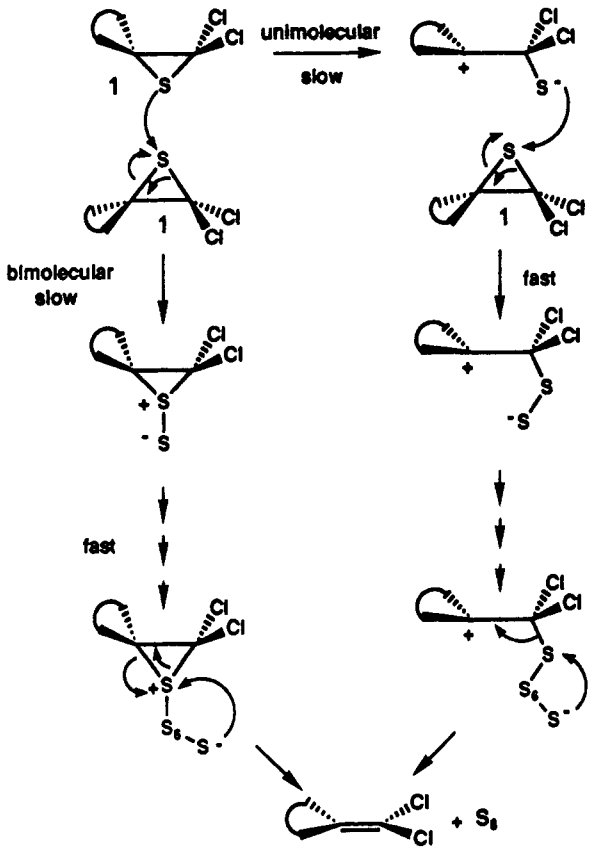
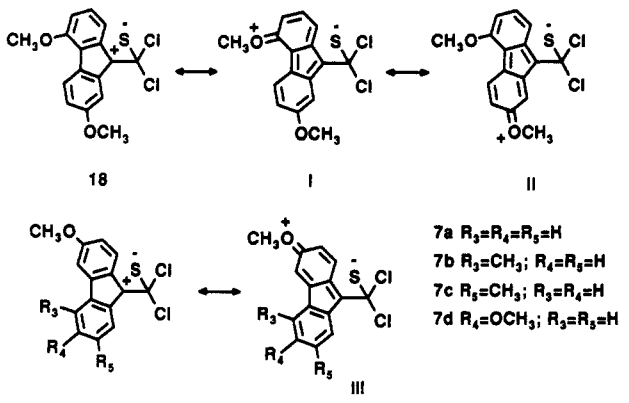
Scheme III



Scheme IV



argument. The fluorine atom could stabilize the dipolar intermediate *via* resonance[18] facilitating desulfurization. Countering this, by its inductive effect, the intermediate would be destabilized and thus inhibit desulfurization. Our experiments show that a mixture of **12** and **14** was obtained, strongly suggesting that the inductive and the resonance effects on the fluorenyl ring system are approximately balanced and episulfide **12** is partially converted to olefin **14**.

A similar explanation can be envisioned for the instability of thiiranes **7**. The presence of methoxy substituents would stabilize the proposed cationic intermediate and enhance its decomposition. The presence of additional activating methyl groups in **7b** and **7c** further increases desulfurization. The synthesis of 2,5-dimethoxy-substituted fluorenylthiirane **7f** was successful, although in poor yield. Initial studies show that when **7f** was heated in toluene at 80 °C for 2 h, no desulfurization occurred. The reaction was followed by ^{1}H NMR and found to be unchanged after heating for 2 h whereas compound **1** completely desulfurized under the same conditions. Although the two methoxy substituents present in **7f** would enhance desulfurization by a resonance effect, a closer examination of the resonance contributors suggests why we do not observe ready desulfurization (Scheme IV).

In order for **7f** to desulfurize, resonance structures **I** or **II** should be strong contributors to the hybrid. However, these contributors destroy the overall aromaticity of the ring system, and therefore, both I and II deliver a small resonance contribution. Conversely, resonance contributor III in compounds **7a–d** does not disrupt the aromaticity of the entire ring system; as a consequence, desulfurization is more likely to occur. Furthermore, it was discovered that introduction of a stabilizing methyl substituent at the 3-position of the fluorenyl group in **1** (thiirane **11**) causes desulfurization. It should be emphasized that in the cases of attempted preparation of **7a–d**, and **11**, the only products isolated were the corresponding alkenes **8a–d** and **13**. The episulfides must have been formed but underwent ready desulfurization.

An interesting result was observed when we studied the reactivity of the diphenyl-substituted thiiranes **15** and **16**. These two compounds are easily prepared in high yield, and the precursors as well as the thiirane are stable for months in the refrigerator without noticeable decomposition. Unlike **1**, **15** does not desulfurize when heated at 80 °C for 45 min. This observation can be explained by the differences in the two aromatic systems which influence their ability to promote the cation generated in the unimolecular rate-determining step.

The planar fluorenyl group in **1** can delocalize the cation more efficiently than the noncoplanar phenyl groups of **15**. It is known from solvolysis reactions of alkyl chlorides containing either the fluorenyl or biphenyl aromatic systems that the fluorenyl substituent is a better transmitter of π electrons in stabilizing carbonium ions.[19] The phenyl groups, meanwhile, are less effective in stabilizing the incipient carbonium ion since the π system is twisted out of the plane. Further supporting this position is the recent observation of Johnston and Lee-Ruff who have demonstrated the comparable stabilities of the two cation systems (fluorenyl and biphenyl).[20] They have reported that when reactivities with the same solvent are compared the diphenylmethyl cation is less reactive than the fluorenyl counterpart.

Conversely, the bis(4-methoxyphenyl)-substituted derivative **16** was found to decompose readily in solution. This would be expected since the *p*-methoxy groups would assist in stabilizing the incipient carbonium ion and facilitate desulfurization.

3′,3′-Dichloro-10,11-dihydrospiro[5*H*-dibenzo[*a*,*d*]cycloheptene-5,2′-thiirane] (**17**) did not desulfurize under the reaction conditions (2 h, 80 °C) but was found to desulfurize to a 50% extent when heated at 100 °C for 8 days. After 17 days, approximately 75% had decomposed. This is consistent with the overall mechanistic picture because the two methylene groups bridging the phenyl

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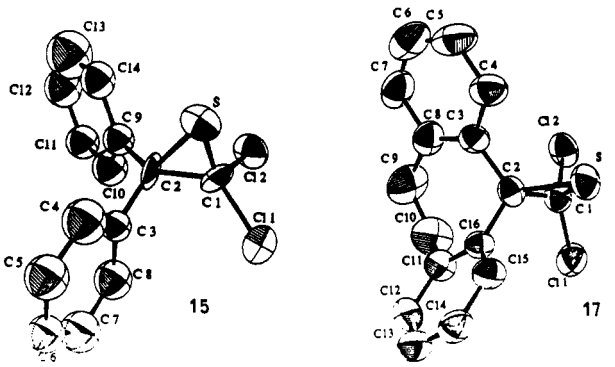

Figure 1. ORTEP representation of thiiranes 15 and 17.

Table I. Atomic Coordinates (x, y, z) and Temperature Factors (B_{eq}) for Compound 15 (Estimated σs Refer to the Last Digit)

atom	x	y	z	B_{eq}
Cl1	0.0877(3)	0.3652(11)	0.0534(3)	5.4(4)
Cl2	−0.0202(3)	0.4118(11)	0.1232(3)	5.5(4)
S	0.0426(3)	0.8129(11)	0.0785(3)	4.4(4)
C1	0.0524(12)	0.543(4)	0.1048(11)	4.4(15)
C2	0.0895(12)	0.685(4)	0.1503(9)	4.2(15)
C3	0.1638(6)	0.676(3)	0.1537(7)	3.6(3)
C4	0.1966(9)	0.8525(22)	0.1334(6)	6.9(3)
C5	0.2647(9)	0.8483(23)	0.1377(6)	6.4(3)
C6	0.3000(6)	0.668(3)	0.1621(7)	5.0(3)
C7	0.2672(9)	0.4909(22)	0.1823(7)	6.8(3)
C8	0.1990(9)	0.4951(23)	0.1781(7)	6.1(3)
C9	0.0665(8)	0.728(3)	0.2127(6)	4.3(3)
C10	0.0771(7)	0.5720(22)	0.2611(9)	6.2(3)
C11	0.0576(7)	0.609(3)	0.3210(7)	5.7(3)
C12	0.0275(8)	0.802(3)	0.3326(6)	6.7(3)
C13	0.0169(7)	0.9581(23)	0.2843(9)	9.6(3)
C14	0.0364(7)	0.9210(25)	0.2243(7)	5.3(3)
Cl1A	0.6579(4)	−0.3601(14)	−0.0320(3)	8.2(5)
Cl2A	0.5726(4)	−0.4533(15)	0.0591(4)	9.5(6)
SA	0.5933(4)	0.0110(14)	0.0270(4)	7.5(5)
C1A	0.6250(15)	−0.252(4)	0.0354(12)	6.3(19)
C2A	0.6619(11)	−0.117(5)	0.0817(12)	5.2(16)
C3A	0.7308(6)	−0.058(3)	0.0698(7)	5.0(3)
C4A	0.7429(8)	0.139(3)	0.0425(7)	6.7(3)
C5A	0.8065(9)	0.1933(21)	0.0342(6)	6.0(3)
C6A	0.8581(6)	0.051(3)	0.0532(7)	5.6(3)
C7A	0.8460(8)	−0.146(3)	0.0805(7)	7.8(3)
C8A	0.7824(9)	−0.2009(21)	0.0888(6)	5.3(3)
C9A	0.6575(7)	−0.143(3)	0.1520(5)	3.4(3)
C10A	0.6796(7)	−0.3271(24)	0.1867(8)	6.6(3)
C11A	0.6777(7)	−0.3386(24)	0.2531(8)	6.2(3)
C12A	0.6536(7)	−0.166(3)	0.2847(5)	6.2(3)
C13A	0.6315(7)	0.018(3)	0.2500(9)	7.8(3)
C14A	0.6334(7)	0.0291(23)	0.1836(8)	8.3(3)

groups cause the π system to become more planar than the diphenyl system but less than that of the fluorenyl system.

Crystal structure determinations of 15 and 17 were carried out. Figure 1 shows the ORTEP representations of both 15 and 17. Atomic coordinates and temperature factors are reported in Tables I and II. As predicted, the phenyl groups in 15 are not coplanar and are arranged in such a fashion as to minimize their interaction. In 17, a similar nonplanarity of the aromatic rings is also found. The aryl groups in 17 are ~60° out of the plane, and the phenyl groups in 15 are >60° out of the plane; of course, the fluorenyl group in 1 is planar. Since the fluorenyl system decomposes readily while the diphenyl system does not desulfurize, we would expect some decomposition to occur with 17 but at a very slow rate.

Consequently, we can summarize the aromatic systems in increasing order of reactivity: diphenyl < dibenzosuberonyl < fluorenyl and diphenyl ≪ bis(4-methoxyphenyl). Bis(4-methoxyphenyl) would be predicted to be more reactive than fluorenyl since the activating methoxy groups would override the resonance effect of the planar fluorenyl ring system. Qualitatively, we can state that amongst the substituted fluorenyl derivatives the increasing order of reactivity would be as follows: fluorenyl < 2,5-dimethoxyfluorenyl < 2-fluorofluorenyl < 3-methylfluorenyl < 3-methoxyfluorenyl < 3-methoxy-5-methylfluorenyl = 3-methoxy-7-methylfluorenyl < 3,6-dimethoxyfluorenyl.

Table II. Atomic Coordinates (x, y, z) and Temperature Factors (B_{eq}) for Compound 17 (Estimated σs Refer to the Last Digit)

atom	x	y	z	B_{eq}
S	0.62296(19)	0.6257(3)	0.06797(7)	5.15(9)
Cl1	0.54225(18)	1.0721(3)	0.09744(7)	5.68(9)
Cl2	0.75718(18)	1.0136(3)	0.01891(6)	5.54(9)
C1	0.6712(6)	0.8961(10)	0.07392(22)	4.4(3)
C2	0.7574(6)	0.7600(9)	0.11535(23)	3.7(3)
C3	0.9152(7)	0.7150(10)	0.10565(23)	4.0(3)
C4	0.9485(7)	0.5357(12)	0.0762(3)	5.5(4)
C5	1.0918(9)	0.4897(14)	0.0675(3)	7.2(5)
C6	1.1976(9)	0.6260(18)	0.0864(4)	7.7(6)
C7	1.1643(8)	0.8035(15)	0.1158(3)	6.8(5)
C8	1.0231(7)	0.8520(12)	0.1267(3)	5.2(4)
C9	1.0055(8)	1.0434(14)	0.1629(4)	7.7(5)
C10	0.8679(9)	1.1112(11)	0.1805(3)	7.2(4)
C11	0.7803(6)	0.9424(10)	0.2072(3)	4.6(3)
C12	0.7550(7)	0.9529(11)	0.2638(3)	5.2(4)
C13	0.6760(7)	0.8005(13)	0.2879(3)	5.2(4)
C14	0.6217(7)	0.6345(11)	0.2568(3)	4.9(3)
C15	0.6462(6)	0.6201(9)	0.20059(24)	4.1(3)
C16	0.7255(6)	0.7735(9)	0.1759(23)	3.6(3)

Experimental Section

X-Ray Crystallographic Data for 15 and 17. Intensity data were collected at room temperature on a AFC6S Rigaku diffractometer using graphite-monochromated CuK$_\alpha$ (γ = 1.540 56 Å) (composed 15) or MoK$_\alpha$ (γ = 0.709 30 Å) (compound 17) radiations using the $\theta/2\theta$ scan mode for 15 and the ω scan mode for 17. Structures were solved by direct methods.[21] Hydrogens were calculated. Solution and refinement were done using NRCVAX system programs.[22] Crystal data, collection and refinement parameters are given in Table III.[23] Crystal 15 decomposed in the beam, and data were collected from four crystals. Phenyl rings in 15 were refined as isotropic rigid groups. For crystal 17 all non-hydrogens were refined anisotropically. Tables of bond lengths and angles, torsion angles, and temperature factors have been deposited as supplementary material.

General Methods. Melting points (mp) were determine using a Gallenkamp melting point apparatus and are uncorrected. Low-resolution electron impact (EI) mass spectra were obtained on a Dupont Instruments 21-492B or Kratos MS25RFA mass spectrometer equipped with a 70-eV ionizing energy source and used in direct-inlet mode. Elemental analyses were performed by Guelph Chemical Laboratories Ltd. (Guelph, Ontario). ^{1}H NMR spectra were recorded on either Varian XL200 or XL300 spectrometers using deuteriochloroform as the reference solvent unless otherwise indicated. ^{13}C NMR spectra were obtained at 75.4 MHz using the Varian XL300, at 67.9 MHz using the JEOL CPF-270, or at 50.3 MHz using the Varian Gemini-200 spectrometers. ^{19}F NMR spectra are reported relative to external dichlorodifluoromethane and were not proton decoupled. Infrared spectra were recorded on an Analect Instruments ASQ-18

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(23) The authors have deposited atomic coordinates for 15 and 17 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, UK.

Table III. Crystal Data for Thiiranes 15 and 17

	compd 15	compd 17
chemical formula	$C_{14}H_{10}SCl_2$	$C_{16}H_{12}SCl_2$
formula wt	281.20	307.23
cryst dimsn (mm)	0.40 × 0.15 × 0.05	0.50 × 0.35 × 0.20
cryst system	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/c$
lattice constants		
a(Å)	20.646(6)[a]	9.351(4)[b]
b(Å)	6.244(3)	6.3151(19)
c(Å)	20.880(6)	24.077(6)
b(°)	99.263(23)	94.03(3)
Z	8	4
h, k, l ranges	−16 16, 0 5, 0 17	−10 10, 0 6, 0 25
density (cald) (g cm^{-3})	1.406	1.439
no. of parameters	119	172
obsd data $I > 2.5s(I)$	827	1053
for significant reflns	RF = 0.091,[c] R_w = 0.083[d]	RF = 0.045,[c] R_w = 0.040[d]

[a] Cell dimensions were obtained from 20 reflections with 2θ angle in the range 40.00–50.00°. No correction was made for absorption. [b] Cell dimensions were obtained from 25 reflections with 2θ angle in the range 20.00–25.00°. No correction was made for absorption.[c] RF = $\Sigma(F_o - F_c)/\Sigma(F_o)$. [d] $R_w = (\Sigma[w(F_o - F_c)^2/\Sigma(wF_o^2)])^{1/2}$.

FTIR spectrometer. Raman spectra were recorded on a S. A. Ramonor spectrometer equipped with a Spectra-Physics Argon ion laser at 514.5 nm or a Bruker IFS-88 FT Raman spectrometer equipped with a ND:YAG laser.

Synthesis of Biphenyloxazolines 2. General Procedure. The preparation of biphenyl oxazolines **2** is based on the method described by Meyers.[3]

2-(2-Phenyl-(4-methoxyphenyl)-4,4-dimethyl-2-oxazoline (2a). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.27 (s, 6H, $C(CH_3)_2$), 3.75 (s, 2H, CH_2), 3.84 (s, 3H, OCH_3), 6.87–6.90 (m, 2H), 7.36–7.39 (m, 5H), 7.70 (d, 1H, J = 8.2 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 28.0, 55.4, 67.2, 79.2, 112.5, 115.5, 120.3, 127.2, 127.9, 128.2, 131.8, 141.2, 143.4, 160.9, 163.7. MS m/z (rel intensity) 281 ($M^{\bullet+}$, 25), 280 ($M^{\bullet+}$ − 1, 100), 195 (28), 152 (11), 94 (11).

2-[2-(2-Methylphenyl)-4-methoxyphenyl]-4,4-dimethyl-2-oxazoline (2b). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.17, 1.19 (2 × s, 6H, $C(CH_3)_2$), 2.11 (s, 3H, CH_3), 3.64 (s, 2H, CH_2), 3.82 (s, 3H, OCH_3), 6.73 (d, 1H, J = 2.5 Hz), 6.89 (dd, 1H, J_1 = 8.6 Hz, J_2 = 2.6 Hz), 7.14–7.20 (m, 4H), 7.77 (d, 1H, J = 8.6 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 20.0, 28.0, 55.3, 66.9, 79.2, 112.6, 115.5, 121.0, 125.0, 127.2, 128.8, 129.3, 131.3, 135.6, 141.2, 143.3, 160.8, 163.3. MS m/z (rel intensity) 295 ($M^{\bullet+}$, 5), 280 ($M^{\bullet+}$ − CH_3, 100), 209 (9).

2-[2-(4-Methylphenyl)-4-methoxyphenyl]-4,4-dimethyl-2-oxazoline (2c). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.28 (s, 6H, $C(CH_3)_2$, 2.38 (s, 3H, CH_3), 3.76 (s, 2H, CH_2), 3.83 (s, 3H, OCH_3), 6.84–6.87 (m, 2H), 7.23 (dd, 4H, J_1 = 13.0 Hz, J_2 = 7.9 Hz), 9.10 (d, 1H, J = 9.1 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 21.2, 28.0, 55.4, 67.1, 79.3, 112.3, 115.5, 120.4, 128.1, 128.7, 131.9, 137.0, 138.3, 143.3, 161.0, 163.8. MS m/z (rel intensity) 295 ($M^{\bullet+}$, 25), 294 ($M^{\bullet+}$ − 1, 100), 280 ($M^{\bullet+}$ − CH_3, 3), 239 (7), 209 (12), 108 (15), 43 (44).

2-[2-(3-Methoxyphenyl)-4-methoxyphenyl]-4,4-dimethyl-2-oxazoline (2d). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.27 (s, 6H, $C(CH_3)_2$), 3.77 (s, 2H, CH_2), 3.81 (s, 3H), 3.84 (s, 3H), 6.85–7.68 (m, 7H, aromatic). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 27.8, 55.1, 55.3, 67.1, 79.3, 112.6, 113.0, 113.8, 115.5, 120.4, 120.9, 129.0, 131.9, 142.8, 142.9, 159.5, 161.1, 163.8. MS m/z (rel intensity) 311 ($M^{\bullet+}$, 30) ($M^{\bullet+}$ − 1, 100) 296 ($M^{\bullet+}$ − CH_3, 9), 255 (10), 225 (16).

2-[2-(2-Methoxyphenyl)-3-methoxyphenyl]-4,4-dimethyl-2-oxazoline (2e). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.38 (s, 6H, $C(CH_3)_2$), 3.88 (s, 3H, OCH_3), 3.89 (s, 3H, OCH_3), 4.08 (s, 2H, CH_2), 6.76–6.98 (m, 4H, aromatic), 7.24 (dd, 2H, J_1 = 7.9 Hz, J_2 = 1.6 Hz), 7.52 (dd, 1H, J_1 = 7.8 Hz, J_2 = 1.6 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 28.4, 56.1, 56.2, 67.0, 78.4, 111.1, 111.7, 112.1, 115.1, 118.0, 119.5, 121.8, 128.4, 133.3, 148.3, 150.3, 155.9, 163.7. MS m/z (rel intensity) 280 ($M^{\bullet+}$ − OCH_3, 23), 149 (100).

2-[2-(4-Methoxyphenyl)-3-methoxyphenyl]-4,4-dimethyl-2-oxazoline (2f). ^{1}H NMR (200 MHz, $CDCl_3$): δ 1.20 (s, 6H, $C(CH_3)_2$), 3.69 (s, 2H, CH_2), 3.73 (s, 3H, OCH_3), 3.82 (s, 3H, OCH_3), 6.89–7.27 (m, 7H, aromatic). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 27.9, 55.1, 55.8, 60.3, 79.9, 112.8, 113.0, 121.8, 128.0, 128.7, 130.1, 130.7, 130.9, 156.7, 158.6, 163.5. MS m/z (rel intensity) 310 ($M^{\bullet+}$ − 1, 7), 163 (100).

Synthesis of Biphenylcarboxylic Acids 3. General Procedure. The preparation of biphenylcarboxylic acids **3** is based on the method described by Meyers[3] unless otherwise noted.

2-Phenyl-4-methoxybenzoic Acid (3a). Mp: 163–165 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.86 (s 3H, OCH_3), 6.82 (d, 1H, J = 2.5 Hz), 6.90 (dd, 1H, J_1 = 8.7 Hz, J_2 = 2.6 Hz), 7.31–7.35 (m, 5H), 7.98 (d, 1H, J = 8.8 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 55.5, 112.6, 116.7, 121.0, 127.3, 127.9, 128.4, 133.4, 141.3, 146.3, 162.4, 172.0. MS m/z (rel intensity) 228 ($M^{\bullet+}$, 100), 211 ($M^{\bullet+}$ − OH, 96), 168 (27), 152 (15), 139 (31).

2-(2-Methylphenyl)-4-methoxybenzoic Acid (3b). Mp: 141–142 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.06 (s, 3H, CH_3), 3.85 (s, 3H, OCH_3), 6.70 (d, 1H, J = 2.5 Hz), 6.92 (dd, 1H, J_1 = 8.5 Hz, J_2 = 2.5 Hz), 7.09–7.25 (m, 4H), 8.05 (d, 1H, J = 8.6 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 19.9, 55.5, 112.8, 116.3, 120.8, 125.3, 127.3, 128.2, 129.5, 133.4, 135.3, 141.4, 162.6, 170.1. MS m/z (rel intensity) 242 ($M^{\bullet+}$, 97), 227 ($M^{\bullet+}$ − CH_3, 51), 225 ($M^{\bullet+}$ − OH, 100), 197 (19), 181 (22), 165 (35), 152 (28), 120 (23).

2-(4-Methylphenyl)-4-methoxybenzoic Acid (3c). Mp: 167–169 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.39 (s, 3H, CH_3), 3.86 (s, 3H, OCH_3), 6.81 (d, 1H, J = 2.5 Hz), 6.90 (dd, 1H, J_1 = 8.7 Hz, J_2 = 2.6 Hz), 7.21 (s, 4H), 7.97 (d, 1H, J = 8.7 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 21.2, 55.5, 112.5, 116.6, 121.0, 128.3, 128.7, 133.4, 137.1, 138.3, 146.2, 162.3, 171.4. MS m/z (rel intensity) 242 ($M^{\bullet+}$, 100), 225 ($M^{\bullet+}$ − OH, 67), 182 (10), 165 (9), 152 (11), 120 (14).

2-(3-Methoxyphenyl)-4-methoxybenzoic Acid (3d). The preparation of **3d** was based on the method described by Schuster.[9] Mp: 128–129 °C (lit.[9] mp 130–131 °C). ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.77 (s, 3H), 3.84 (s, 3H), 6.79–7.84 (m, 7H, aromatic). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 55.1, 55.4, 112.6, 112.8, 114.2, 116.4, 121.1, 123.2, 129.0, 132.9, 143.2, 145.3, 159.3, 162.0, 172.8. MS m/z (rel intensity) 258 ($M^{\bullet+}$, 83), 241 ($M^{\bullet+}$ − OH, 42), 86 (34), 72 (100).

2-(2-Methoxyphenyl)-3-methoxybenzoic Acid (3e). Mp: 194–196 °C (lit.[3] 196–197 °C). ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.70 (s, 3H, OCH_3), 3.74 (s, 3H, OCH_3), 6.92 (d, 1H, J = 8.2 Hz), 7.01 (d, 1H, J = 7.4 Hz), 7.15 (dd, 2H, J_1 = 7.6 Hz, J_2 = 2.1 Hz), 7.33 (t, 1H, J = 8.3 Hz), 7.38 (t, 1H, J = 8.1 Hz), 7.52 (d, 1H, J = 7.8 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 55.6, 56.2, 110.9, 115.1, 120.3, 122.2, 125.2, 128.2, 128.3, 128.9, 131.0, 131.8, 156.7, 157.3, 169.8. MS m/z (rel intensity) 258 ($M^{\bullet+}$, 100), 227 ($M^{\bullet+}$ − OCH_3, 48), 211 (12), 197 (7), 184 (9), 168 (21), 165 (58), 139 (12).

2-(4-Methoxyphenyl)-3-methoxybenzoic Acid (3f). Mp: 170–172 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.77 (s, 3H, OCH_3), 3.85 (s, 3H, OCH_3), 6.90–7.55 (m, 7H, aromatic). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 55.1, 56.0, 113.3, 114.5, 122.1, 128.1, 128.2, 130.7, 131.2, 131.8, 157.2, 158.8, 172.3. MS m/z (rel intensity) 258 ($M^{\bullet+}$, 100), 225 (9), 197 (12), 184 (7), 122 (11).

Synthesis of Fluorenones 4. General Procedure. The preparation of fluorenones **4** is based on the method described by Schuster.[9]

3-Methoxy-9-fluorenone (4a). Mp: 95–96 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.85 (s, 3H, OCH_3), 6.67 (dd, H, J_1 = 8.2 Hz, J_2 = 2.2 Hz), 6.94 (d, 1H, J = 2.2 Hz), 7.20–7.30 (m, 2H), 7.42 (s, 1H), 7.57 (d, 1H, J = 8.3 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 55.8, 107.0, 112.9, 120.0, 123.8, 126.2, 127.1, 129.2, 134.1, 135.3, 143.3, 146.9, 165.3, 192.5. MS m/z (rel intensity) 210 ($M^{\bullet+}$, 100), 180 (13), 167 (15), 152 (9), 139 (28).

3-Methoxy-5-methyl-9-fluorenone (4b). Mp: 138–140 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.56 (s, 3H, CH_3), 3.90 (s, 3H, OCH_3), 6.72 (dd, 1H, J_1 = 8.3 Hz, J_2 = 2.2 Hz), 7.14–7.22 (m, 3H), 7.50 (d, 1H, J = 8.0 Hz), 7.64 (d, 1H, J = 8.3 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 20.1, 55.7, 111.0, 111.4, 121.6, 126.2, 127.6, 128.9, 133.5, 135.7, 136.9, 140.9, 147.6, 165.1, 192.8. MS m/z (rel intensity) 224 ($M^{\bullet+}$, 100), 181 (15), 170 (6), 165 (17), 152 (20).

3-Methoxy-7-methyl-9-fluorenone (4c). Mp: 118–120 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.36 (s, 3H, CH_3), 3.89 (s, 3H, OCH_3), 6.69 (dd, 1H, J_1 = 8.2 Hz, J_2 = 2.2 Hz), 6.96 (d, 1H, J = 2.2 Hz), 7.30 (m, 2H), 7.42 (s, 1H), 7.57 (d, 1H, J = 8.3 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 21.5, 55.8, 106.8, 112.4, 119.9, 124.6, 126.1, 127.2, 134.4, 135.5, 139.4, 140.6, 147.1, 170.0. MS m/z (rel intensity) 224 ($M^{\bullet+}$, 100), 181 (15), 165 (11), 153 (13).

3,6-Dimethoxy-9-fluorenone (4d). Mp: 141–143 °C (lit.[9] mp 142–144 °C). ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.89 (s, 6H, OCH_3), 6.73 (dd, 2H, J_1 = 8.0 Hz, J_2 = 2.0 Hz), 6.98 (s, 2H), 7.57 (d, 2H, J = 8.3 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 55.7, 107.0, 112.9, 125.7, 128.3, 145.9, 164.9, 191.4. MS m/z (rel intensity) 240 ($M^{\bullet+}$, 100), 211 (9), 197 (17), 169 (17), 126 (9).

4,5-Dimethoxy-9-fluorenone (4e). Mp: 184–137.5 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 4.06 (s, 6H, 2 × OCH_3), 7.51 (t, 2H, J = 8.0 Hz), 8.06 (dd, 2H, J_1 = 7.9 Hz, J_2 = 1.2 Hz), 8.93 (dd, 2H, J_1 = 8.3 Hz, J_2 = 1.5 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 56.0, 116.8, 117.2, 122.6, 124.3, 128.5, 129.2, 129.6. MS m/z (rel intensity) 240 ($M^{\bullet+}$, 6), 226 (100), 211 (49), 155 (19), 139 (8), 127 (13). IR (cm^{-1}): 1724 (C=O).

2,5-Dimethoxy-9-fluorenone (4f). Mp: 160–163 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.82 (s, 3H, OCH_3), 3.93 (s, 3H, OCH_3), 3.93 (s, 3H, OCH_3), 6.90–7.55 (m, 5H), 7.66 (d, 1H, J = 8.2 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 55.5, 55.6, 109.4, 116.5, 117.9, 119.9, 125.1, 127.2, 128.1, 129.2, 135.2, 135.8, 136.3, 154.7, 160.0. MS m/z (rel intensity) 240 ($M^{\bullet+}$, 100), 225 (63), 197 (20), 126 (11).

Synthesis of Hydrazones 5. General Procedure. The preparation of hydrazones **5** is based on the method of described by Schuster.[9]

3-Methoxy-9-fluorenone Hydrazone (5a). Mp: 118–125 °C (mixture of both isomers). ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.89, 3.91 (2 × s, 6H, OCH_3, both isomers), 6.81–7.94 (m, 14H, both isomers). ^{13}C NMR (75.4, MHz, $CDCl_3$): major isomer δ 55.6, 106.4, 112.6, 119.5, 120.7, 123.6, 126.8, 128.1, 128.4, 138.3, 140.2, 141.0, 143.5, 161.1, minor isomer δ 74.7, 104.9, 113.9, 120.4, 121.8, 125.6, 127.9, 129.6, 131.0, 138.6, 139.8, 141.6, 145.9, 160.7. MS m/z (rel intensity) 224 ($M^{\bullet+}$, 100), 209 ($M^{\bullet+}$ – NH, 23), 195 (30), 180 (19), 165 (11), 152 (43).

3-Methoxy-5-methyl-9-fluorenone Hydrazone (5b). In some cases, hydrazone **5b** was contaminated by the Wolff–Kishner reduction product (3-methoxy-5-methylfluorene) which was removed by column chromatography (1:1 CH_2Cl_2/hexanes eluent). Mp: 128–134 °C (mixture of both isomers). ^{1}H NMR (200 MHz, $CDCl_3$): major isomer (NNH_2 syn to H_1) δ 2.65 (s, 3H, CH_3), 3.91 (s, 3H, OCH_3), 6.19 (s, 2H, NNH_2), 6.83 (m, 2H, both isomers), 7.12–7.23 (m, 4H, both isomers), 7.43, (d, 1H, J = 2.4 Hz), 7.60 (d, 1H, J = 7.8 Hz), 7.89 (d, 1H, J = 8.5 Hz), minor isomer (NNH_2 syn to H_8) δ 2.69 (s, 3H, CH_3), 3.89 (s, 3H, OCH_3), 6.24 (s, 2H, NNH_2), 7.32, (d, 1H, J = 2.2 Hz), 7.68 (d, 1H, J = 7.8 Hz), 7.81 (d, 1H, J = 8.5 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$): major isomer δ 20.8, 55.6, 110.6, 110.9, 118.3, 124.0, 126.5, 127.7, 131.3, 131.4, 132.8, 139.1, 140.9, 146.0, 160.4, minor isomer δ 21.2, 55.6, 109.7, 111.9, 121.4, 123.3, 127.6, 131.1, 132.4, 133.8, 136.2, 138.8, 144.5, 145.9, 160.8. MS m/z (rel intensity) 238 ($M^{\bullet+}$, 100), 223 ($M^{\bullet+}$ – CH_3, 19), 209 (32), 195 (17), 165 (27), 152 (19).

3-Methoxy-7-methyl-9-fluorenone Hydrazone (5c). Mp: 118–123 °C (mixture of both isomers). ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.36 (s, 3H, CH_3), 3.89 (s, 3H, OCH_3), 6.69 (dd, 1H, J_1 = 8.2 Hz, J_2 = 2.2 Hz), 6.96 (d, 1H, J = 2.2 Hz), 7.30 (m, 2H), 7.42 (s, 1H), 7.57 (d, ^{1}H, J = 8.3 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 21.5, 55.8, 106.8, 112.4, 119.9, 124.6, 126.1, 127.2, 134.4, 135.5, 139.4, 140.6, 147.1, 165.2, 170.0. MS m/z (rel intensity) 238 ($M^{\bullet+}$, 100), 223 ($M^{\bullet+}$ – CH_3, 18), 209 (29), 195 (16), 165 (26), 152 (25).

3,6-Dimethoxy-9-fluorenone Hydrazone (5d). Mp: 204–204.5 °C (lit.[9] mp 202–203 °C). ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.89 (s, 3H, OCH_3), 3.93 (s, 3H, OCH_3), 6.10 (s, 2H, NNH_2), 6.85 (dd, 2H, J_1 = 8.5 Hz, J_2 = 2.5 Hz), 7.13 (s, 1H), 7.23, (s, 1H), 7.62 (d, 1H, J = 8.4 Hz), 7.87 (d, 1H, J = 8.5 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 55.9 (2 × CH_3), 106.5, 106.8, 113.9, 114.7, 124.0, 126.3, 131.3, 131.8, 143.4, 144.8, 154.7, 163.2, 163.3. MS m/z (rel intensity) 254 ($M^{\bullet+}$, 100), 239 ($M^{\bullet+}$ – NH, 21), 225 (17), 210 (17), 139 (11), 129 (27), 112 (11).

2,5-Dimethoxy-9-fluorenone Hydrazone (5f). In somes cases, hydrazone **5f** was contaminated by the Wolff–Kishner reduction product (2,5-dimethoxyfluorene) which was removed by column chromatography (CH_2Cl_2 eluent). ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.88 (s, 3H, OCH_3), 3.99 (s, 3H, OCH_3), 6.88 (d, 1H, J = 8.2 Hz), 6.97 (d, 1H, J = 8.2 Hz), 7.24 (d, 1H, J = 8.0 Hz), 7.28 (s, 1H), 7.48 (d, 1H, J = 8.0 Hz), 7.87 (d, 1H, J = 8.0 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$): major isomer δ 55.4, 55.5, 104.8, 112.7, 115.3, 117.9, 124.5, 127.7, 129.0, 131.7, 138.9, 145.7, 155.2, 159.4, 169.8, minor isomer δ 55.3, 55.7, 110.9, 112.6, 113.2, 113.7, 122.3, 124.9, 128.2, 131.0, 133.5, 139.3, 154.8, 158.9, 169.8.

Synthesis of Diazo Compounds 6. General Procedure. The preparation of diazo compounds **6** is based on the method described by Schuster.[9] Hydrazones **5** were dissolved in 10 mL of anhydrous THF, and 0.25 g sodium sulfate was added to the solution. Yellow mercuric oxide (2 equiv) was then added followed by 3 drops of ethanolic KOH. The mixture was stirred at room temperature for 45 min, decanted from the mercuric sludge, and immediately cooled to 0 °C. In some cases, a second portion of mercuric oxide was necessary and the mixture stirred until a violet of reddish tint was obtained.

Attempted Synthesis of Substituted Thiiranes 7. General Procedure. The cooled diazo compounds **6** (1 equiv) were treated dropwise with thiophosgene (1.5 equiv, *caution: toxic*) until the evolution of nitrogen ceased. After the solvent was evaporated followed by flash chromatography, the products were identified and characterized.

Dichloro(3-methoxy-9-fluorenylidene)methane (8a). Flash chromatography was performed using 1:1 CH_2Cl_2/hexanes eluent: mp 86–89 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.91 (s, 3H, OCH_3), 6.74 (dd, 1H, J_1 = 8.20 Hz, J_2 = 2.2 Hz), 7.03 (d, 1H, J = 2.4 Hz), 7.15–7.50 (m, 4H), 7.62 (d, 1H, J = 8.3 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 55.8, 107.1, 112.9, 120.1, 123.9, 126.3, 127.2, 128.3, 129.3, 134.1, 135.4, 137.8, 143.4, 147.0, 165.4. MS m/z (rel intensity) 280 (11), 278 (64), 276 ($M^{\bullet+}$, 100), 233 (41), 198 (12), 163 (29).

Dichloro(3-methoxy-5-methyl-9-fluorenylidene)methane (8b). Flash chromatography was performed using 3:2 hexanes/CH_2Cl_2 eluent. Mp: 96–96.5 °C. R_f: 0.75. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.43 (s, 3H, CH_3), 3.89 (s, 3H, OCH_3), 6.79 (dd, 1H, J_1 = 8.7 Hz, J_2 = 2.6 Hz), 7.15 (d, 1H, J = 2.5 Hz), 7.19 (d, 1H, J = 7.8 Hz), 7.53 (d, 1H, J = 7.7 Hz), 8.10 (s, 1H), 8.18 (d, 1H, J = 8.8 Hz). ^{13}C NMR (67.9 MHz, $CDCl_3$): δ 22.0, 55.5, 104.8, 112.4, 119.3, 119.7, 119.8, 126.5, 126.9, 129.4, 129.7, 133.8, 137.3, 137.6, 142.2, 160.7. MS m/z (rel intensity) 294 (11), 292 (65), 290 ($M^{\bullet+}$, 100), 247 (44), 212 (21), 176 (36), 88 (17).

Dichloro(3-methoxy-7-methyl-9-fluorenylidene)methane (8c). Flash chromatography was performed using 3:2 hexanes/CH_2Cl_2 eluent. Mp: 82–85 °C. R_f: 0.64. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.67 (s, 3H, CH_3), 3.90 (s, 3H, OCH_3), 6.82 (dd, 1H, J_1 = 8.9 Hz, J_2 = 2.5 Hz), 7.17–7.22 (m, 2H), 7.40 (d, 1H, J = 2.5 Hz), 8.23 (d, 1H, J = 8.6 Hz), 8.31 (d, 1H, J = 7.6 Hz). ^{13}C NMR (67.9 MHz, $CDCl_3$): δ 21.3, 55.5, 110.0, 110.8, 119.3, 123.4, 126.6, 127.1, 129.8, 131.9, 132.9, 133.6, 137.6, 137.8, 142.9, 160.3. MS m/z (rel intensity) 294 (11), 292 (65), 290 ($M^{\bullet+}$, 100), 247 (36), 212 (25), 176 (40).

Dichloro(3,6-dimethoxy-9-fluorenylidene)methane (8d). The product was obtained by filtration. Mp: 122–123 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.90 (s, 6H, OCH_3), 6.84 (dd, 2H, J_1 = 8.5 Hz, J_2 = 2.5 Hz), 7.17 (d, 2H, J = 2.3 Hz), 8.20 (d, 2H, J = 8.9 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 55.5, 105.1, 113.1, 118.1, 126.8, 130.2, 133.2, 141.6, 160.6. MS m/z (rel intensity) 310 (11), 308 (65), 306 ($M^{\bullet+}$, 100), 263 (29), 220 (11), 153 (15), 129 (27), 112 (10).

3′,3′-Dichloro-2,5-dimethoxyspiro[fluorene-9,2′-thiirane] (7f). Flash chromatography was performed using 1:1 hexanes/CH_2Cl_2 eluent. ^{1}H NMR (200 MHz, $CDCl_3$): δ 3.87 (s, 3H, OCH_3), 3.98 (s, 3H, OCH_3), 6.91 (d, 1H, J = 8.5 Hz), 6.92 (d, 1H, J = 8.5 Hz), 7.20 (t, 1H, J = 8.1 Hz), 7.91 (s, 1H), 7.92 (d, 1H, J = 8.0 Hz), 8.17 (d, 1H, J = 8.5 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 55.4, 55.6, 65.5, 91.6, 111.7, 112.2, 114.0, 118.3, 124.5, 127.1, 132.7, 134.7, 137.3, 138.2, 154.7, 158.7. MS m/z (rel intensity) 310 (2), 309 (12), 308 (12), 307 (65), 306 ($M^{\bullet+}$ – S, 65), 305 ($M^{\bullet+}$ – SH, 100), 290 (59), 262 (12), 247 (10), 150 (13), 76 (15).

Dichloro(3-methyl-9-fluorenylidene)methane (13). Flash chromatography was performed using hexanes eluent. Mp: 67–70 °C. ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.43 (s, 3H, CH_3), 7.11 (d, 1H, J = 7.2 Hz), 7.29–7.38 (m, 2H), 7.48 (s, 1H), 7.65 (d, 1H, J = 6.9 Hz), 8.16 (d, 1H, J = 7.9 Hz), 8.29 (d, 1H, J = 7.1 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 21.6, 119.4, 120.2, 121.2, 125.5, 125.7, 127.3, 128.3, 128.6, 133.9, 134.1, 136.8, 139.2, 140.2, 140.3. MS m/z (rel intensity) 264 (11), 262 (64), 260 ($M^{\bullet+}$, 100), 225 ($M^{\bullet+}$ – Cl, 37), 190 (34), 189 (71), 163 (10), 94 (36). Anal. Calcd for $C_{15}H_{10}Cl_2$: C, 68.99; H, 3.86. Found: C, 68.90; H, 3.73.

Dichloro(2-fluoro-9-fluorenylidene)methane (14). Flash chromatography (4:1 hexanes/CH_2Cl_2 eluent) yielded a ~1:3 mixture of 12 and 14 determined by ^{13}C NMR analysis. The mixture could not be separated as both compounds have identical R_f values. Mp: 114–120 °C. ^1H NMR of 14 only (200 MHz, $CDCl_3$): δ 7.06–7.68 (m, 5H, aromatic), 8.02 (dd, 1H, J_1 = 10.8 Hz, J_2 = 2.5 Hz), 8.30 (d, 1H, J = 7.9 Hz). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 113.4 (d, J = 26.3 Hz), 116 (d, J = 23.3 Hz), 119.4, 120.4 (d, J = 9.0 Hz), 123.6, 125.8, 127.2, 129.4, 133.6, (d, J = 2.8 Hz), 136.2, 136.5, 138.1 (d, J = 9.2 Hz), 139.4, 162.5 (d, J = 243.9). ^{19}F NMR (282.2 MHz, $CDCl_3$): δ 63.68. MS m/z (rel intensity) 268 (11), 266 (64), 264 ($M^{\bullet+}$, 100), 229 ($M^{\bullet+}$ – Cl, 7), 194 ($M^{\bullet+}$ – 2 × Cl, 53), 183 (11), 168 (6), 132 (10), 114 (8), 97 (21).

2,2-Dichloro-3,3-bis(4-methoxyphenyl)thiirane (16). Flash chromatography was performed using 1:1 CH_2Cl_2/hexanes eluent. Mp: 86–87 °C. ^1H NMR (200 MHz, $CDCl_3$): δ 3.79 (s, 6H, OCH_3), 6.87 (d, 4H, J = 8.9 Hz), 7.51 (d, 4H, J = 8.9 Hz). ^{13}C NMR (67.9 MHz, $CDCl_3$): δ 55.6, 66.4, 82.0, 113.7, 131.1, 131.6, 159.6. MS m/z (rel intensity) 311 (2), 309 (13), 308 ($M^{\bullet+}$ – S, 4), 307 ($M^{\bullet+}$ – SH, 20), 238 ($M^{\bullet+}$ – SCl_2, 16), 223 (7), 69 (18), 66 (100), 57 (88), 41 (30). Raman: 665 cm^{-1}. Anal. Calcd for $C_{16}H_{14}O_2SCl_2$: S, 9.39. Found: S, 9.37. **1,1-Dichloro-2,2-bis(4-methoxyphenyl)ethylene.** The second fraction was identified as the desulfurized product. Mp: 128–132 °C. ^1H NMR (200 MHz, $CDCl_3$): δ 3.88 (s, 6H, OCH_3), 6.95 (d, 4H, J = 8.9 Hz), 7.78 (d, 4H, J = 8.9 Hz). ^{13}C NMR (67.9 MHz, $CDCl_3$): δ 55.4, 113.4, 113.7, 128.4, 130.7, 132.2, 162.8. MS m/z (rel intensity) 308 ($M^{\bullet+}$, 0.2) 242 (23), 227 (24), 211 (10), 135 (100), 107 (12), 92 (17), 77 (20).

3′,3′-Dichloro-10,11-dihydrospiro[5*H*-dibenzo[*a*,*d*]cycloheptene-5,2′-thiirane] (17). Flash chromatography was performed using 2:1 hexanes/CH_2Cl_2 eluent. Mp: 113–114 °C. ^1H NMR (200 MHz, $CDCl_3$): δ 2.98–3.16 (m, 2H), 3.64–3.82 (m, 2H), 7.11–7.41 (m, 8H). ^{13}C NMR (75.4 MHz, $CDCl_3$): δ 31.9, 69.0, 82.8, 126.2, 128.9, 129.5, 129.7, 136.5, 138.8. MS m/z (rel intensity) 306 ($M^{\bullet+}$, 3), 277 (2), 276 (3), 275 (5), 274 ($M^{\bullet+}$ – S, 14), 273 ($M^{\bullet+}$ – SH, 38), 272 ($M^{\bullet+}$ – H_2S, 23), 271 ($M^{\bullet+}$ – Cl, 100), 236 (63), 221 (11), 202 (31), 191 (41). Raman: 627, 685 cm^- Anal. Calcd for $C_{16}H_{12}SCl_2$: C, 62.54; H, 3.94. Found: C, 62.14; H, 3.60.

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Supplementary Material Available: ^1H NMR spectra (26 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 or ordering information.

Thermal Decomposition of 3′,3′-Dichlorospiro[fluorene-9,2′-thiirane]: Kinetics and Mechanism

Warren Chew and David N. Harpp*

Department of Chemistry, McGill University, Montréal, Québec, Canada H3A 2K6

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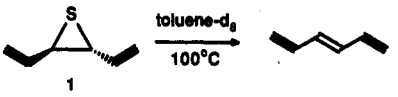
Kinetic studies on the thermal decomposition of 2,2-dichloro-3-(9-fluorenylidene)thiirane in 12 solvents have been investigated in detail. A two-term rate equation has been derived to account for the overall rate changes. Both a uni- and bimolecular ionic mechanism involving the concatenation of sulfur atoms is proposed to account for the observed kinetic behavior. Activation parameters were calculated and rationalized with respect to differences in solvation of the ground and transition states. A linear, isokinetic relationship was found indicating a similar mechanism of decomposition in these solvents. Rates of reaction were also found to be linearly correlated with dielectric constant as well as the π^* scale of Kamlet and Taft. The rate of desulfurization is decreased in the presence of acetic acid, and a radical mechanism is discounted from a rate study in the presence of radical inhibitors.

Introduction

Many thiiranes thermally decompose to elemental sulfur and the corresponding alkene, but only three reports on the mechanism of extrusion have been reported to date.

Bergman's[1] work suggests that 1,2-diethynylthiirane (1) decomposes in a bimolecular fashion at high concentrations of thiirane. As the concentration of thiirane decreases



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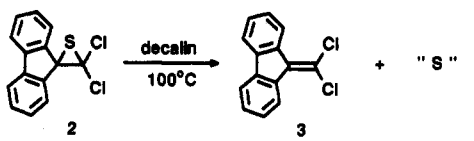
during the reaction, it was proposed that the bimolecular step changes to a unimolecular process. A simple cheletropic extrusion of a sulfur atom was ruled out as a likely pathway; the authors concluded that the reaction involves a more complicated mechanism.

Lutz and Biellmann[2] studied the thermally-induced extrusion reaction of 3′,3′-dichlorospiro[fluorene-9,2′-thiirane] **2** in decalin at 100 °C querying whether the loss of sulfur was a unimolecular process (Scheme I). Clean kinetic behavior was not observed from their results, and it was suggested that sulfur loss is not a cheletropic extrusion of a sulfur atom but that a more complex process was involved. It was proposed that an "unknown species" acquires a sulfur atom which reacts further with another molecule of episulfide.

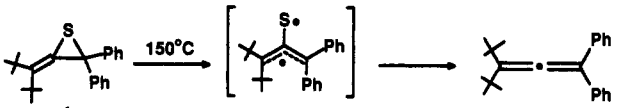
Finally, the mechanism of extrusion of a related molecule, an allene episulfide, was examined by Ando and co-workers.[3] The thermally catalyzed desulfurization of **4** in *o*-dichlorobenzene at 150 °C led the authors to postulate a thioallyl radical intermediate. The observed rate acceleration in diglyme was rationalized by the presence of a dipole moment of the C–S bond biradical intermediate having a modest zwitterionic contribution. A similar kinetic study was undertaken by the same authors on thiirane **5**, but only 2,4-dimethyl-3-mercaptopenta-1,3-diene (**6**) was obtained via an intramolecular 1,4-hydrogen

Scheme I



2 3

shift and no allene was recovered.[4] As part of our investigation of sulfur-extrusion mechanisms,[5] we examined the decomposition reaction of **2**, and a detailed kinetic study was undertaken for several reasons. First, the synthesis of this compound as well as a number of substituted analogs[5h] is fairly straightforward and documented in the literature. Second, this particular thiirane can be stored in the refrigerator for several months without noticeable decomposition. Although it is known that thiiranes containing aromatic and electron-withdrawing substituents are usually unstable, the stability of this thiirane is ideal as it allows study on its thermal decomposition under a variety of conditions. Finally, a detailed kinetic study should allow clarification of the conclusions



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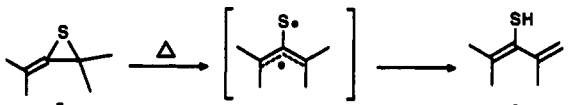

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(1) Vollhardt, K. P. C.; Bergman, R. G. *J. Am. Chem. Soc.* **1973**, *95*, 7538.
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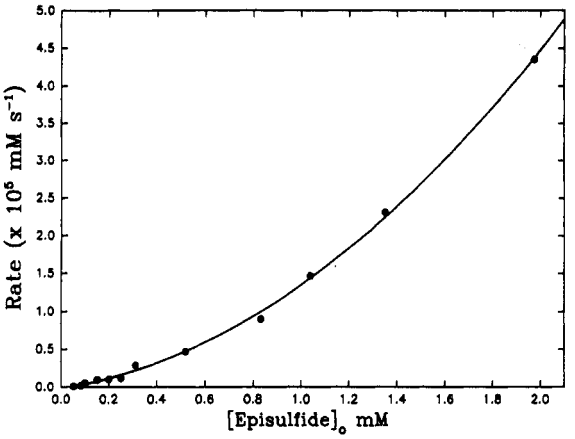

Figure 1. Rate behavior in the decomposition of **2** in toluene at 80 °C.

made by Lutz and Biellman[2] and hopefully provide strong evidence regarding the nature of the desulfurization. It should then be possible to establish a general rate law governing the overall mechanism of the thermal decomposition of thiiranes. The effect of solvent on the decomposition of **2** was also studied to distinguish whether the extrusion of sulfur proceeds via an ionic or radical mechanism.

Results and Discussion

The rate of decomposition of **2** was conveniently obtained by measuring the increase in absorbance with time of the olefin products **3** at λ = 325 nm;[6] the method of initial rates was used. The thermal decomposition reaction was conducted in 12 different solvents all involving runs at 80 °C. A typical rate profile in toluene is shown in Figure 1.

By inspection, the decomposition of **2** is *not* a first-order reaction (in agreement with that observed by Lutz and Biellmann[2]) and thus is not a simple unimolecular decomposition. From this detailed kinetic study, we examined four possible rate laws to fit the data, and we conclude that the best overall correlation is consistent with a two-term rate expression containing a first- and second-order term (eq 1). Values of the rate constants, k_1

$$\text{rate} = k_1[\text{E}] + k_2[\text{E}]^2 \qquad (1)$$

[E] = concentration episulfide (mM)

$$k_1 = \text{s}^{-1}$$

$$k_2 = \text{mM}^{-1}\,\text{s}^{-1}$$

and k_2, were obtained by curve-fitting the data using the Marquardt–Lerenberg interactive algorithm[7] and are listed in Table I.

Table II shows the relative rates of the data obtained from eq 1 (Table I). In general, the unimolecular rate constants in the solvents do show the expected trends with respect to their solvent polarities. The most polar solvents, DMF and DMSO, have the highest rates. The nonpolar aromatic solvents all have similar slow rates; 1,2,4-trimethylbenzene and *m*-xylene are unexpectedly even lower. It has been reported recently that the 9-fluorenyl cation can undergo electrophilic aromatic substitution reactions with benzene, toluene, and mesitylene.[9] Evidence was provided for capture of the fluorenyl cation with these solvents. Our observation of the slower rates in the methylbenzenes (Table II) could possibly be linked to the trapping of the fluorenyl cation by these solvents since our proposed intermediate involves a fluorenyl cation[5f] (vide infra). Electrophilic substitution would inhibit formation of olefin **3**, and thus the rate of reaction would diminish. We explored this possibility further by conducting product studies on the desulfurization of episulfide **2** in toluene, 1,2,4-trimethylbenzene, and the xylenes. Unfortunately, no indication of trapping of the fluorenyl cation was observed and only the olefin **3** plus elemental sulfur was obtained. The failure to detect any other products does not discount the proposed dipolar mechanism, but perhaps it is likely that the linking of sulfur atoms and subsequent extrusion of elemental sulfur[5g] (vide infra) is much faster than electrophilic reaction with the solvent molecules. The relative rates in the bimolecular term also show the expected trends with the exception of decalin and bromobenzene. All show somewhat higher rates than both 1,2,4-trimethylbenzene and *m*-xylene. The rationale for the higher rates in these solvents is not clear.

Table I. Rate Constants (k_1 and k_2) Derived from eq 1. All Rate Data Were Determined at 80 °C

	rate = k_1[E] + k_2[E]^2	
solvent	k_1[a,8]	k_2[b,8]
decalin	0.72 ± 0.51	2.0 ± 1.0
DMF	109 ± 32	173 ± 116
DMSO	36 ± 21	82 ± 29
o-dichlorobenzene	0.52 ± 0.20	0.99 ± 0.33
bromobenzene	0.50 ± 0.27	2.5 ± 1.0
toluene	0.45 ± 0.17	0.90 ± 0.43
1:1 decaline/toluene	0.83 ± 0.17	0.61 ± 0.84
1,1,2,2-tetrachloroethane	1.9 ± 0.3	2.2 ± 0.5
1,2,4-trimethylbenzene	0.11 ± 0.07	0.21 ± 0.05
o-xylene	0.71 ± 0.20	0.41 ± 0.54
m-xylene	0.09 ± 0.08	0.22 ± 0.09
p-xylene	0.63 ± 0.21	0.42 ± 0.20

Table II. Relative Rates Calculated from Rate Constants using eq 1. All Rate Data Were Determined at 80 °C

solvent	k_{rel} (k_1)	k_{rel} (k_2)
DMF	1211	824
DMSO	400	390
1,1,2,2-tetrachloroethane	21	10
1:1 decalin/toluene	9	3
o-xylene	8	2
decalin	8	10
p-xylene	7	2
o-dichlorobenzene	6	5
bromobenzene	6	12
toluene	5	4
1,2,4-trimethylbenzene	1	1
m-xylene	1	1

[a] In $s^{-1} \times 10^5$. [b] In $mM^{-1}\,s^{-1} \times 10^5$.

(6) λ_{max} was at 320 nm. It was not used due to absorbance values that were too high at higher initial concentrations of episulfide.

(7) SigmaPlot Scientific Graphing System Version 4.1, Jandel Scientific Corporation, Corte Madera, CA 94925.

(8) Errors were determined as described in Harris, D. C. *Quantitative Chemical Analysis*, 2nd ed.; W. H. Freeman and Co.: New York, 1987; pp 31, 43. The estimated errors in the rates were ±15%.

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