spectrum of this solution at 35 °C showed signals at δ 8.08–7.25 (m, 7 H, Ar), 2.70 (s, 3 H), 2.31 (s, 6 H), and 1.95 (s, 3 H) (Table II). This NMR spectrum was also quite different from that taken in CCl_4: δ 1.63 (s, 6 H, two C-methyls), 1.56 (s, 6 H, two S-methyls). The signals at δ 2.70 and 1.95 were assigned to two *C*-methyls of **1**, and the signal at δ 2.31 was ascribed to two equivalent *S*-methyls. The same NMR spectrum was obtained when olefin **3** was dissolved in TFA.

The TFA solution of carbocation **1** precipitated crystals of olefin **3** in almost quantitative yield on standing in air at room temperature. Pouring the solution into ice–water gave alcohol **2** (35%) and olefin **3** (50%).

A solution of alcohol **2** in CF_3CO_2D (TFA-*d*) at room temperature did not show the ^1H NMR signals at δ 2.70 and 1.95. Evaporation of this solution gave white crystals whose ^1H NMR spectrum (in $CDCl_3$) agreed with that expected for pentadeuterated olefin **3**-d_5. A solution of this olefin in TFA exhibited the same NMR spectrum as that of cation **1**, and also yielded olefin **3** on standing.



3-d_5

The H–D exchange experiments confirm the assignments of the ^1H NMR signals at δ 2.70 and 1.95 (two nonequivalent C-methyls) and 2.31 (two equivalent S-methyls). This is based on the reasoning that in strong acid neither the SCH_3 nor the S^+CH_3 group undergoes H–D exchange, whereas exchange is possible for the C^+CH_3 group, probably via the olefin. This assignment was supported by ^{13}C NMR data for enriched alcohol **2** (Table III).

^1H NMR of 1 at Lower Temperatures. In Figure 2 (see supplementary material) are shown ^1H NMR spectra of carbocation **1** in TFA at different temperatures. The singlet at δ 2.31 (SCH_3) begins to broaden at 30 °C and is split into two peaks at 20 °C. This splitting is complete at 5 °C (Δδ 0.12 ppm) and no further change was observed down to −30 °C in TFA or to −60 °C in TFA/SO_2. This change is reversible, whereas the signals for the two C-methyls (δ 2.70 and 1.95) are unchanged throughout this temperature range.

^{13}C NMR of 1. The ^{13}C NMR spectrum of cation **1** was recorded at −20 °C because the cation is not sufficiently stable at room temperature for measurements of long duration. The measurements were carried out at 25 MHz in CF_3CO_2H–$CDCl_3$ (4:1, vol, concentrations ca. 20%) with Me_4Si as an internal standard (Table III). Alcohol **2** enriched with ^{13}C (ca. 60%) at the α-carbon was used for assignment of the α-carbon peak and for measurement of C–C coupling constants. The chemical shift for the α-carbon was 91.3 ppm, indicating considerable shielding of the carbenium carbons. The two signals at 25.5 and 30.9, doublets due to C–C coupling, were assigned to two C-methyls. The two signals at 16.1 and 20.2 ppm were assigned to two S-methyls, which are not equivalent, as in the ^1H NMR spectrum below 30 °C.

Table III. ^{13}C NMR Parameters for Carbocation 1

C	$R^+SbCl_6^-$ in CD_3NO_2[a]	$R^+CF_3CO_2^-$ in CF_3CO_2H[b]		
	shift, δ[c]	shift, δ[c]	$^1J_{CH}$, Hz[d]	$^1J_{CC}$, Hz[d]
S-Me	16.5	16.1	141.6 (q)	
	20.6	20.2	146.5 (q)	
Cα-Me	25.5	25.5[e]	130 ± 2 (q)[f]	35.4 (d)
	30.9	30.9[e]	130 ± 2 (q)[f]	35.4 (d)
C9	77.9	78.7	(s)	
Cα	91.0	91.3[g]	(s)	
	123.3	123.3	158.7 (d)	
C2, C4	124.1	123.5	166.0 (d)	
C5, C6	124.9	124.7	162.4 (d)	
C7, C8	127.1	126.6	160.5 (d)	
	129.3	129.6	157.4 (d)	
	132.7	133.0	162.4 (d)	
C3	135.2	135.4	163.6 (d)	
C1, C4a	139.8	140.1	(s)	45.2 (C1)
	140.9	140.2	(s)	
C4b, C8a	142.6	141.5	(s)	
C9a	143.0	143.0	(s)	
	150.7	150.6	(s)	

[a] At −10 °C. [b] At −20 °C. [c] Measured in ppm relative to internal Me_4Si. [d] Precision is ±0.6 Hz. [e] These peaks become multiplets in TFA-*d* by C–D coupling. [f] These coupling constants are not accurate (overlap of peaks). [g] Assigned with the use of α-^{13}C-enriched (ca. 60%) sample.

Isolation of Hexachloroantimonate of 1. We were able to isolate carbocation **1** as its stable crystalline hexachloroantimonate by passing dry hydrogen chloride into a solution of olefin **3** in dichloromethane at −60 °C, adding antimony pentachloride, and allowing it to stand. The precipitated salt was recrystallized from nitromethane, giving analytically pure salt as orange-red plates. This salt can be stored for several weeks in a desiccator at room temperature without deterioration. The ^1H NMR spectrum of this salt in nitromethane-d_3 or dichloromethane-d_2 (Table II) was similar to that of cation **1** in TFA, except that the singlet for *S*-Me was shifted 0.1 ppm downfield. The electronic absorption spectrum of the salt in dichloromethane (Table I) was also essentially the same as that of **1** in TFA, with 6–7-nm shifts to longer wavelengths. The intensities of these bands are lower and decrease further during the measurement, indicating decomposition of the salt. The half-life of the salt in this solvent was estimated to be about 1 h at 15 °C.

Discussion

Structure of 1 in Solution. Carbocation **1** is a stable species that can exist in TFA at room temperature for several hours. In contrast, carbocations that lack sulfur atoms around the cationic center are quite unstable. For example, 9,9-dimethyl-1-isopropenylfluorene shows essentially the same ^1H NMR spectrum in TFA and in $CDCl_3$. Moreover, its isopropenyl group does not undergo H–D isotopic exchange in TFA-*d* (see Experimental Section). Cumyl alcohol, which was reported to exist as cumyl cation[6] in fluorosulfonic acid at −40 °C, changed instantaneously into a dimeric cyclic species on dissolution in TFA at room temperature, probably via cumyl cation as an intermediate.

The stability of cation **1** is attributed to transfer of electrons from the two neighboring sulfur atoms to the cationic center. Complete electron transfer would lead to a sulfonium ion, whereas partial transfer would give a carbenium ion. Since the two S-methyl groups of cation **1** are seen equivalent in ^1H NMR at 35 °C, the ion cannot be a sulfonium species at this temperature.[7] This

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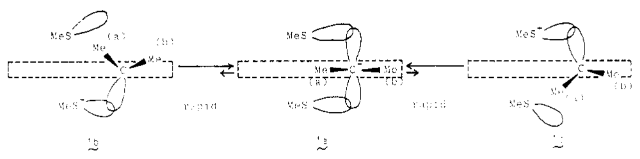
(5) Olah, G. A.; Pittman, C. U., Jr.; Waack, R.; Doran, M. *J. Am. Chem. Soc.* **1966**, *88*, 1488–1495.

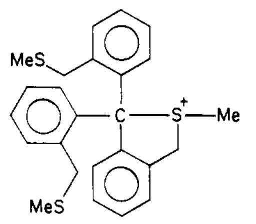
(6) Farnum, D. G. *J. Am. Chem. Soc.* **1967**, *89*, 2970–2975.

Scheme II. Views from Within the Plane of the Fluorene Nucleus



equivalence could be explained by either (a) partial transfer of electrons from sulfur to form a stabilized cation **1a**, or (b) interconversion between two sulfonium ions **1b** and **1c** at a rate high enough to give only a single NMR peak.

The fact that cation 1 shows strong electronic absorption bands at long wavelengths is strong evidence for the view that it is not a sulfonium species. Furthermore, the interconversion of a pair of sulfonium ions would be sluggish at lower temperatures, which should be reflected in its NMR spectrum. Breslow et al.[2] observed that tris[*o*-[(methylthio)methyl]phenyl]carbenium ion changes gradually into sulfonium species **4** on lowering the temperature. In 1, the ^{1}H NMR singlet for the two S-methyl groups (δ 2.31 at 35 °C) is split into two peaks (δ 2.29 and 2.41) at 5 °C and does not change further to -60 °C. However, this splitting ($\Delta\delta$ 0.12) is too small to be ascribed to a difference between a sulfide methyl and a sulfonium methyl, and is probably due to conformational change of the S-methyl groups. In addition, the chemical shifts for the two C-methyl groups are unchanged throughout this temperature range.



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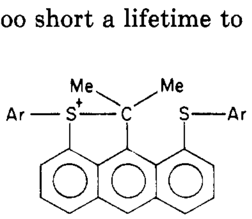
The electronic spectrum of 1 in TFA is essentially unchanged between 20 and -20 °C, indicating that the ion does not change within this temperature range. The rapid interconversion between two sulfonium forms of several 2-thioniaaceanthrenes **5** has been reported by Martin and Basalay.[3a] When the parent olefin of **5** was dissolved in TFA-*d*, only one deuterium was incorporated into ion **5**. In contrast, when alcohol **2** or olefin **3** is dissolved in this solvent, the hexadeuterio ion is obtained. Thus in ion **5** a carbenium species intermediate between the two sulfonium forms has too short a lifetime to undergo isotopic exchange.



5

These observations indicate that cation 1 is not a sulfonium but a carbenium ion. However, as judged from ^{1}H and ^{13}C NMR data, the positive charge appears to be extensively delocalized over the two sulfur atoms, with only a small portion remaining on the carbenium carbon. The chemical shift of the methyl proton of cumyl cation in strong acid was reported to be 3.48 ppm downfield from Me_4Si,[8] while the corresponding values for the two C^+-methyl groups of cation 1 in TFA are 1.95 and 2.70. The ^{13}C chemical shifts for the carbenium carbons of cumyl cation (255 ppm), trityl cation (212 ppm), and *tert*-butyl cation (330 ppm)[9] are significantly greater than that for 1 (91 ppm). This delocalization is surely related to the unusual stability of cation 1. Deshielding of the two S-methyl groups of cation 1 is observed in both ^{1}H and ^{13}C NMR chemical shifts. The ^{13}C–^{13}C coupling constant for the C^+-CH_3 of cation 1 is 35.4 Hz, while the corresponding value for trivalent (sp^2) C–CH_3's is reported to be 60–40 Hz.[10]

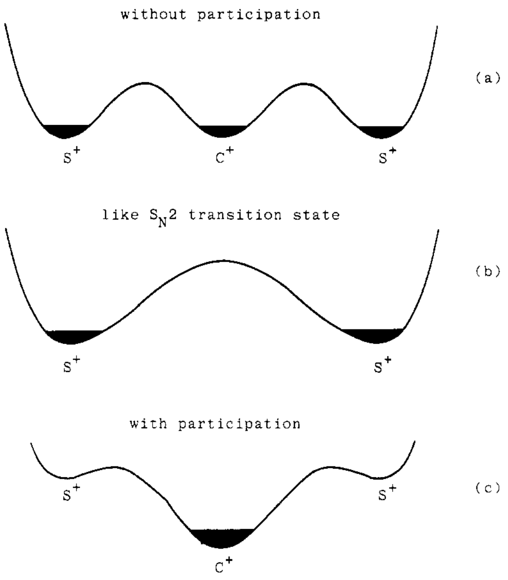


Figure 1. Schematic representation of energy diagrams for trityl ion system (a),[2] thioniaaceanthrene system (b),[3a] and the present system (c). Darkened portions indicate regions where these ions spend most of the time.

A possible conformation for 1 is shown as **1a** (Scheme II). Nonbonding electrons of the two sulfurs participate from both sides of the plane of the sp^2 carbon, which is thus pentacoordinated as in the transition states of S_N2 displacements. The bonds of this pentacoordinated carbon are electron rich, in contrast to the electron-deficient bonds formed by the protonation of alkanes in strong acid.[11]

In the schematic energy diagram for the trityl ion 4 (Figure 1, part a), the carbenium form is stable without assistance from the neighboring sulfur atoms. Hence, although facile interconversion between sulfonium and carbenium species could be observed, ion 4 could not become a hypervalent carbon species during the transition between the two sulfonium forms. In the thioniaaceanthrene system 5 (Figure 1, part b), the intermediate carbenium form is probably not stable since the plane of the carbenium center becomes perpendicular to the plane of the anthracene ring with loss of its conjugation with the ring on going from one sulfonium form to the other. Therefore ion 5 also could not stay as a carbenium intermediate (S_N1 process) but merely passes through it as a transition state of the S_N2 type. In 1 (Figure 1, part c), the two sulfonium forms are highly strained[7] relative to 4 and 5, and 1 can be an intermediate carbenium species

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[7] In fact the molecular model shows that the sulfonium form is highly strained.

[8] Olah, G. A.; Comisarow, M. B.; Kim, C. J. *J. Am. Chem. Soc.* **1969**, *91*, 1458–1469.

[9] Olah, G. A.; White, A. M. *J. Am. Chem. Soc.* **1969**, *91*, 5801–5810.

[10] Stothers, J. B. "Carbon-13 NMR Spectroscopy"; Academic Press: New York, 1972; p 371.

[11] Olah, G. A. *J. Am. Chem. Soc.* **1972**, *94*, 808–820.

stabilized by electrons from the two sulfur atoms and from the fluorene nucleus by conjugation.

Structure of 1 in the Crystalline State. X-ray crystallographic analysis of the crystalline hexachloroantimonate of cation 1 revealed that the two S–C$^+$ distances are different, with the shorter one (1.94 Å) close to that of a covalent C–S bond (1.82 Å). The electronic absorption (reflection method) of this crystal was also quite different from that of solutions of 1 hexachloroantimonate and trifluoroacetate, although there was a weak band in the visible region which appeared as a shoulder at ca. 430 nm. These results suggest that in a crystalline lattice cation 1 primarily a sulfonium structure with a little carbenium character, and that on dissolution it reverts to carbenium species 1a.

Experimental Section

Spectroscopic Measurements. Electronic absorption spectra were recorded on a Hitachi Model EPS-3T spectrophotometer. Solid-state electronic absorption spectra were recorded on a Shimadzu Model MPS-2000 spectrophotometer equipped with an apparatus for reflection measurements; the zero absorption line was corrected with barium oxide. ^{1}H NMR spectra were measured on Hitachi Model R-24 (60 MMz) and JEOL Model PS-100 (100 MHz) spectrometers, the latter being equipped with a JEOL Model VT-3C for measurements at different temperatures. ^{13}C NMR spectra were recorded on a JEOL Model PFT-100 (25 MHz) spectrometer equipped with a variable-temperature apparatus VT-3C. Chemical shifts were recorded in ppm from internal Me_4Si as standard, and precision of coupling constants is 0.6 Hz. For measurements of coupling constants between adjacent ^{13}C nuclei, ^{13}C-enriched (ca. 60%) samples were used.

Preparation of Materials. Methyl 9-Fluorenone-1-carboxylate. Hydrogen chloride was passed into a methanol solution (1.5 L) of 9-fluorenone-1-carboxylic acid[12] (40 g) and heated under reflux for 12 h to afford 38 g (89% yield) of the crude ester. Recrystallization from *n*-hexane gave pure material as bright yellow needles: mp 87–88 °C; IR (KBr) 1732 (ester), 1713 (ketone), 1618, 1448, 1287, 1195, 1142, 1090, 915, 750, and 733 cm^{-1}; ^{1}H NMR (CCl_4) δ 7.6–7.2 (m, 7 H, ArH), 3.92 (s, 3 H, OMe). Anal. ($C_{15}H_{10}O_3$) C, H.

Methyl 9,9-Bis(methylthio)fluorene-1-carboxylate. Method A. A mixture of 15 g (63 mmol) of methyl 9-fluorenone-1-carboxylate, 50 g of 30% methanol solution of methanethiol, and 10 mL of boron trifluoride etherate (47% in ether) was allowed to stand for one day at room temperature in a tightly stoppered flask. After evaporation of the solvent, the residue was collected, washed with an aqueous solution sodium hydroxide and then with water to give the crude product (20 g, 100%). Recrystallization from methanol gave 16.4 g (80%) of white needles: mp 98–99 °C; IR (KBr) 1735 (C═O), 1450, 1430, 1415, 1260, 1193, 1145, 1104, 1064, 764, and 637 cm^{-1}; ^{1}H NMR (CCl_4) δ 7.75–7.20 (m, 7 H, ArH), 3.90 (s, 3 H, OMe), 1.50 (s, 6 H, SMe). Anal. ($C_{17}H_{16}O_2S_2$) C, H, S.

Method B. In a glass-stoppered flask a mixture of 8.75 g of 9-fluorenone-1-carboxylic acid,[12] 25 g of a methanol solution (30%) of methanethiol, and 10 mL of an ethereal solution (45%) of boron trifluoride was stirred at room temperature for 2 days. The reaction mixture was poured into water, and extracted with dichloromethane. The extract was washed with an aqueous solution of sodium carbonate and then with water and dried over anhydrous sodium sulfate. Evaporation of the solvent gave 10.6 g (85.9%) of crude product. Recrystallization from methanol gave 9.61 g (77.9%) of white needles: mp 96–97 °C.

Grignard Reaction of Methyl 9,9-Bis(methylthio)fluorene-1-carboxylate. To a Grignard solution prepared from magnesium (0.925 g) and methyl iodide (5.4 g) in ether (60 mL) was added an ethereal solution (180 mL) of the ester (3 g). The mixture, deep violet in color, was stirred for 2 h at room temperature. After the solution was quenched with dilute hydrochloric acid, the organic layer was washed with water and dried over anhydrous sodium sulfate, and the solvent was evaporated to give 2.5 g of yellow oil. Column chromatography on silica gel gave the following four compounds.

9,9-Bis(methylthio)-1-isopropenylfluorene (3). Elution with hexane gave this olefin in 5% yield: mp 59–60 °C (from hexane); mass spectrum, *m/e* 298; IR (KBr) 1645 (C═C), 1582, 1454, 1434, 1420, 1410, 1366 (Me), 960, 902 (═CH$_2$), 757 and 550 cm^{-1}; ^{1}H NMR (CCl_4) δ 7.76–6.97 (m, 7 H, ArH), 5.34 (m, 1 H, ═CH$_2$), 5.12 (m, 1 H, ═CH$_2$), 2.26 (q, 3 H, CMe), 1.61 (s, 6 H, S-Me). Anal. ($C_{18}H_{18}S_2$) C, H, S. This olefin can also prepared from 9,9-bis(methylthio)-α,α-dimethyl-1-fluorenemethanol (2) in an almost quantitative yield by dissolving it in TFA and pouring the solution into glacial acetic acid at room temperature.

1-Acetyl-9,9-bis(methylthio)fluorene. The hexane–benzene (1:1) fraction afforded this ketone in 30% yield: mp 125–127 °C (from hexane); IR (KBr) 1706 (C═O), 1417, 1356, and 760 cm^{-1}; ^{1}H NMR (CCl_4) δ 7.6–7.0 (m, 7 H, ArH), 2.74 (s, 3 H, COMe), 1.50 (s, 6 H, SMe). Anal. ($C_{17}H_{16}OS_2$) C, H, S. This ketone can be converted quantitatively into alcohol 2 by reaction with methylmagnesium iodide in the usual manner.

9,9-Bis(methylthio)-α,α-dimethyl-1-fluorenemethanol (2). This alcohol was eluted by benene (50% yield): mp 144–145 °C (from hexane); IR (KBr) 3400 (OH), 1455, 1435, 1415, 1405, 1380, 1355, 1180, 1130, 960, 765, and 755 (vs) cm^{-1}; ^{1}H NMR (CCl_4) δ 7.7–7.3 (m, 7 H, ArH), 5.12 (s, 1 H, OH), 1.70 (s, 6 H, C-Me), 1.62 (s, 6 H, S-Me). Anal. ($C_{18}H_{20}OS_2$) C, H. S.

α,α-Dimethyl-9-fluorenone-1-methanol. Elution with ethyl acetate gave this keto alcohol in 10% yield: mp 107–108 °C (from hexane); IR (KBr) 3350 (OH), 1694 (C═O), 1576, 1457, 1380, 1290, 1186, 923, 690, and 670 cm^{-1}; ^{1}H NMR (CCl_4) δ 7.8–7.2 (m, 7 H, ArH), 5.62 (s, 1 H, OH), 1.58 (s, 6 H, C-Me). Anal. ($C_{16}H_{14}O_2$) C, H.

1-Isopropenyl-9,9-dimethylfluorene. Gaseous hydrogen chloride was passed through a mixture of 2.4 g of methyl 9-fluorenone-1-carboxylate, 1 g of ethanedithiol, and 50 mL of glacial acetic acid for 5 h at room temperature. The reaction mixture was poured into water, extracted with dichloromethane, washed with an aqueous solution of sodium hydroxide, and dried over anhydrous sodium sulfate. Evaporation of the solvent gave 2.9 g (92%) of crude product. Recrystallization from tetrahydrofuran afforded the ethylene dithioacetal of methyl 9-fluorenone-1-carboxylate as colorless plates: mp 128–129 °C; IR (KBr) 1730 (C═O), 1430, 1255, 1180, 1140, 1060, 760, 745, 740 and 640 cm^{-1}; ^{1}H NMR (CCl_4) δ 7.8–7.1 (m, 7 H, ArH), 3.85 (s, 3 H, OMe), 3.77 (m, 4 H, CH_2CH_2). Anal. ($C_{17}H_{14}O_2S_2$) C, H, S.

To a solution of methylmagnesium iodide in large excess (4.9 g of magnesium and 43 g of methyl iodide in 20 mL of ether) was added dropwise a solution of the ethylene dithioacetal of methyl 9-fluorenone-1-carboxylate (0.94 g) in tetrahydrofuran (20 mL). After refluxing for 4 h the excess Grignard reagent was quenched by adding methanol and then dilute hydrochloric acid. The organic layer was washed with water and dried over anhydrous sodium sulfate and the solvent was distilled off to yield 1.1 g of brown oil. Column chromatography on silica gel afforded 0.38 g (54%) of 1-isopropenyl-9,9-dimethylfluorene, together with 27% of the corresponding alcohol. Recrystallization from hexane gave pure olefin: mp 47–48 °C; mass spectrum, *m/e* 234; IR (KBr) 1640 (C═C), 1450, 1410, 1370, 910, 765, and 750 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.7–6.9 (m, 7 H, ArH), 5.30 (m, 1 H, olefinic), 4.96 (m, 1 H, olefinic), 2.10 (q, 3 H, α-Me), 1.54 (s, 6 H, 9-Me). Anal. ($C_{18}H_{18}$) C, H.

Preparation of ^{13}C-Enriched Compounds. 1-Iodo-9,9-bis(methylthio)fluorene. After dry hydrogen chloride was passed for 2 h at 0 °C into a methanol solution (50 mL) of 1-iodo-9-fluorenone[13] (5 g), 25 g of a methanol solution (30%) of methanethiol was added at this temperature, and the mixture was stirred for 3 days at 40 °C in a tightly stoppered flask. White crystals came out and weighed 5.09 g. An additional crop (0.73 g) was obtained from the filtrate. Column chromatography on silica gel gave 5.82 g (92%) of crude product. Recrystallization from ethanol gave colorless prisms: mp 110–111 °C; IR (KBr) 2925, 1560, 1443, 1435, 1420, 1406, 1024, 745 (vs), 630, and 502 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.97–6.84 (m, 7 H, ArH), 1.43 (s, 5 H,

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SMe). Anal. ($C_{15}H_{13}IS_2$) C, H, I.

[α-^{13}C]-9,9-Bis(methylthio)fluorene-1-carboxylic Acid. Method A. To a Grignard solution prepared from magnesium (760 mg) and methyl iodide (2 mL) in ether (5 mL) was added dropwise an ethereal solution (40 mL) of 1-iodo-9,9-bis(methylthio)fluorene (2 g). After refluxing for 4 h, carbonation was carried out by passing ^{13}C-enriched (ca. 60%) carbon dioxide, generated from barium carbonate-^{13}C and concentrated hydrochloric acid, into this mixture. After hydrolysis with dilute sulfuric acid, the ethereal layer was extracted with an aqueous solution of sodium carbonate. The extract was acidified and the precipitate was collected to give crude product (0.88 g, 56%). Recrystallization from hexane gave white crystals: mp 129–130 °C; IR (KBr) 1690 (^{12}C=O), 1665 (^{13}C=O), 1420, 1275, 1150, 910, 770, and 635 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 10.22 (broad s, 1 H, CO_2H), 8.02–7.20 (m, 7 H, ArH), 1.54 (s, 6 H, SMe).

Method B. To a suspension of 1.15 g (3 mmol) of 9,9-bis(methylthio)-1-iodofluorene in dry ether (30 mL) was added under nitrogen a solution of butyllithium in hexane (15%, 1.12 mL) through a syringe at −55 °C. After stirring for 20 min at this temperature, ^{13}C-enriched (ca. 60%) carbon dioxide was passed into the mixture for 0.5 h. Stirring was continued for 2 h at this temperature and then for another 1 h at room temperature. Workup as in method A gave 629 mg (69.2%) of the acid.

Methyl [α-^{13}C]-9,9-Bis(methylthio)fluorene-1-carboxylate. A mixture of [α-^{13}C]-9,9-bis(methylthio)fluorene-1-carboxylic acid (2 g) and sulfuric acid (3 mL) in methanol (20 mL) was heated under reflux for 2 h to afford 1.96 g of crude product containing some methyl [α-^{13}C]-9-fluorenone-1-carboxylate. Recrystallization of this mixture from methanol gave 1.03 g (49.2%) of the desired ester as white needles: mp 96.0–96.5 °C; IR (KBr) 1738 (^{12}C=O), 1695 (^{13}C=O), 1420, 1255, 1190, 1140, 762, 748 and 738 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.90–7.10 (m, 7 H, ArH), 3.95 (s, ^{12}C-OMe), 3.94 (d, $^3J_{COCH}$ = 4.9 Hz, ^{13}C-OMe), 1.53 (s, 6 H, SMe).

[α-^{13}C]-9,9-Bis(methylthio)-α,α-dimethyl-1-fluorenemethanol (2-α-^{13}C). To a solution of methylmagnesium iodide (0.945 g of magnesium, 5.5 g of methyl iodide and 30 mL of ether) cooled in an ice bath was added dropwise an ethereal solution (70 mL) of the ^{13}C-enriched ester (1.535 g) prepared above. The mixture was stirred for 20 min in the ice bath and then for 3 h at room temperature. Hydrolysis with dilute hydrochloric acid and extraction with ether gave 1.68 g of reddish orange paste. Column chromatography on silica gel gave the following products: [α-^{13}C]-9-methylthio-α,α-dimethyl-1-fluorenemethanol, 135 mg (10%); [α-^{13}C]-9,9-bis(methylthio)-1-acetylfluorene, 321 mg (22%); [α-^{13}C]-9,9-bis(methylthio)-α,α-dimethyl-1-fluorenemethanol, 593 mg (39%). The ^{13}C-enriched ketone (321 mg) was converted to the alcohol **2**-α-^{13}C (338 mg) by repeated Grignard reaction. The combined yield of the ^{13}C alcohol **2**-α-^{13}C was 61% (931 mg). Recrystallization from hexane–benzene (1:1) gave white needles (659 mg, 43%): mp 140.0–140.5 °C; IR (KBr) 3420 (OH), 1453, 1433, 1417, 1406, 1383, 1360, 1123, 956, 762 and 755 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.80–7.20 (m, 7 H, ArH), 5.12 (broad s, 1 H, OH), 1.79 (s, ^{12}C-Me), 1.78 (d, $^2J_{CH}$ = 4.0 Hz, ^{13}C-Me), 1.61 (s, 6 H, SMe); ^{13}C content, ca 60%.

Generation of Carbocation 1. About 10 mg of alcohol **2** or olefin **3** was dissolved in 0.2 mL of TFA (or TFA-*d*) in an NMR tube at room temperature and its ^{1}H NMR spectrum was recorded immediately at 35 °C.

Isolation of Olefin 3 and Olefin 3-d_5 from a Solution of Carbocation 1. In a typical experiment 327 mg of alcohol **2** was dissolved in 2 mL of TFA and the solution was allowed to stand on an evaporating dish under a hood at room temperature. Chromatography on silica gel afforded 185 mg (60%) of white crystals. Recrystallization from hexane–carbon tetrachloride gave pure olefin **3**, mp 59–60 °C, which was identified by mixture melting point with the authentic specimen. The same experiment with TFA-*d* afforded pentadeuterio olefin **3**-d_5: mp 58.0–59.0 °C; mass spectrum, *m/e* 303; IR (KBr) 2225 cm^{-1} (C–D) [laking 1645 (C=C), 1366 (CMe), and 902 cm^{-1} (C=CH_2)]; ^{1}H NMR ($CDCl_3$) δ 7.70–6.97 (m, 7 H, ArH), 1.59 (s, 6 H, SMe) [lacking =CH_2 and CMe]. This olefin **3**-d_5 was further confirmed by converting it into olefin **3** by the procedure described above.

Reaction of Ion 1 with Water. A solution of alcohol **2** (106 mg) in TFA (3 mL) was poured into ice–water and extracted with ether. The ethereal layer was washed with an aqueous solution of sodium carbonate and then with water and dried over anhydrous sodium sulfate. After evaporation of the solvent, the residual oil was submitted to column chromatography on silica gel to give 28.5% yield of alcohol **2** and 45.3% yield of olefin **3**.

Reaction of Cumyl Alcohol on Dissolution into TFA. Cumyl alcohol (2 g) was dissolved in TFA (7 mL) and stirred for 5 min at room temperature. After removal of the solvent in vacuo, the residual colorless oil was submitted to column chromatography on silica gel. The hexane fraction gave 1.31 g (75%) of 1,1,3-trimethyl-3-phenylindan: white crystals (from hexane); mp 53.5–54.0 °C (lit.[14] mp 52 °C); IR (KBr) 2940, 1495, 1480, 1445, 765, 760 and 700 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 7.3–7.1 (m, 9 H, ArH), 2.40 and 2.17 (AB q, *J* = 13 Hz, 2 H, CH_2), 1.67 (s, 3 H, Me), 1.33 (s, 3 H, Me), 1.03 (s, 3 H, Me). Anal. ($C_{10}H_{20}$) C, H. α-Methylstyrene in TFA gave the same product.

Isolation of Carbocation 1 as Hexachloroantimonate. In a 100-mL three-necked round-bottomed flask equipped with a gas-inlet tube, a dropping funnel, and a glass filter were placed 298 mg (1 mmol) of olefin **3** and 8 mL of freshly distilled dichloromethane. Carefully dried hydrogen chloride gas was passed through this solution at −55 °C for 0.5 h and antimony pentachloride (299 mg, 1 mmol) in 8 mL of dichloromethane was added dropwise to this brownish solution at this temperature. When 16 mL of carbon tetrachloride was added to this solution with constant stirring, a fine yellow precipitate began to separate. After stirring for another 0.5 h and warming to room temperature, the precipitate was collected on the filter by inclining the apparatus. Washing thoroughly with cold carbon tetrachloride and drying in a vacuum desiccator gave practically pure salt, 583 mg (92% yield). Recrystallization from nitromethane between +20 and −20 °C afforded an analytically pure sample as orange-yellow plates: mp 63–65 °C dec. Anal. Calcd for $C_{18}H_{19}Cl_6S_2Sb$: C, 34.10; H, 3.02; Cl, 33.55. Found: C, 34.32; H, 2.98; Cl, 32.73. Electronic absorption spectra and ^{1}H and ^{13}C NMR spectral data are listed in Table I, Table II, and Table III, respectively. This salt is remarkably stable at room temperature and can be stored for several weeks in a desiccator. In an open vessel, however, it begins to decompose after half a day and becomes resinous within five days. In solution (eg., CH_2Cl_2, CH_3NO_2) decomposition proceeds with a half-life of about 30 min at room temperature.

Satisfactory analytical data (±0.4% for C, H, S, I) have been submitted for all new compounds.

Registry No. **1**·$CF_3CO_2^-$, 95512-58-6; **1**·$SbCl_6^-$, 95512-59-7; **2**, 65223-17-8; **2**-α-^{13}C, 95512-55-3; **3**, 65223-18-9; **3**-d_5, 65223-21-4; MeSH, 74-93-1; 9-oxofluorene-1-carboxylic acid, 1573-92-8; methyl 9-oxofluorene-1-carboxylate, 5406-90-6; methyl 9,9-bis(methylthio)fluorene-1-carboxylate, 65223-19-0; 1-acetyl-9,9-bis(methylthio)fluorene, 95512-49-5; α,α-dimethyl-9-oxofluorene-1-methanol, 95512-50-8; 1-isopropenyl-9,9-dimethylfluorene, 65223-22-5; 1,2-ethanedithiol, 540-63-6; methyl 9-oxofluorene-1-carboxylate ethylene dithioacetal, 65223-20-3; 1-iodo-9,9-bis(methylthio)fluorene, 95512-51-9; 1-iodo-9-fluorenone, 52086-21-2; [α-^{13}C]-9,9-bis(methylthio)fluorene-1-carboxylic acid, 95512-52-0; methyl [α-^{13}C]-9,9-bis(methylthio)fluorene-1-carboxylate, 95512-53-1; methyl [α-^{13}C]-9-oxofluorene-1-carboxylate, 95512-54-2; [α-^{13}C]-9-(methylthio)-α,α-dimethyl-1-fluorenemethanol, 95512-56-4; [α-^{13}C]-9,9-bis(methylthio)-1-acetylfluorene, 95512-57-5; cumyl alcohol, 536-60-7; 1,1,3-trimethyl-3-phenylindan, 3910-35-8; α-methylstyrene, 98-83-9.

Supplementary Material Available: ^{13}C NMR data for alcohol **2** and olefin **3** in $CDCl_3$ at 25 °C (2 pages). Ordering information is given on any current masthead page.

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