chlorotoluene, and 50 mL of ethanol. The mixture was stirred and heated to 50 °C, 0.2 g of 10% Pd/C catalyst (50% water, 0.09 mmol Pd) was added, and the heterogeneous system was mixed for 1 h at the above temperature. After being cooled, the aqueous phase was separated, the solvent evaporated under vacuum, and the crude product washed with water and distilled. Pure toluene (4.18 g; 91%) was obtained.

Registry No. PhCl, 108-90-7; p-MeC_6H_4Cl, 106-43-4; m-MeC_6H_4Cl, 108-41-8; p-ClC_6H_4Cl, 106-46-7; p-BrC_6H_4Cl, 106-39-8; p-$H_2NC_6H_4Cl$, 106-47-8; PhBr, 108-86-1; p-MeC_6H_4Br, 106-38-7; o-MeC_6H_4Br, 578-57-4; PhI, 591-50-4; PhF, 462-06-6; p-$IC_6H_4NO_2$, 636-98-6; p-$O_2NC_6H_4Me$, 99-99-0; $PhCH{=}CH_2$, 100-42-5; p-$FC_6H_4NO_2$, 350-46-9; $PhNO_2$, 98-95-3; $PhC{\equiv}CH$, 536-74-3; $HCO_2H{\cdot}K$, 590-29-4; Pd, 7440-05-3.

Oxyfunctionalization of Hydrocarbons. 17.[1] Acid-Dependent High Regioselectivity Hydroxylation of Naphthalene with Hydrogen Peroxide Giving 1- or 2-Naphthol

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The acid-catalyzed hydroxylation of naphthalene with 90% hydrogen peroxide was investigated. Regioselectivity of the reaction depends on the acidity of the system and the solvent used. In anhydrous hydrogen fluoride or 70% HF–30% pyridine solution at −10 to +20 °C 1-naphthol is the product formed in >98% selectivity. In contrast, 2-naphthol is obtained in hydroxylation in superacid ($HF–BF_3$, $HF–SbF_5$, $HF–TaF_5$, $FSO_3H–SbF_5$) solution at −60 to −78 °C in >98% selectivity. When 1-naphthol reacted under the latter conditions 1,5- and 1,7-dihydroxynaphthalene were obtained, while 2-naphthol gave 1,6-dihydroxynaphthalene (along with only minor amounts of 1,7-dihydroxynaphthalene). The mechanism of the reactions is discussed, contrasting electrophilic hydroxylation of naphthalene, giving predominantly 1-substitution, with reaction of protonated naphthalenes (i.e., naphthalenium ions) with hydrogen peroxide.

Introduction

Studies of electrophilic aromatic oxygenation using various peroxide reagents have been reported. These include hydrogen peroxide in the presence of sulfuric acid[2] or boron trifluoride etherate,[3] peracids,[4] peracids with Lewis acid promoters,[5] diisopropyl peroxydicarbonate,[6] aroyl peroxides,[7] dicyclohexyl peroxydicarbonate–ferric chloride,[8] alkyl peroxides,[9] and dialkyl peroxides.[10] More recently, effective electrophilic hydroxylation of aromatics was carried out using hydrogen peroxide and hydrogen fluoride,[11] aluminum chloride[12] or superacid catalysts.[13] Application of hydrogen peroxide with pyridinium polyhydrogen fluoride was also described.[14]

Few reports appeared in the literature on the direct hydroxylation of naphthalene. Williams et al. have reported the reaction of aroyl peroxides with naphthalene via homolytic substitution.[15] Friedel–Crafts oxygenation of naphthalene with diisopropyl peroxydicarbonate gives a low yield of naphthols. Vesely and Schmering reported hydroxylation with hydrogen peroxide–hydrogen fluoride under carbon dioxide pressure.[11]

In our continued study of electrophilic oxyfunctionalization of hydrocarbons, we report now the investigation of the acid-catalyzed hydroxylation of naphthalene with 90% hydrogen peroxide and the surprising observation of extremely high regioselectivity in obtaining either 1- or 2-naphthol, dependent on the acidity of the catalyst systems and the solvent used.[16]

Results and Discussion

Naphthalene was treated with 90% hydrogen peroxide at temperatures between −78 and 0 °C in solutions of various acids and superacids such as fluorosulfuric acid–sulfuryl chloride fluoride, fluorosulfuric acid–sulfur dioxide, fluorosulfuric acid, fluorosulfuric acid–methylene chloride, fluorosulfuric acid–antimony pentafluoride (1:1) sulfuryl chloride fluoride, hydrogen fluoride, hydrogen fluoride–sulfuryl chloride fluoride, 70% hydrogen fluoride–30% pyridine, hydrogen fluoride–boron trifluoride, hydrogen fluoride–tantalum pentafluoride, hydrogen fluoride–antimony pentafluoride, and trifluoromethanesulfonic acid–sulfuryl chloride fluoride. 1- and 2-naphthol were obtained, together with some dihydroxynaphthalenes and poly-

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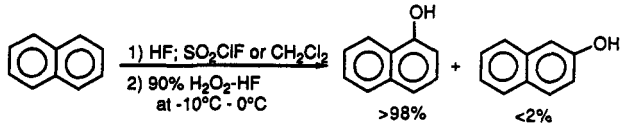
0022-3263/91/1956-6148$02.50/0

Table I. Superacid-Catalyzed Hydroxylation of Naphthalene with 90% H_2O_2

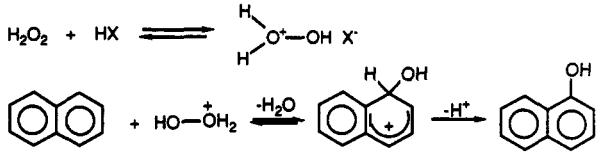
solvent for H_2O_2	solvent for naphthalene	reaction temp, °C	% yield naphthols	% normalized naphthol isomer distribution: 1-naphthol	% normalized naphthol isomer distribution: 2-naphthol	1,6-dihydroxy-naphthalene	polymeric (oxylized) byproduct
FSO_3H (2)/SO_2ClF	FSO_3H (2)/SO_2ClF	-78	49	38.6	61.4		4.7
FSO_3H (2)/SO_2 (2)	FSO_3H (2)/SO_2 (2)	-78	82	66.6	33.4		7.8
FSO_3H (2)	FSO_3H (4)	-78	40	7.5	92.5	18.5	4.7
FSO_3H-SbF_5 (1:1) (2)/SO_2ClF (2)	FSO_3H-SbF_5 (1:1) (2)/SO_2ClF (2)	-78	59	7.5	92.5	5.8	trace
FSO_3H (2)/SO_2ClF (2)	SO_2ClF (2)	-78	74	65.7	34.3		15.6
FSO_3H (2)	CH_2Cl_2 (2)	-78	67	66.2	33.8		15.6
HF (2)	HF (4)	-10 to 0	43	98.4	1.6		9.4
HF (3)	SO_2ClF (2)	-78	15	68.7	31.3		6.3
70% HF/30% pyridine	70% HF/30% pyridine	0 to 20	26	98.4	1.6	9.5	1.2
HF-BF_3 (4)	HF-BF_3 (4)	-78	49	18	82	6	9.4
HF-BF_3 (4)	HF-BF_3 (4)	-60	64	5	95	1.5	16.0
HF-BF_3 (4)	HF-BF_3 (4)	-50	53	2	98	18.7	12.5
HF-BF_3 (4)	HF-BF_3 (4)	-40	17	3	93	51.8	31.3
CF_3SO_3H	CF_3SO_3H-SO_2ClF	-50	80	62	38		17.2
HF-SbF_5	HF-SbF_5	-78	50	1.8	98.2		
HF-TaF_5	HF-TaF_5	-78	39	3	97		

meric/oxydized materials. The isomer distribution and yield of naphthols obtained are summarized in Table I.

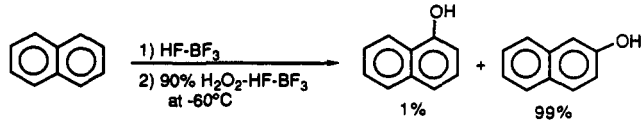
The isomer distribution of naphthols depends on the acid medium used and the sequence of addition of the reagents. When 90% hydrogen peroxide in anhydrous hydrogen fluoride or in 70% HF-30% pyridine solution was added to a solution of naphthalene in methylene chloride (or its suspension in hydrogen fluoride or sulfuryl chloride fluoride) at 0–20 °C, a 26–43% yield of naphthols was obtained containing nearly exclusively (>98%) 1-naphthol with <2% 2-naphthol after workup. The reaction indicates typical electrophilic substitution of naphthalene.



It has been recognized that the actual electrophilic hydroxylating agent in hydrogen peroxide–acid systems is the hydroperoxonium ion ($H_3O_2^+$, i.e., protonated hydrogen peroxide)[12] accounting for the mechanism.



In contrast, when a solution of 90% hydrogen peroxide in a superacid (HF-BF_3, HF-SbF_5, HF-TaF_5, FSO_3H, FSO_3H-SbF5, HF-SbF_5) was added to a solution of naphthalene in the same superacid at low temperature (-60 to -78 °C), the isomer distribution of 40–59% of naphthols obtained showed a nearly complete change to 2-naphthol, i.e., 99% 2-naphthol and 1% of 1-naphthol (together with 1.5% of 1,6-dihydroxynaphthalenes).



In the reaction at more elevated temperatures, the yield of the dihydroxylated as well as polymeric products increased. Similar results were obtained in reactions in other superacid media, except that when using fluorosulfuric acid where sulfonation and oxidation also take place.

It was previously recognized that the nature of the products in the sulfonation or Friedel–Crafts reactions of naphthalene depend on the reaction conditions, particularly the reaction temperature and solvents used. Kinetically controlled electrophilic reactions tend to give the 1-substituted products, whereas thermodynamically influenced reversible reactions, as well as those subject to steric hindrance by peri positions, result in increased 2-substitution.

To explain the observed drastic change in the regioselectivity from 1- to 2-naphthol in the hydroxylation of naphthalene the following possibilities can be considered: rearrangement of the hydroxyl group from the 1-position to the thermodynamically more stable 2-position; steric retardation of the attack at the 1-position by peri-hydrogen interaction with a bulky solvated reagent; nucleophilic quenching of protonated naphthalene (i.e., naphthalenium ion) by hydrogen peroxide (σ-substitution), or electrophilic hydroxylaftion of the naphthalenium ion in the unprotonated ring.

To differentiate the possibilities and eliminate pathways in control experiments we found that in hydrogen fluoride–boron trifluoride solution from -78 to 0 °C neither 1- nor 2-naphthol isomerized to the other. If the bulkiness of the solvated hydroxylating reagent were reponsible for a formation of 2-naphthol, adding a solution of hydrogen peroxide in superacid to a solution of naphthalene in either methylene chloride or superacid should give predominantly 2-naphthol. However, hydroxylation in methylene chloride solution resulted in much increased 1-naphthol formation. In contrast, in neat superacid 2-naphthol is the predominant product.

It is well-known that aromatics in superacidic media are easily protonated to form stable arenium ions. ^{13}C NMR spectroscopy is particularly useful in elucidating the structure of carbocationic intermediates under superacidic, stable ion conditions. The ^{13}C NMR spectrum of the red solution of naphthalene in hydrogen fluoride–boron trifluoride at -78 °C recorded before adding a solution of hydrogen peroxide in the same acid indicated formation of 1-protonated naphthalenium ion (A) (being identical with the previously reported spectrum[17]).

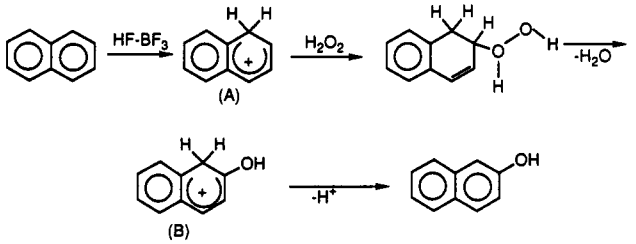
A possible explanation for the nearly exclusive formation of 2-naphthol in the reaction in superacidic media is that hydrogen peroxide still present in equilibrium with the

(17) Olah, G. A.; Staral, J. S.; Asencio, G.; Liang, G.; Forsyth, D. A.; Mateescu, G. D. *J. Am. Chem. Soc.* 1978, *100*, 6299.

Table II. Hydroxylation of Naphthols by 90% H_2O_2 in HF-BF_3

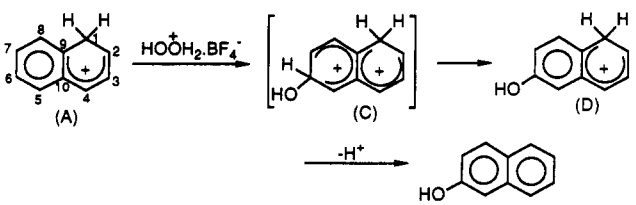
naphthol	reaction temp, °C	time, min	product	yield, %	recovered naphthol, %
1-naphthol	-78	30			99
1-naphthol	-50	30	1,5-dihydroxynaphthalene	2.7	95
			1,7-dihydroxynaphthalene	2.2	
2-naphthol	-78	30			quant
2-naphthol	-50	30	2,6-dihydroxynaphthalene	18.5	80.5
			1,7-dihydroxynaphthalene	1.0	

protonated hydroperoxonium ion acts as a nucleophilic reagent at the 2-position of A to give 1-protonated 2-hydroxynaphthalenium ion (B) followed by the deprotonation to 2-naphthol (σ-substitution, using Kovacic's terminology[18]).



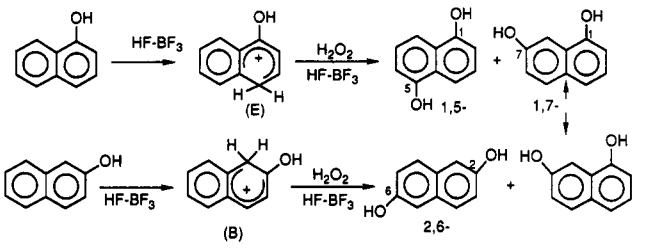
In superacidic media, however, the concentration of unprotonated hydrogen peroxide would be low. Furthermore, if this mechanism were operating, the intermediate hydroxynaphthalenium ion B could also undergo nucleophilic attack by hydrogen peroxide at the ring already containing a hydroxyl group. The dihydroxylated compound obtained was, however, only 1,6-dihydroxynaphthalene, nor was 1,2- or 1,4-naphthoquinone detected in the reaction products. 2-Naphthol is also easily protonated by hydrogen fluoride-boron trifluoride to form the naphthalenium ion B. When treated with 90% hydrogen peroxide in hydrogen fluoride–boron trifluoride at -50 °C, it gives 2,6- and 1,7-dihydroxynaphthalenes (Table II). These observations make nucleophilic attack on the naphthalenium ion by unprotonated hydrogen peroxide in superacidic solutions ion improbable.

There also exists the possibility of the electrophilic hydroxylating agent attacking the unprotonated ring of the naphthalenium ion A. Consideration of the ^{13}C NMR chemical shifts of naphthalenium ion A compared with naphthalene indicates that significant charge is localized in the ion at C_2 and C_4 and lesser charge at the formally conjugated C_5, C_7 and C_9 positions. Electrophilic attack by protonated hydrogen peroxide would be depressed not only by overall charge–charge repulsion, but also by the counter ion BF_4^-, which will be attracted to the vicinity of the positively charged ring. Due to additional steric hindrance of C_8 by peri-interaction, only electrophilic attack at C_6 to give the dicationic intermediate C would be preferred followed by deprotonation, giving 2-naphthol.



The hydroxylation of naphthalene with excess of 90% hydrogen peroxide in hydrogen fluoride–boron trifluoride at -40 °C gave 1,6-dihydroxynaphthalene in 51.8% yield, together with 1-naphthol (0.5%) and 2-naphthol (16%). In contrast, 1-naphthol at -50 °C gave 1,5- and 1,7-dihydroxynaphthalenes, while 2-naphthol gave 2,6-dihydroxynaphthalene, along with minor amounts of 1,7-dihydroxynaphthalene (Table II).

The orientation for the hydroxylation of naphthols can be best interpreted in terms of electrophilic attack by the hydroxylating agent at the positions with least positive charge localization in the corresponding naphthalenium ions.



Formation of 1,6-dihydroxynaphthalene in the hydroxylation of naphthalene consequently might occur by secondary electrophilic attack by the hydroxylating agent on the intermediate D.

The acid-catalyzed hydroxylation of naphthalene in sulfur dioxide solution preferentially gives 1-naphthol. It is known that strongly solvated carbocations are formed from alkyl fluoride–antimony pentafluoride systems in sulfur dioxide solution.[19] Thus, in sulfur dioxide solution the naphthalenium ion may be also strongly solvated with the positive charge less delocalized into the ring system resulting in preferential α-attack by the electrophile.

In summary, the acid-catalyzed hydroxylation of naphthalene with 90% H_2O_2 was found to give, depending on the acidity of the system and solvent used, in very high regioselectivity either 1- or 2-naphthol. The mechanistic aspects of these reactions were also studied.

Experimental Section

Naphthalene (Matheson) and 1- and 2-naphthol (Mallinckrodt) were commercial products of high purity. Hydrogen peroxide (90%) was obtained from the FMC Co. HF (Harshaw), BF_3 (Matheson), SO_2, SO_2, SO_2ClF, and CH_2Cl_2 were also commercially available. Antimony pentafluoride and fluorosulfuric acid were double distilled and stored in Teflon bottles.

Gas chromatographic analyses of trimethylsilylated naphthols were carried out using a column packed with 5% OV 101 on chromosorb W. The retention times (in s) using a column temperature of 154 °C and the pressure of 53 psi of trimethylsilylated naphthols were the following (showing the positions of TMSO groups) 1, 673; 2, 740; 1,4, 1079; 1,6, 1099; 1,7, 1123; 1,5, 1208; 2,7, 1460; 2,6, 1511 (s).

Hydroxylation of Naphthalene with 90% H_2O_2–FSO_3H or H_2O_2–HF. To a vigorously stirred solution of naphthalene (0.64 g, 5 mmol) in dichloromethane (2 mL) was added a solution of 90% H_2O_2 in fluorosulfuric acid (2 mL) dropwise at given temperatures (kept constant by external cooling). Hydroxylation with HF systems were similarly carried out with compositions and proportions indicated in Table I. It was noted that when HF or SO_2ClF were used as solvents, naphthalene did not completely dissolve and the reactions were carried out in a well-stirred but heterogeneous systems. After a 30-min reaction time, the reaction mixture was quenched with ice–water and extracted with ether. A small amount of insoluble material that formed was removed by filtration. The combined ether extracts were washed with 5%

(18) (a) Olah, G. A. *Friedel-Crafts Chemistry*; Wiley-Interscience: New York, 1973; p 203.

(19) Olah, G. A.; Donovan, D. J. *J. Am. Chem. Soc.* **1978**, *100*, 5163; **1964**, *86*, 1650; **1965**, *87*, 1262; **1966**, *88*, 1000, 3819.

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*-$CH_3C_6H_4SO_2^-$.

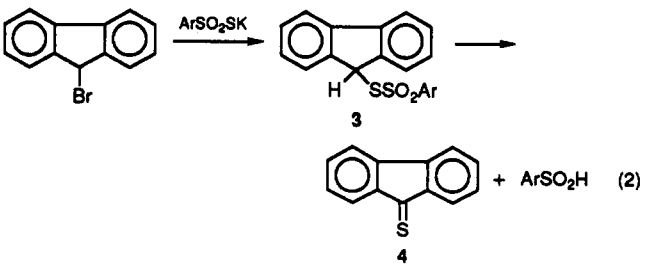
Reaction of potassium *p*-toluenethiosulfonate with a diarylmethyl bromide normally leads (eq 1) to the formation of a diarylmethyl *p*-toluenethiosulfonate (**1**).[2,3] We were therefore surprised to discover that when 9-bromofluorene was used the product was *not* 9-fluorenyl *p*-toluenethiosulfonate. 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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