sodium bicarbonate solution to remove acid and subsequently extracted with 10% aqueous sodium hydroxide. The organic layer was separated, dried, and then rotary evaporated leaving unreacted naphthalene. Following acidification of the alkali solution and ether extraction, the separated ethereal layer was dried and evaporated to give the hydroxylated products. For analysis they were first O-trimethylsilylated by *N,O*-bis(trimethylsilyl)trifluoroacetamide (Pierce) and then analyzed as the trimethylsilyl ethers by GC.

Hydroxylation of Naphthalene with 90% H_2O_2 in HF–BF_3 and Other Superacid Solutions. Finely pulverized naphthalene (0.64 g, 5 mmol) was dissolved in hydrogen fluoride (6 mL) saturated with boron trifluoride at −78 °C. A clear red solution resulted. Separately, 90% H_2O_2 (0.38 g, 6 mmol) was added dropwise over a 20-min period at −78 °C to vigorously stirred hydrogen fluoride (8 mL) saturated with boron trifluoride, using a Vortex-Genie mixer. The latter solution was then added with good stirring to the solution of naphthalene and stirred for 30 min at −78 °C. The reaction mixture was then quenched with ice–water, extracted with ether, and worked up as before.

Other hydroxylations with superacid systems were similarly carried out (results summarized in Tables I and II).

Registry No. 1-Naphthol, 90-15-3; 2-naphthol, 135-19-3; naphthalene, 91-20-3; 1,6-dihydroxynaphthalene, 575-44-0; 1,5-dihydroxynaphthalene, 83-56-7; 1,7-dihydroxynaphthalene, 575-38-2; 2,6-dihydroxynaphthalene, 581-43-1; fluorosulfonic acid, 7789-21-1; hydrofluoric acid, 7664-39-3; boron trifluoride, 7637-07-2; antimony pentafluoride, 7783-70-2; tantalum pentafluoride, 7783-71-3; hydrogen peroxide, 7722-84-1.

9-Fluorenyl 9-(*p*-Tolylsulfonyl)-9-fluorenyl Disulfide: The Unexpected Product of the Reaction of 9-Bromofluorene and Potassium *p*-Toluenethiosulfonate and the Mechanism of Its Formation[1]

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Received May 3, 1991

Reaction of potassium *p*-toluenethiosulfonate with 9-bromofluorene leads, not to the expected 9-fluorenyl *p*-toluenethiosulfonate (**3**), but rather to a product shown to be 9-fluorenyl 9-(*p*-tolylsulfonyl)-9-fluorenyl disulfide (**7**, R = 9-fluorenyl) (eq 11). This disulfide of unusual structure is shown to arise as a result of the following reaction sequence: (a) initial formation of **3**; (b) a facile elimination of **3** (due to the acidity of the 9-H), forming *p*-toluenesulfinic acid and 9-thiofluorenone (**4**); (c) addition of *p*-$CH_3C_6H_4SO_2^-$ to **4** to give α-sulfonyl thiolate ion **16**; and (d) reaction of **16** with remaining **3** (in a rapid displacement at the dicoordinate sulfur) to give **7** plus regeneration of *p*-$CH_3C_6H_4SO_2^-$.

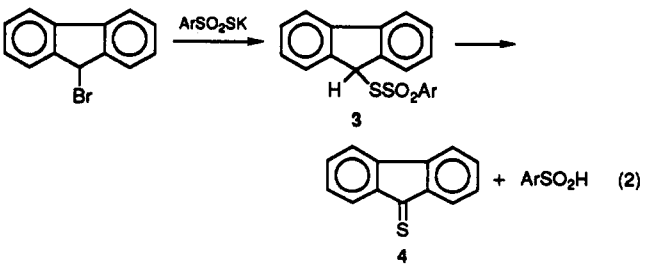
Reaction of potassium *p*-toluenethiosulfonate with a diarylmethyl bromide normally leads (eq 1) to the formation of a diarylmethyl *p*-toluenethiosulfonate (**1**).[2,3] We were therefore surprised to discover that when 9-bromofluorene was used the product was *not* 9-fluorenyl *p*-toluenethiosulfonate. Elucidation of the unusual structure of the final product actually formed and of the anomalous course of the reaction form the subject of this paper.

$$Ar'_2CHBr + p\text{-}CH_3C_6H_4SO_2SK \rightarrow Ar'_2CHSSO_2C_6H_4CH_3\text{-}p + KBr \quad (1)$$
1

Results and Discussion

Reaction of 9-Bromofluorene with Potassium *p*-Toluenethiosulfonate. 9-Bromofluorene was allowed to react with an equimolar amount of potassium *p*-toluenethiosulfonate in acetonitrile at reflux for 4 h.[4] Workup of the reaction mixture afforded (in >90% yield) a compound (**2**) shown by mass spectral and combustion analysis to have the molecular formula $C_{33}H_{24}O_2S_3$. The ^1H NMR of **2** consisted of a *p*-tolyl methyl group (δ 2.20, s, 3 H), one fluorenyl 9-H (δ 5.39, s, 1 H), and 20 aromatic protons distributed as a complex set of multiplets between δ 6.83 and 8.35. Strong bands in the infrared at 1310 and 1145 cm^{-1} indicated a sulfonyl group was present in **2**. Compound **2** therefore possesses a *p*-tolyl residue, three sulfur atoms, one of which is an SO_2 group, and two fluorenyl residues, one of which no longer has a hydrogen at C-9. The ^{13}C NMR of **2** (see Experimental Section) is also in accord with this structural assessment.

In considering how **2** might arise, we were attracted by the possibility that 9-bromofluorenone and *p*-$CH_3C_6H_4SO_2SK$ might indeed react initially to form the expected thiosulfonate (**3**), but that, because of the acidity of the fluorenyl 9-H, **3** would undergo elimination[3a] much more readily than a typical diarylmethyl thiosulfonate **1**, giving 9-thiofluorenone (**4**), eq 2. Compound **2** would then arise from a further reaction involving **4**.



$$\text{4} + ArSO_2H \quad (2)$$

Formation of 2 from 9-Thiofluorenone. To test this possibility equimolar amounts of 9-thiofluorenone (**4**),[5] 9-bromofluorene, and potassium *p*-toluenethiosulfonate were allowed to react at room temperature in acetonitrile

(1) This research was supported by the National Science Foundation, Grants CHE-8610116 and CHE-9000175.

(2) Kice, J. L.; Kupczyk-Subotkowska, L. *J. Org. Chem.* **1991**, *56*, 1424.

(3) (a) Kice, J. L.; Weclas, L. *J. Org. Chem.* **1985**, *50*, 32. (b) Much higher (~80%) yields of **1** than reported in ref 3a can be obtained by a change in the workup procedure used to isolate **1**.

(4) The same reaction product (**2**) was also obtained by allowing the reaction to proceed at room temperature for 24 h or in other solvents (MeOH, DMSO).

(5) Campaigne, E.; Reid, W. B. *J. Am. Chem. Soc.* **1946**, *68*, 769.

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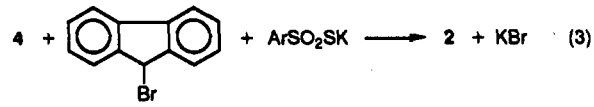
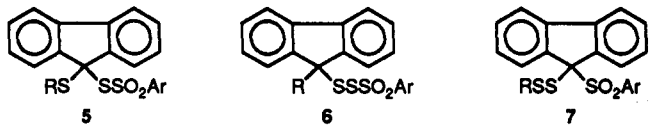
for 1.5 h. Workup gave **2** in 99% yield. This establishes that formation of **2** from 9-bromofluorene and *p*-$CH_3C_6H_4SO_2SK$ first involves the sequence shown in eq 2; this is followed by a set of reactions whose overall stoichiometry can be represented by eq 3 (Ar = *p*-tolyl). (The actual sequence of reactions leading from **4** to **2** will be discussed later after the correct structure for **2** has been established.)

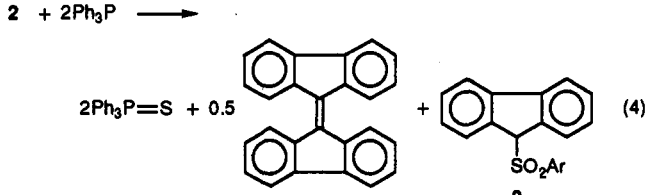


Several possible structures, **5**–**7** (R = 9-fluorenyl), can be suggested for **2**.



Three different experimental approaches have been pursued to obtain information regarding the correct structure for **2**: (1) Examination of the products formed when **2** was treated with triphenylphosphine; (2) comparison of the ^{13}C NMR spectrum of **2** with those of selected model compounds having structural features in common with **5**–**7**; (3) determination of the products resulting from the reaction of other substrates with **4**. The results from each approach will first be presented and then the collective evidence will be discussed in terms of its implications for the structure of **2**.

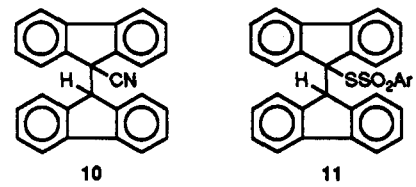
Reaction of 2 with Triphenylphosphine. Treatment of **2** (0.4 mmol) with triphenylphosphine (0.8 mmol) in acetonitrile at reflux for 3 h resulted in the formation of 0.15 mmol of difluorenylidene[6] (**8**), 0.28 mmol of *p*-tolyl 9-fluorenyl sulfone[7] (**9**, Ar = *p*-tolyl), and triphenylphosphine sulfide, eq 4. Sulfone **9** was also obtained when



2 was reacted with an equimolar amount of triphenylphosphine. A separate experiment showed that 9-thiofluorene reacts with triphenylphosphine to form $Ph_3P{=}S$ and **8** (eq 5). Thus, **2** apparently reacts with Ph_3P to give $Ph_3P{=}S$, **9**, and thiofluorenone, and the thioketone then reacts with additional Ph_3P as shown in eq 5 to give **8**.

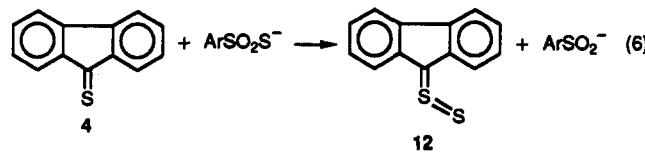
^{13}C NMR of Compounds Related Structurally to 5–7. The ^{13}C chemical shifts for the two C-9 carbons of the fluorenyl groups in **2** are at 53.58 and 79.63 ppm. The ^{13}C chemical shifts for the C-9 carbons in **10** and **11**, two compounds structurally related to **6**, are at 50.98 and 52.48 ppm (**10**) and 54.24 and 68.91 ppm (**11**). The ^{13}C chemical shift for the C-9 carbons in di-9-fluorenyl sulfide is 48.31 ppm.

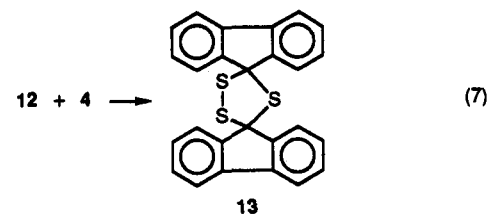
Reaction of Thiofluorenone with (a) Other Halides and Potassium *p*-Toluenethiosulfonate and (b) Thiosulfonate Esters and Sodium *p*-Toluenesulfinate. We first investigated the products formed when thiofluorenone (**4**) was allowed to react with *p*-$CH_3C_6H_4SO_2S^-$ in the presence of other halides than 9-bromofluorene.



Reaction of equimolar amounts of $(p\text{-}ClC_6H_4)_2CHBr$, 9-thiofluorenone, and potassium *p*-toluenethiosulfonate in acetonitrile at room temperature led to the formation of a product analogous to **2** (i.e., containing one aralkyl residue from the halide, a *p*-tolyl group, a fluorenyl residue from the thioketone, and three sulfur and two oxygen atoms). The yield was significantly lower (49%) than in the case of 9-bromofluorene. When *n*-propyl bromide was the halide no product analogous to **2** was obtained. Under such conditions the product isolated was spiro[bis(fluorene)-1,2,4-trithiolane][8] (**13**). A small amount of **13** was also isolated from the reaction involving (4,4′-dichlorodiphenyl)methyl bromide.

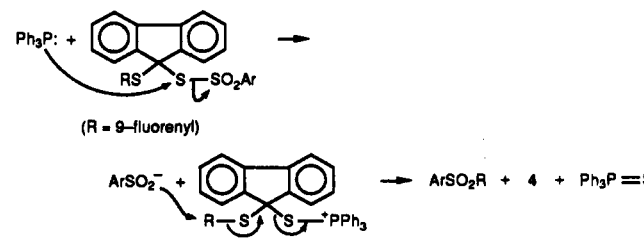
Huisgen and Rapp[8] have shown that thiofluorenone (**4**) can abstract a sulfur atom readily from certain species to form thiosulfine **12** and that **12** reacts readily with **4** to give **13**. Since a separate experiment showed that reaction of $ArSO_2SK$ (1 mmol) with **4** (2 mmol) gave **13** in 95% yield, the origin of **13** is presumed to be the reaction sequence in eqs 6 and 7.





The ^1H NMR spectrum of the product, **14** ($C_{33}H_{24}Cl_2O_2S_3$), from the reaction involving $(p\text{-}ClC_6H_4)_2CHBr$ showed a *p*-tolyl methyl group (δ 2.17), a singlet for the C*H* proton of the $(p\text{-}ClC_6H_4)_2CH$ group at δ 5.55, and 20 aromatic protons distributed as a set of doublets (δ 6.79 and 6.93, 2 H each) and multiplets (δ 7.21–7.56, 14 H; 8.11, 2 H). Strong bands in the infrared at 1317 and 1140 cm^{-1} indicated a sulfonyl group was part of the structure. In the ^{13}C NMR the chemical shift for the methine carbon of the $(p\text{-}ClC_6H_4)_2CH$ group was at 58.78 ppm, while δ for

(6) Trost, B. M.; Kinson, P. L. *J. Org. Chem.* **1972**, *37*, 1273.
(7) Bavin, P. M. G. *Can. J. Chem.* **1960**, *38*, 917.
(8) Huisgen, R.; Rapp, J. *J. Am. Chem. Soc.* **1987**, *109*, 902.
(9) Formation of **9** from **5** upon treatment with Ph_3P could *conceivably* happen in the following manner:



the C-9 carbon of the fluorenyl group was at 78.90 ppm.

(4,4'-Dichlorodiphenyl)methyl p-toluenethiosulfonate (1, Ar' = p-ClC_6H_4), prepared via eq 1,[3] did *not* react with 4 in acetonitrile at room temperature. However, when $CH_3C_6H_4SO_2^-$ was also present 14 was formed in 84% yield. Thus, although 4 and 1 (Ar' = p-ClC_6H_4) *alone* don't form 14, in the presence of p-$CH_3C_6H_4SO_2^-$ 14 is formed in excellent yield. This observation is valuable in clarifying the mechanism by which 2 is formed in the reaction of 9-bromofluorene with p-$CH_3C_6H_4SO_2S^-$.

The ^1H and ^{13}C NMR spectra of 2 and 14 indicate that these compounds have the same type of structure, the only difference being that the fluorenyl group of 2 that possesses a hydrogen at C-9 has been replaced by a p-$(ClC_6H_4)_2CH$– group in 14. Reaction of 14 (0.3 mmol) with Ph_3P (0.6 mmol) gave $Ph_3P{=}S$, 0.22 mmol of p-tolyl 9-fluorenyl sulfone (9), and $(p\text{-}ClC_6H_4)_2C{=}S$. The exact amount of thioketone formed was not determined.

Thiofluorenone, $ArSO_2SK$, and n-propyl bromide give only 13, no product analogous to 2 being formed. However, when the thiosulfonate n-$PrSSO_2Ar$ (1 mol) and 4 (2 mol) were allowed to interact in acetonitrile at room temperature in the presence of $ArSO_2Na$, a compound (15a), whose NMR and infrared spectra showed that it contained an n-propyl group, a p-tolylsulfonyl group, and a fluorenyl group doubly substituted at C-9 and that it had a structure analogous to 2 or 14, but whose elemental analysis ($C_{23}H_{22}O_2S_4$) indicated the presence of one additional dicoordinate sulfur, was isolated in 43% yield. A similar experiment using p-$O_2NC_6H_4CH_2SSO_2Ar$ as the thiosulfonate gave, in 82% yield, 15b ($C_{27}H_{21}NO_4S_4$), a compound whose NMR and infrared spectra showed that its structure was similar to 15a, but with the n-propyl group of 15a replaced by a p-nitrobenzyl group. An important byproduct of the reactions leading to 15a and 15b was p-tolyl 9-fluorenyl sulfone (9).

The origin of these products (15) with a structure akin to 2 and 14, but with one additional sulfur atom, will be discussed after settling the correct structure for 2 and the mechanism for its formation.

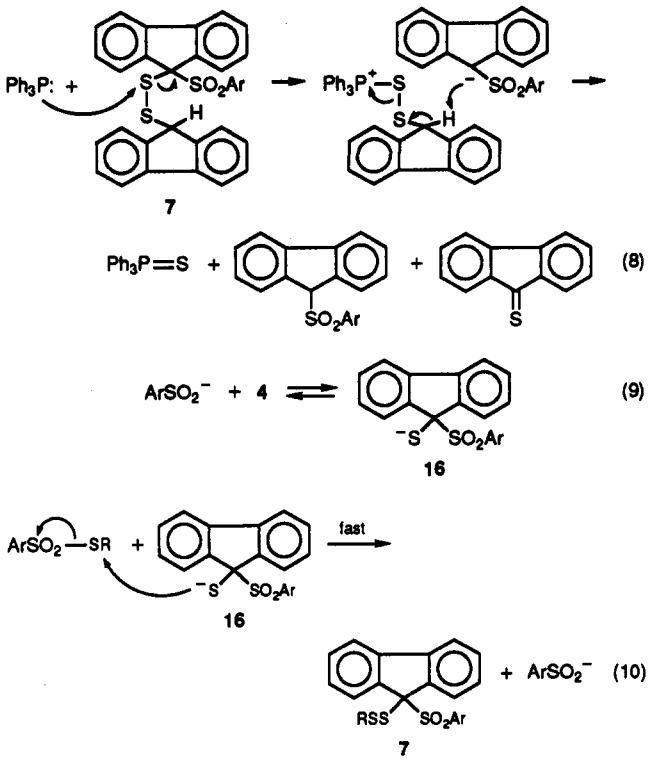
Structure of 2. The fact that treatment of 2 with Ph_3P gives p-tolyl 9-fluorenyl sulfone (9) in high yield (0.7 mmol/mmol of 2) is not compatible with 2 having structure 6. The ^{13}C chemical shift (79.63 ppm) for the tertiary 9-C in 2 also seems further downfield than would be expected for the tertiary 9-C in 6, given the chemical shift (68.91 ppm) for the analogous carbon in 11.

While it is possible to devise a reaction scheme (see ref 9) whereby reaction of Ph_3P with 5 could lead to 9, this scheme predicts that the same reaction with 14 would lead to p-chlorobenzhydryl p-tolyl sulfone. In actuality, reaction of Ph_3P with 14 also gives 9 in high yield. Thus, the behavior of the reaction of the phosphine is inconsistent with 14 having structure 5 (R = $[p\text{-}ClC_6H_4]_2CH$–).

On the other hand, the formation of 9 from 2 and 14 upon reaction with Ph_3P can be explained if 2 and 14 have structure 7. This is evident from the reaction sequence shown in eq 8.

The evidence therefore points to 2 (R = 9-fluorenyl) and 14 (R = $[p\text{-}ClC_6H_4]_2CH$–) having structure 7. Both are 9-(p-tolylsulfonyl)-9-fluorenyl disulfides.

Mechanism of Formation of 2 (7). Now that the structure of 2 has been established to be 7 (R = 9-fluorenyl), the mechanism for its formation remains to be determined. The fact that 4 and $(p\text{-}ClC_6H_4)_2CHSSO_2Ar$ form 14 (7, R = $(p\text{-}ClC_6H_4)_2CH$) in almost 85% yield in the presence of $ArSO_2^-$, but *not* in its absence, can be explained by the mechanism shown in eqs 9 and 10. This



involves reversible addition of the sulfinate ion to 4 to give the α-sulfonyl thiolate ion 16 (eq 9) followed by nucleophilic attack of this thiolate on the dicoordinate sulfur of the thiosulfonate (eq 10), a type of substitution that is known[10] to be generally very rapid. Note that eq 10 regenerates the arenesulfinate ion consumed in eq 9, so that the sequence of eqs 9–10 does not result in any net consumption of sulfinate ion.

When the system used to react with 4 is (p-$ClC_6H_4)_2CHBr$ plus $ArSO_2S^-$, the arenesulfinate required for eq 9 is generated by the reaction of 4 with $ArSO_2S^-$ (eq 6) that gives thiosulfine 12 plus $ArSO_2^-$. This is the reason that some 13, resulting from eq 7, is found in the product under those conditions. The thiosulfonate ($ArSO_2SR$, R = $(p\text{-}ClC_6H_4)_2CH$) needed for eq 10 is formed by reaction of $ArSO_2S^-$ with $(p\text{-}ClC_6H_4)_2CHBr$. The fact that the two key reagents required, $ArSO_2^-$ and $RSSO_2Ar$, have to be generated in situ leads to the yield of 14 being substantially lower (49%) than when $ArSO_2^-$ and the thiosulfonate are introduced directly (84%).

In the case of n-propyl bromide plus $ArSO_2S^-$, where the rate of reaction of the halide with $ArSO_2S^-$ (eq 1) is much slower than for $(p\text{-}ClC_6H_4)_2CHBr$,[12] the thiosulfonate $RSSO_2Ar$ is not formed rapidly enough, and the only reactions observed are the formation of $ArSO_2^-$ and thiosulfine 12 (eq 6) and the subsequent reaction of 12 with 4 (eq 7), leading to the formation of 13.

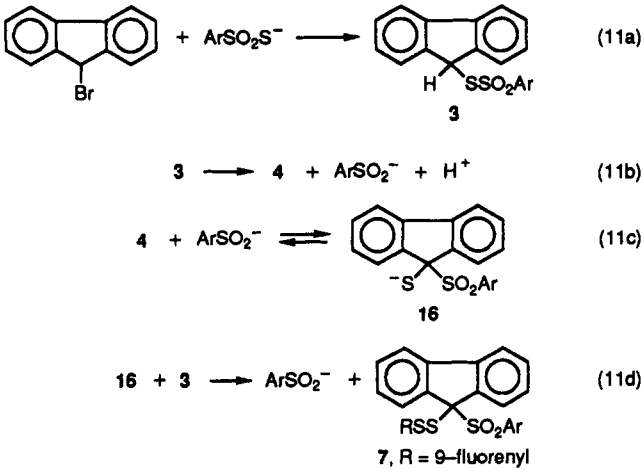
Unlike the other thiosulfonates, 3 (due to the acidity of the fluorenyl 9-H) is able to generate $ArSO_2^-$ quite readily by elimination (eq 2). As a result, in the 9-bromofluorene-$ArSO_2SK$ system, $ArSO_2^-$ doesn't have to be either added or generated (by eq 6) in order for the reaction to proceed. Furthermore, since the elimination that generates $ArSO_2^-$ from 3 also generates the required thioketone 4, all that is needed for a high yield of 7 in the

(10) (a) Parsons, T. F.; Buckman, J. D.; Pearson, D. E.; Field, L. *J. Org. Chem.* **1965**, *30*, 1923. (b) Kice, J. L.; Rogers, T. E. *J. Am. Chem. Soc.* **1974**, *96*, 8015.

(11) Birnie, J. M.; Campbell, N. *Proc. R. Soc. Edinburgh, Sect. A* **1969**, *68*, 120.

(12) Scholz, D. *Liebigs Ann. Chem.* **1984**, 259.

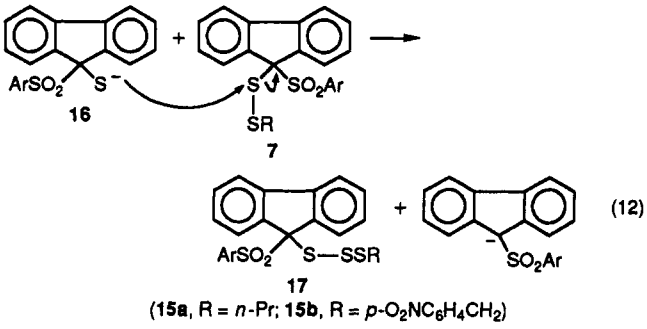
9-bromofluorene system is the aralkyl halide and $ArSO_2^-SK$. These two react together initially to form **3** (eq 11a); **3** undergoes elimination gradually to afford **4** and $ArSO_2^-$ (eq 11b); the arenesulfinate adds to the carbon of the C=S of **4** to give **16** (eq 11c); and **16** then reacts rapidly (eq 11d) with some of the remaining **3** to give **7** (R = 9-fluorenyl).



(11a) (11b) (11c) (11d)

For the system to lead to **7** in high yield the elimination in eq 11b, while occurring readily, must be slower than the rate of the other reactions in eq 11.

Structure and Mechanism of Formation of 15. Comparison of the ^1H and ^{13}C NMR and infrared spectra of **15a** and **15b** with those of **2** and **14** indicates that **15** differ from **2** and **14** by having a structure (**17**) in which a trisulfide functionality (RSSS–) has replaced the disulfide moiety (RSS–) present in **7**. These compounds are thought to be formed by the reaction of initially formed **7** with additional **16** in the manner shown in eq 12. The



(12)

(**15a**, R = *n*-Pr; **15b**, R = *p*-$O_2NC_6H_4CH_2$)

fact that 9-fluorenyl *p*-tolyl sulfone (**9**) is also a product in those reactions in which **17** is formed provides important support for eq 12 as the mechanism for the formation of **17**. Maximization of the yield of **17** requires the use of 2 mol of thiofluorenone per 1 mol of thiosulfonate $RSSO_2Ar$.

Models suggest that when R is a branched and relatively bulky secondary alkyl group, such as $(p\text{-}ClC_6H_4)_2CH$– or 9-fluorenyl, attack of **16** on the necessary sulfur in **7** is sterically hindered. This is thought to be the reason that formation of **17** is observed when R equals *n*-propyl or *p*-nitrobenzyl, but not when R is $(p\text{-}ClC_6H_4)_2CH$– or 9-fluorenyl.

Experimental Section

Reaction of 9-Bromofluorene with Potassium *p*-Toluenethiosulfonate. 9-Bromofluorene (1.23 g, 5 mmol) and 1.13 g (5 mmol) of $CH_3C_6H_4SO_2SK$ (Aldrich) in 30 mL of acetonitrile were stirred and heated at reflux for 4 h. About half the solvent was evaporated under reduced pressure, and the precipitate was filtered off, washed with 10 mL of acetonitrile, and then treated with chloroform. Most of the precipitate dissolved in chloroform. That which did not (KBr) was filtered off and washed with a little chloroform. The washings were added to the chloroform filtrate, and the chloroform was removed under reduced pressure, giving 1.24 g (91%) of 9-fluorenyl 9-(*p*-tolylsulfonyl)-9-fluorenyl disulfide (**2**, or **7**), mp 199–200 °C, after recrystallization from 5:1 acetonitrile–chloroform: IR (KBr) 1310 and 1145 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.20 (s, 3 H), 5.39 (s, 1 H), 6.83 (d, 2 H), 7.02 (d, 2 H), 7.26–7.65 (m, 10 H), 7.67 (d, 2 H), 7.86 (d, 2 H), 8.35 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.48, 53.58, 79.63, 120.00, 120.11, 125.53, 127.39, 127.50, 127.80, 128.31, 128.49, 129.70, 130.14, 132.37, 138.74, 140.38, 140.90, 143.68, 144.30; mass spectrum *m/e* 548 (M^+). Anal. Calcd for $C_{33}H_{24}O_2S_3$: C, 72.23; H, 4.41; S, 17.52. Found: C, 71.98; H, 4.37; S, 18.02.

Reaction of 9-Thiofluorenone with Potassium *p*-Toluenethiosulfonate and 9-Bromofluorene. 9-Thiofluorenone[5] (0.98 g, 5 mmol), $CH_3C_6H_4SO_2SK$ (1.13 g, 5 mmol), and 9-bromofluorene (1.23 g, 5 mmol) were added to 20 mL of acetonitrile, and the mixture was stirred at room temperature for 1.5 h. The precipitate that formed was filtered off, washed with a little acetonitrile, and then treated with chloroform. After filtration the chloroform was evaporated to give 2.70 g (99%) of **2**, mp 198–200 °C.

Reaction of 2 with Triphenylphosphine. A mixture of 0.22 g (0.4 mmol) of **2** and 0.21 g (0.8 mmol) of triphenylphosphine in 20 mL of acetonitrile was stirred and heated under reflux for 3 h. After the mixture was cooled to room temperature, 50 mL of water was added and the precipitate that separated was filtered off. Several recrystallizations of the precipitate, which was a mixture of Ph_3P=S and *p*-tolyl 9-fluorenyl sulfone (**9**), from ether–acetonitrile gave 0.09 g (0.28 mmol, 70%) of pure **9** as a white, crystalline solid: mp 224–226 °C (lit.[7] mp 226–228 °C); IR (KBr) 1290 and 1170 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ 2.19 (s, 3 H), 5.41 (s, 1 H), 6.83 (d, 2 H), 6.95 (d, 2 H), 7.39 (m, 6 H), 8.01 (m, 2 H).

The filtrate was extracted with chloroform, and the chloroform was evaporated to give an orange-red oil that was a mixture of **8** and Ph_3P=S. Column chromatography of this oil on silica gel using hexane–ethyl acetate as eluant afforded 0.050 g (0.15 mmol, 75%) of difluorenylidene (**8**), mp 184–186 °C (lit.[6] mp 186–187.5 °C).

Reaction of Thiofluorenone with Triphenylphosphine. 9-Thiofluorenone (0.20 g, 1 mmol) and triphenylphosphine (0.26 g, 1 mmol) were added to 20 mL of acetonitrile and heated at reflux for 3 h. The mixture was cooled to room temperature, and the precipitate of Ph_3P=S was filtered off. The filtrate was evaporated under reduced pressure, and the residue was subjected to column chromatography (SiO_2) using hexane–ethyl acetate as eluant. There was obtained 0.10 g (63%) of difluorenylidene[6] (**8**), mp 184–186 °C.

Reaction of Difluorenylidene with Cyanide. Difluorenylidene (0.09 g, 0.27 mmol) was dissolved in 15 mL of DMSO, and 0.14 g (2.7 mmol) of sodium cyanide and 1.37 mL of 1 N perchloric acid were added. The mixture was refluxed for 0.5 h and cooled to room temperature, 100 mL of water was added, and the mixture was extracted with ethyl acetate. The extracts were dried ($MgSO_4$), and the solvent was removed under reduced pressure. Crystallization of the residue from chloroform–hexane gave 0.05 g (77%) of 9-cyano-9,9′-bifluorene (**10**), mp 228–229 °C (lit.[11] mp 228 °C): IR (KBr) 2240 cm^{-1} (CN); ^1H NMR ($CDCl_3$) δ 4.81 (s, 1 H), 7.05–7.55 (m, 16 H); ^{13}C NMR ($CDCl_3$) δ 50.98, 52.48, 119.52, 120.15, 121.32, 124.21, 125.27, 126.81, 127.80, 128.42, 129.48, 140.71, 140.82, 141.92. Anal. Calcd for $C_{27}H_{17}N$: C, 91.24; H, 4.82. Found: C, 90.88; H, 4.96.

Reaction of (4,4′-Dichlorodiphenyl)methyl Bromide with 4 and Potassium *p*-Toluenethiosulfonate. Thiofluorenone (0.98 g, 5 mmol), $CH_3C_6H_4SO_2SK$ (1.13 g, 5 mmol), and (4,4′-dichlorodiphenyl)methyl bromide[3a] (1.58 g, 5 mmol) were added to 30 mL of acetonitrile and stirred at room temperature for 2.5 h. The initial dark green suspension gradually changed to a light yellow solution containing a white precipitate. The precipitate was filtered off, washed with a little acetonitrile, and then treated with chloroform. The part of the precipitate that did not dissolve in $CHCl_3$ (KBr) was removed by filtration. The chloroform filtrate was evaporated, giving a residue that was a mixture of **14** and **13**. These two compounds were separated by a series of fractional crystallizations from acetonitrile–chloroform (5:1). There was obtained 0.12 g (0.3 mmol) of spiro[bis(fluorene)-1,2,4-trithiolane]

(13), mp 180–185 °C dec (lit.[8] mp 185–186 °C dec) and 1.53 g (2.5 mmol, 49%) of (4,4′-dichlorodiphenyl)methyl 9-(p-tolylsulfonyl)-9-fluorenyl disulfide (14), mp 191–192 °C dec: IR (KBr) 1317 and 1140 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ 2.17 (s, 3 H), 5.55 (s, 1 H), 6.79 (d, 2 H), 6.93 (d, 2 H), 7.21–7.56 (m, 14 H), 8.11 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.45, 58.78, 78.90, 120.07, 127.50, 127.83, 128.38, 128.86, 129.74, 130.21, 130.39, 132.22, 133.54, 137.93, 138.74, 140.75, 144.37. Anal. Calcd for $C_{33}H_{24}Cl_2O_2S_3$: C, 63.97; H, 3.90; S, 15.52. Found: C, 63.94; H, 4.15; S, 15.55.

Evaporation of the acetonitrile filtrate from the reaction mixture gave a residue that was recrystallized from ether to give 0.76 g (1.8 mmol) of (4,4′-dichlorodiphenyl)methyl p-toluenethiosulfonate, mp 122–125 °C (lit.[3] mp 123–125 °C).

Reaction of Thiofluorenone with (4,4′-Dichlorodiphenyl)methyl p-Toluenethiosulfonate. Thiofluorenone (0.20 g, 1.0 mmol), (4,4′-dichlorodiphenyl)methyl p-toluenethiosulfonate[3] (0.21 g, 0.5 mmol) and 0.09 g of sodium p-toluenesulfinate (Aldrich) were added to 20 mL of acetonitrile, and the mixture was stirred at room temperature for 2 h. At the end of that time the mixture was filtered, and the filtrate was evaporated to about half its original volume. The material that precipitated out during the evaporation was filtered off and recrystallized from acetonitrile–chloroform. There was obtained 0.26 g (84%) of 14, mp 191–192 °C dec.

In a separate experiment, 0.04 g (0.21 mmol) of thiofluorenone and 0.09 g (0.21 mmol) of (4,4′-dichlorodiphenyl)methyl p-toluenethiosulfonate were added to 10 mL of acetonitrile and the suspension was stirred at room temperature for 5 h. Evaporation of the solvent and examination of the residue by ^1H NMR showed that no reaction had occurred and no 14 had been formed.

Reaction of Thiofluorenone with Potassium p-Toluenethiosulfonate. A mixture of 0.20 g (1 mmol) of 4 and 0.11 g (0.5 mmol) of $CH_3C_6H_4SO_2SK$ in 20 mL of acetonitrile was stirred at room temperature for 2 h. Water (20 mL) was added, and the cream-colored precipitate was filtered off and dried, giving 0.20 g (95%) of 13, mp 182–185 °C.

Compound 13 (1.0 g, 2.4 mmol) was also obtained when 5 mmol of n-propyl bromide, 5 mmol of thiofluorenone, and 5 mmol of potassium p-toluenethiosulfonate were stirred in 30 mL of acetonitrile for 3 h at room temperature.

Reaction of Thiofluorenone with n-Propyl p-Toluenethiosulfonate. Thiofluorenone (1.96 g, 10 mmol), 1.15 g (5 mmol) of n-propyl p-toluenethiosulfonate[12] (prepared by the reaction of n-propyl bromide with $CH_3C_6H_4SO_2SK$[3]), and 0.89 g of sodium p-toluenesulfinate were added to 50 mL of acetonitrile, and the mixture was stirred at room temperature for 2 h. The reaction mixture was filtered, and the filtrate was evaporated under reduced pressure. The residue was chromatographed on silica gel using hexane–methylene chloride as the eluant. After recrystallization from methanol there was obtained 0.98 g (43%) of 15a, mp 95–96 °C: IR (KBr) 1315, 1285 and 1145 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ 0.90 (t, 3 H), 1.60 (m, 2 H), 2.17 (s, 3 H), 2.67 (t, 2 H), 6.79 (d, 2 H), 6.93 (d, 2 H), 7.26–7.60 (m, 6 H), 8.16 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 12.96, 21.41, 22.03, 41.87, 79.01, 120.00, 127.39, 127.61, 128.23, 129.74, 129.92, 132.48, 138.81, 140.75, 144.12. Anal. Calcd for $C_{23}H_{22}O_2S_4$: C, 60.23; H, 4.83. Found: C, 60.86; H, 5.01.

Examination of the ^1H NMR of the crude product prior to chromatography showed the presence of p-tolyl 9-fluorenyl sulfone as an important additional reaction product.

Reaction of Thiofluorenone with p-Nitrobenzyl p-Toluenethiosulfonate. Thiofluorenone (0.20 g, 1.0 mmol), p-nitrobenzyl p-toluenethiosulfonate[13] (0.16 g, 0.5 mmol), and 0.09 g (0.50 mmol) of sodium p-toluenesulfinate were stirred in acetonitrile (20 mL) at room temperature for 2 h. The reaction mixture was then filtered, and the filtrate was evaporated to about half its original volume. The material that had precipitated was filtered off and recrystallized (acetonitrile–chloroform). There was obtained 0.23 g (82%) of p-nitrobenzyl 9-(p-tolylsulfonyl)-9-fluorenyl trisulfide (15b), mp 174–175 °C: IR (KBr) 1520, 1345 (NO_2), 1310, 1140 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ 2.18 (s, 3 H), 4.21 (s, 2 H), 6.80 (d, 2 H), 6.92 (d, 2 H), 7.26–7.55 (m, 10 H), 8.18 (m, 2 H); ^{13}C NMR ($CDCl_3$) δ 21.45, 43.00, 78.35, 120.15, 123.70, 126.33, 127.36, 127.80, 128.34, 129.66, 130.21, 130.47, 132.11, 138.41, 140.64, 144.37, 154.22. Anal. Calcd for $C_{27}H_{21}NO_4S_4$: C, 58.78; H, 3.84; N, 2.54. Found: C, 58.32; H, 3.76; N, 2.56.

Remaining in the acetonitrile solution after removal of 15b was p-tolyl 9-fluorenyl sulfone (9).

Reaction of Triphenylphosphine with 14. Triphenylphosphine (0.6 mmol) and 14 (0.3 mmol) were added to 20 mL of acetonitrile and heated under reflux for 2.5 h. Formation of $(p\text{-}ClC_6H_4)_2C{=}S$ was indicated by the development of a dark blue-green color. The reaction mixture was subsequently cooled to room temperature, 50 mL of water was added, and the precipitate was filtered off. Recrystallization of the precipitate from ether–acetonitrile gave 0.21 mmol of 9, mp 224–226 °C (identical in all respects with the material isolated from the reaction of 2 with Ph_3P). Spectrophotometric examination of the precipitate prior to recrystallization indicated the presence of sizeable amounts triphenylphosphine sulfide.

Preparation of 9-Bromo-9,9′-bifluorene. 9-Hydroxy-9,9′-bifluorene was prepared in 69% yield from fluorene and 9-fluorenone using the procedure described by Minabe and Suzuki,[14] mp 194–196 °C (lit.[15] mp 195–196 °C). The alcohol was converted to 9-bromo-9,9′-bifluorene in 64% yield using the procedure of Carey et al.,[15] mp 163–165 °C (lit.[15] mp 165–166 °C).

Preparation of Thiosulfonate 11. Potassium p-toluenethiosulfonate (0.67 g, 3 mmol) and 9-bromo-9,9′-bifluorene (1.23 g, 3 mmol) were added to 20 mL of acetonitrile, and the mixture was stirred and heated at reflux for 3 h. The precipitate of potassium bromide was filtered off, and the acetonitrile was evaporated under reduced pressure. The residue was recrystallized first from ether and then from acetonitrile–ether (1:2), affording 0.57 g (37%) of thiosulfonate 11, mp 174–175 °C dec: IR (KBr) 1330 and 1140 cm^{-1} (SO_2); ^1H NMR ($CDCl_3$) δ 2.32 (s, 3 H), 4.94 (s, 1 H), 6.85–7.48 (m, 20 H); ^{13}C NMR ($CDCl_3$) δ 21.52, 54.24, 68.91, 119.20, 119.52, 124.90, 126.19, 126.48, 126.73, 127.03, 127.98, 128.60, 129.04, 129.70, 140.48, 141.45, 142.07, 142.80, 143.68. Anal. Calcd for $C_{33}H_{24}O_2S_2$: C, 76.71; H, 4.68; S, 12.41. Found: C, 76.06; H, 4.89; S, 12.30.

Registry No. 1 (Ar′ = C_6H_4Cl-p), 93454-46-7; 2, 135561-65-8; 3, 135561-66-9; 4, 830-72-8; 8, 746-47-4; 9, 102001-66-1; 10, 17454-96-5; 11, 135561-67-0; 13, 164-79-4; 14, 135561-68-1; 15a, 135561-69-2; 15b, 135561-70-5; Ph_3P, 603-35-0; $p\text{-}MeC_6H_4SO_2SK$, 28519-50-8; $(p\text{-}ClC_6H_4)_2CHBr$, 6306-46-3; $p\text{-}MeC_6H_4SO_2SPr$, 90494-81-8; $p\text{-}MeC_6H_4SO_2SCH_2C_6H_4NO_2\text{-}p$, 31378-00-4; 9-bromofluorene, 1940-57-4; difluorenylidene, 746-47-4; 9-bromo-9,9′-bifluorene, 13295-92-6; 9-hydroxy-9,9′-bifluorene, 981-46-4; fluorene, 86-73-7; 9-fluorenone, 486-25-9.

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