5-Arylthianthreniumyl Perchlorates as a Benzyne Precursor

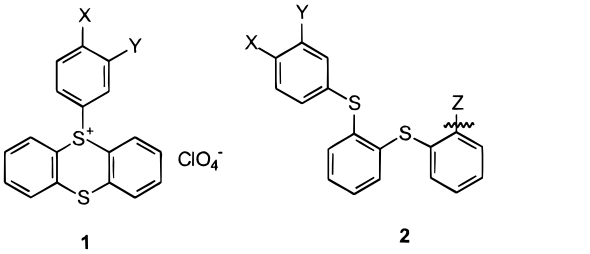
Kab Sig Kim, Sung Min Ha, Jong Yup Kim, and Kyongtae Kim*

Department of Chemistry, Seoul National University, Seoul 151-742, Korea

Received February 19, 1999

Introduction

It has been reported that 5-arylthianthreniumyl perchlorates **1**, prepared from thianthrene cation radical perchlorate and aromatics having an electron-donating group in acetonitrile at room temperature, can be utilized as useful starting materials for the synthesis of numerous polyarylthioethers such as 2-(alkyl and arylthio)-2′-(arylthio)diphenyl sulfides **2a** and bis[2-[2-(arylthio)-phenylthio]]diphenyl sulfides **2b**.[1]



compound **1** compound **2**

In a continuation of our study exploring the synthetic utility of **1**, we are now interested in the synthesis of azacrown compounds **2c**, which may be useful model compounds for studying the effects of a lariat consisting of arylthio groups in complexation with metal ions[2] by the foregoing method.

For preliminary information, compound **1a** (X = OMe, Y = H) was treated with diethylamine, whose structure around the nitrogen atom is similar to that of **2c**, and **2c** in the presence of LDA in THF at reflux. We now wish to disclose the findings from these reactions.

Results and Discussion

LDA (2 M in *n*-hexane) was added dropwise into a mixture of **1a** and diethylamine in THF at reflux under a nitrogen atmosphere. Since a considerable amount of LDA would be expected to deteriorate at a high reaction temperature, the addition of the same amount of LDA was repeated four times every 40−50 min. From the reaction mixture were obtained thianthrene (**3**) (8%), 2-(4-anisylthio)-3′-(diethylamino)diphenyl sulfide (**4a**) (57%), and 2-(4-anisylthio)-2′-(diethylamino)diphenyl sulfide (**5a**) (11%) (Scheme 1).

Scheme 1

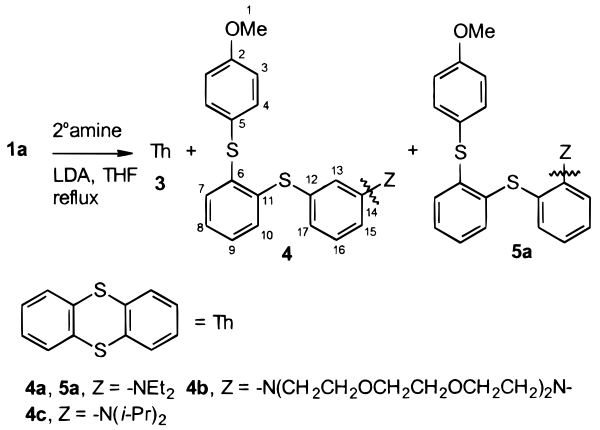


Table 1. Characteristic ^{1}H (300 MHz) and ^{13}C (75 MHz) NMR Spectral Data of 4 and 5 in $CDCl_3$

		^{13}C NMR (δ, ppm)	
compd	^{1}H NMR (δ, ppm)	C-11	C-12
4a	7.12 (t, J = 8.20 Hz, *H*C-16)	135.50	136.53
5a	6.63 (d, J = 8.06 Hz, *H*C-14) 6.72 (d, J = 7.75 Hz, *H*C-17)	136.18	130.55
4b	7.14 (t, J = 7.93 Hz, *H*C-16 and *H*-C′-16)	134.15	135.58
4c	7.13 (t, J = 8.12 Hz, *H*C-16)	134.39	135.06

Compounds **4a** and **5a** were liquids, and their structures were determined on the basis of spectroscopic (IR, ^{1}H and ^{13}C NMR) and analytical data. ^{1}H and ^{13}C NMR spectral data are particularly informative regarding the structure of **4a** (Table 1).

Close examination of the ^{1}H NMR spectra of **4a** and **5a** revealed that **4a** exhibited a triplet (*H*C-16 couples with *H*C-15 and *H*C-17), whereas **5a** exhibited two doublets (*H*C-14 and *H*C-17 couple with *H*C-15 and *H*C-16, respectively). It is interesting to note that the ^{13}C NMR band of C-12 of **5a** showed an upfield shift of about 5 ppm in comparison with that of **4a** owing to the presence of an ortho amino group, while little difference in the corresponding chemical shifts was observed from C-11 of **4a** and **5a**. Similar treatment of **1a** with 4,13-diaza-18-crown-6 in the presence of LDA under the same conditions as the foregoing gave **4b** (55%) and **4c** (36%), whose structures were determined on the basis of spectroscopic and elemental analyses. However, the relative stereochemistry between two lariats of **4b** is uncertain. X-ray crystallographic analyses of **4b** have been unsuccessful.

The formation of **4a**−**c** as major compounds is reminiscent of the benzyne mechanism, which has been extensively studied.[3] To demonstrate the involvement of a benzyne intermediate, **1a** was treated with LDA in the

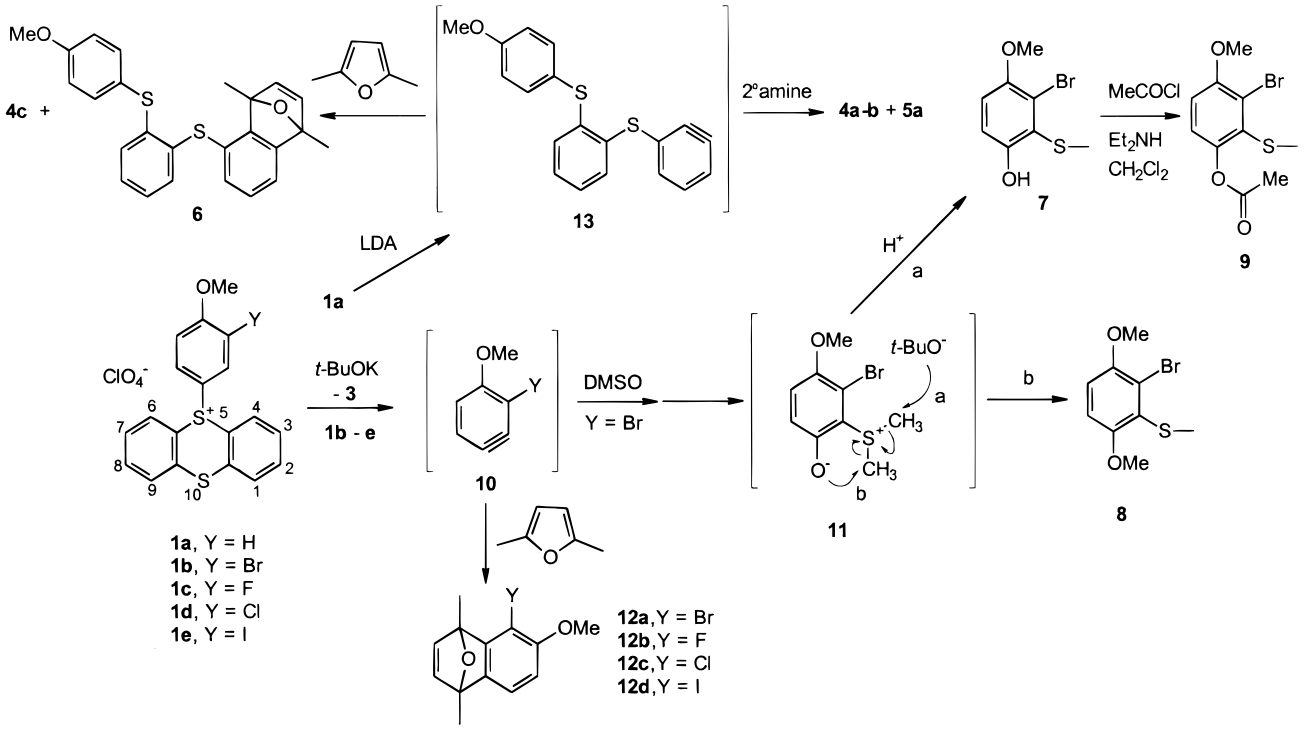
(1) (a) Kim, K.; Rim, H. J. *Tetrahedron Lett.* **1990**, *31*, 5631. (b) Shin, S. S.; Kim, M. N.; Kim, H. O.; Kim, K. *Tetrahedron Lett.* **1993**, *34*, 8469.

(2) (a) *Cation Binding by Macrocycles*; Inoue, Y., Gokel, G. W., Eds.; Marcel Dekker: New York, 1990. (b) *Crown Compound*; Cooper, S. R., Ed.; VCH: New York, 1992.

(3) (a) Gilchrist, T. L. *The Chemistry of triple-bonded functional groups Part 1*; Patai, S., Rappoport, Z., Eds.; John Wiley & Sons: New York, 1983; Supplement C, Chapter 11, pp 383−419 and references cited therein. (b) Caubére, P. *Acc. Chem. Res.* **1974**, *7*, 301. (c) Hoffmann, R. W. *Dehydrobenzene and Cycloalkynes*; Academic Press: New York, 1967. (d) Campbell, C. D.; Rees, C. W. *J. Chem. Soc. C* **1969**, 742. (e) Wittig, G.; Hoffmann, R. W. *Organic Syntheses*; Wiley: New York, 1973; Collect. Vol. V, p 60.

10.1021/jo990322p CCC: $18.00
Published on Web 07/29/1999

Scheme 2



presence of 2,5-dimethylfuran[4] to give a benzyne-trapped compound **6** (34%) and **4c** (42%) (Scheme 2). The formation of **6** clearly indicates the involvement of benzyne as an intermediate.

On the other hand, treatment of **1b** (X = OMe, Y = Br) with *t*-BuOK in DMSO at room temperature gave 3-bromo-4-methoxy-2-(methylthio)phenol (**7**) (79%) and 2-bromo-1,4-dimethoxy-3-methylthiobenzene (**8**) (3%). Acetylation of **7** using acetyl chloride in the presence of Et_2NH at room temperature gave acetate **9** (94%). The ^1H NMR (300 MHz, $CDCl_3$) spectral data for **7** showed a singlet (6.76 ppm) and two doublets (6.94 and 6.92 ppm, J = 9.01 Hz), whereas the data for **9** exhibited two doublets (6.92 and 7.05 ppm, J = 8.60 Hz) of aromatic protons.

The formation of **7** can be explained in terms of nucleophilic attack of *t*-BuO^- on the acidic proton between two electron-withdrawing groups, i.e., bromo and thianthreniumyl moieties, concomitant with loss of the thianthreniumyl moiety to generate (3-bromo-4-methoxy) benzyne (Y = Br) **10** (Scheme 2). Subsequent reaction of **10** with DMSO would give **7** via the intermediate **11** (path a) analogous to the intermediate proposed for the reactions of 4-bromo[2,2]paracyclophane with *t*-BuOK in DMSO.[5] The formation of **8** can be explained in terms of an intramolecular nucleophilic attack of phenoxide on the methyl group of a dimethylsulfonium ion (path b). To the best of our knowledge, this is the first example of this type of methyl transfer from a sulfonium ion to phenoxide in benzyne chemistry, albeit in low yield. It is believed that the bromo substituent (Y = Br) of **10** governs the orientation[6] of the nucleophilic attack of DMSO on benzyne to eventually give **7**.

The intermediate **10** (Y = Br) was trapped by 2,5-dimethylfuran to give **12a** in 75% yield. Similarly, the reactions of **1c** (Y = F), **1d** (Y = Cl), and **1e** (Y = I) under the same conditions as for **1b** gave fluoro (**12b**), chloro (**12c**), and iodo (**12d**) compounds in 88, 73, and 58% yields, respectively. In the case of **1a** (Y = H), it is thought that LDA attacks a proton at C-4, concomitant with cleavage of a C−S bond to give 3-[2-(4-anisylthio)-phenylthio] benzyne **13**, which reacts with amines to give regioisomers **4a**,**b** and **5a**.

Experimental Section

General Procedures. THF was distilled under nitrogen immediately prior to use from sodium/benzophenone. Column chromatography was conducted with silica gel (70−230 mesh), unless otherwise stated.

Thianthrene cation radical perchlorate and 5-arylthianthreniumyl perchlorates (**1a**−**e**) were prepared according to the literature method.[7]

General Procedure for the Reactions of 5-(4-Anisyl)-thianthreniumyl Perchlorate (1a) with Secondary Alkylamines in the Presence of LDA. LDA (0.60 mmol, 2 M in *n*-hexane) was dropwise added into a mixture of **1a** and secondary alkylamine in THF (50 mL) at reflux under nitrogen atmosphere. The addition of the same amount of LDA was repeated four times for the reaction with diethylamine and six times for the reaction with 4,13-diaza-18-crown-6 every 40−50 min. Removal of the solvent in vacuo gave a residue that was chromatographed on a silica gel column (1.5 × 7 cm).

Reaction with Diethylamine. A mixture of **1a** (600 mg, 1.42 mmol), diethylamine (310 mg, 4,26 mmol), and LDA in THF was heated for 4 h at reflux. Chromatography of the reaction mixture using a mixture of EtOAc and *n*-hexane (1:9) gave thianthrene (**3**) (26 mg, 9%), 2-(4-anisylthio)-3′-(*N*,*N*-diethylamino)diphenyl sulfide (**4a**) (320 mg, 57%), and 2-(4-anisylthio)-2′-(*N*,*N*-diethylamino)diphenyl sulfide (**5a**) (59 mg, 11%). **4a**: oily liquid; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.09 (t, J = 7.06 Hz, 6H), 3.29 (q, J = 7.04 Hz, 4H), 3.82 (s, 3H), 6.55−6.61 (m, 3H), 6.84−6.87 (m, 1H), 6.95 (d, J = 8.86 Hz, 2H), 7.04−7.07 (m, 2H), 7.12 (t, J = 8.20 Hz, 1H), 7.19−7.22 (m, 1H), 7.37 (d, J = 8.89 Hz, 2H); ^{13}C NMR

(4) Newman, M. S.; Kannan, R. *J. Org. Chem*. **1976**, *41*, 3356.

(5) (a) Cram, D. J.; Day, A. C. *J. Org. Chem*. **1966**, *31*, 1227. (b) Winterfeldt, C. *Chem. Ber*. **1965**, *98*, 1581.

(6) (a) Roberts, J. D.; Vaughan, C. W.; Carlsmith, L. A.; Semenow, D. A. *J. Am. Chem. Soc*. **1956**, *78*, 611. (b) Wotiz, J.; Huba, F. *J. Org. Chem*. **1959**, *24*, 595. (c) Biehl, E. R.; Razzuk, A.; Jovanovic, M. V.; Khanapure, S. P. *J. Org. Chem*. **1986**, *51*, 5157.

(7) Silver, J. J.; Shine, H. J. *J. Org. Chem*. **1971**, *36*, 2923.

($CDCl_3$, 75 MHz) δ 12.79, 45.28, 55.77, 111.97, 114.99, 116.04, 118.78, 124.63, 127.05, 128.53, 129.39, 130.72, 133.30, 135.50, 136.53, 136.63, 142.16, 149.54, 161.36; IR (neat) 3048, 2968, 1589, 1489, 1434, 1347, 1251, 1171 cm^{-1}; MS *m*/*z* 395 (M^+, 55.0), 380 (100). Anal. Calcd for $C_{23}H_{25}NOS_2$: C, 69.83; H, 6.37; N, 3.54; S, 16.21. Found: C, 69.78; H, 6.35; N, 3.40; S, 16.05. **5a**: oily liquid; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.00 (t, J = 7.09 Hz, 6H), 3.05 (q, J = 7.06 Hz, 4H), 3.75 (s, 3H), 6.63 (d, J = 8.06 Hz, 1H), 6.72 (d, J = 7.75 Hz, 1H), 6.83−6.89 (m, 3H), 6.98−7.10 (m, 4H), 7.35 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 12.54, 47.80, 55.35, 115.16, 122.98, 123.27, 124.49, 125.58 (two carbons), 127.14 (two carbons), 128.92, 130.55, 135.94, 136.18, 136.76, 145.71, 148.21, 160.25; IR (neat) 3051, 2969, 2930, 2833, 1585, 1491, 1441, 1368, 1247, 1174, 1031 cm^{-1}; MS *m*/*z* 395 (M^+, 100), 380 (41.7). Anal. Calcd for $C_{23}H_{25}NOS_2$: C, 69.83; H, 6.37; N, 3.54; S, 16.21. Found: C, 69.74; H, 6.36; N, 3.42; S, 16.30.

Reaction of 1a with LDA in the Presence of 2,5-Dimethylfuran. LDA (0.6 mmol, 2 M in *n*-hexane) was dropwise added into a suspension of **1a** (209 mg, 0.49 mmol) in 2,5-dimethylfuran at reflux under nitrogen atmosphere. After the addition of the same amount of LDA was repeated four times as described in the general procedure, chromatography of the reaction mixture using a mixture of EtOAc and *n*-hexane (1:9) gave 2-(4-anisylthio)-3′-(*N*,*N*-diisopropylamino)diphenyl sulfide (**4c**) (26 mg, 12%) [oily liquid; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.15 (s, 6H), 1.17 (s, 6H), 3.74 (hept, J = 6.76 Hz, 2H), 3.82 (s, 3H), 6.73−6.77 (m, 3H), 6.84−6.88 (m, 1H), 6.91 (d, J = 8.71 Hz, 2H), 7.03−7.07 (m, 2H), 7.13 (t, J = 8.12 Hz, 1H), 7.23−7.26 (m, 1H), 7.42 (d, J = 8.69 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 21.65, 47.89, 55.78, 115.57, 117.07, 120.19, 120.49, 123.90, 126.45, 128.08, 128.48, 129.63, 132.91, 134.39, 135.06, 136.43, 141.82, 149.28, 160.48; IR (neat) 3050, 2968, 2930, 2830, 1580, 1490,1444, 1370, 1249, 1170,1032 cm^{-1}; MS *m*/*z* 423 (M^+, 28.3), 408 (100). Anal. Calcd for $C_{25}H_{29}NOS_2$: C, 70.80; H, 6.90; N, 3.31; S, 15.14. Found: C, 70.80; H, 6.88; N, 3.25; S, 15.00] and 1,4-dimethyl-5-[2-(4-anisylthio)phenylthio]-1,4-dihydronaphthalene (**6**) (47 mg, 23%): oily liquid; ^1H NMR ($CDCl_3$, 300 MHz) 1.81 (s, 3H), 1.90 (s, 3H), 6.23−6.72 (m, 3H), 6.78−6.87 (m, 4H), 6.88−6.95 (m, 3H), 7.00 (d, J = 6.81 Hz, 1H), 7.31 (d, J = 8.70 Hz, 2H); ^{13}C NMR ($CDCl_3$, 75 MHz), 15.20, 17.16, 55.36, 88.10, 90.69, 115.09, 118.11, 123.88, 125.48, 126.29, 126.65, 126.75, 129.65, 129.79, 130.90, 135.15, 137.01, 137.61, 146.76, 146.83, 154.52, 154.68, 159.89; IR (neat) 3055, 2975, 2932, 1591, 1492, 1442, 1247, 1032 cm^{-1}; MS *m*/*z* 418 (M^+, 46.7), 402 (11.3), 235 (100), 221 (67.5). Anal. Calcd for $C_{25}H_{22}O_2S_2$: C, 71.74; H, 5.30; S, 15.32. Found: C, 71.68; H, 5.36; S, 15.37. Elution with a mixture of MeOH and $CHCl_3$ (1:9) gave unreacted **1a** (62 mg, 30%).

Reaction with 1,4,10,13-Tetraoxa-7,16-diazacyclooctadecane. A mixture of **1a** (970 mg, 2.29 mmol), the foregoing diazacyclooctadecane (100 mg, 0.38 mmol), and LDA in THF was heated for 4 h at reflux. Chromatography of the reaction mixture using a mixture of EtOAc and *n*-hexane (1:3) gave **3** (7 mg, 8%) and 2-(4-anisylthio)-3′-(*N*,*N*-diisopropylamino)diphenyl sulfide (**4c**) (58 mg, 36%). Subsequent elution with EtOAc gave *N*,*N*-di[3-[2-(4-anisylthio)phenylthio]]phenyl-1,4,10,13-tetraoxa-7,16-diazacyclooctadecane (**4b**) (190 mg, 55%): mp 141−144 °C (EtOH); ^1H NMR ($CDCl_3$, 300 MHz) δ 3.50−3.64 (m, 24H), 3.82 (s, 6H), 6.56 (d, J = 8.49 Hz, 2H), 6.63 (overlap of singlet and doublet, 4H), 6.85−6.88 (m, 2H), 6.91 (d, J = 8.72 Hz, 2H), 6.99−7.08 (m, 4H), 7.14 (t, J = 7.93 Hz, 2H), 7.20−7.23 (m, 2H), 7.42 (d, J = 8.93 Hz, 4H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 51.22, 55.36, 68.95, 70.91, 110.53, 113.71, 115.15, 118.39, 123.49, 126.09, 127.60, 128.23, 130.00, 132.20, 134.15, 135.58, 135.92, 141.09, 148.59, 160.06; IR (neat) 2856, 1579, 1480, 1434, 1246, 1099, 1026 cm^{-1}. FAB MS *m*/*z* 907 (M^+, 10.8), 154 (100). Anal. Calcd for $C_{50}H_{54}N_2O_6S_4$: C, 66.19; H, 6.00; N, 3.09; S, 14.14. Found: C, 66.05; H, 5.97; N, 2.99; S, 14.21.

Reaction of 5-(3-Bromo-4-methoxyphenyl)thianthreniumyl Perchlorate (1b) with Potassium *tert*-Butoxide. To a solution of **1b** (989 mg, 1.69 mmol) in DMSO (30 mL) was added *t*-BuOK (417 mg, 3.71 mmol). The mixture was stirred for 1.5 h at room temperature, followed by addition of water (30 mL). The mixture was extracted with EtOAc (9 × 30 mL) and worked up as usual. Chromatography (1.5 × 10 cm) of the reaction mixture using *n*-hexane gave **3** (323 mg, 88%). Subsequent elution with a mixture of EtOAc and *n*-hexane (1:9) gave a mixture of 3-bromo-4-methoxy-2-(methylthio)phenol (**7**) and 2-bromo-1,4-dimethoxy-3-methylthiobenzene (**8**), which was separated by elution with the same solvent mixture (1:40) to give **7** (309 mg, 73%): oily liquid; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.33 (s, 3H), 3.85 (s, 3H), 6.76 (s, 1H), 6.90 (d, J = 9.00 Hz, 1H), 6.95 (d, J = 9.02 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.69, 57.55, 113.84, 115.66, 120.16, 123.10, 150.90, 152.27; IR (neat) 3376, 3064, 2912, 1560, 1462, 1426, 1315, 1266, 1195, 1174, 1088, 1045, 973, 906, 802, 715, 587, 542 cm^{-1}; MS *m*/*z* 248 (M^+, 100%), 250 (M^+ + 2, 100), 233 (58.2) and **8** (14 mg, 3%): oily liquid; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.44 (s, 3H), 3.87 (s, 3H), 3.89 (s, 3H), 6.84 (d, J = 9.05 Hz, 1H), 6.88 (d, J = 9.03 Hz, 1H); IR (neat) 2912, 1568, 1466, 1432, 1371, 1290, 1136, 1078, 1046, 1018, 952, 819, 805, 747 cm^{-1}; MS *m*/*z* 262 (M^+, 90.5) 264 (M^+ + 2, 90.8), 249 (30.3), 168 (100).

3-Bromo-4-methoxy-2-(methylthio)phenyl Acetate (**9**). To a solution of **7** (113 mg, 0.454 mmol) and acetyl chloride (39 mg, 0.499 mmol) in CH_2Cl_2 (30 mL) was added triethylamine (51 mg, 0.499 mmol). The mixture was stirred for 30 min at room temperature, followed by addition of water (2 mL). After removal of the solvent, the residue was extracted with CH_2Cl_2 (2 × 30 mL) and dried over $MgSO_4$. Evaluation of the solvent gave **9** (124 mg, 94%), which was recrystallized from a mixture of *n*-hexane and CH_2Cl_2: mp 89−91 °C; ^1H NMR ($CDCl_3$, 300 MHz) δ 2.33 (s, 3H), 2.37 (s, 3H), 3.90 (s, 3H), 6.89 (d, J = 8.91 Hz, 1H), 7.04 (d, J = 8.91 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 18.36, 20.87, 56.73, 112.07, 120.79, 121.58, 132.40, 146.47, 154.82, 169.81; IR (KBr) 3064, 2920, 2824,1762, 1556, 1456, 1432, 1360, 1302, 1275, 1258, 1202, 1086, 1038, 1010, 973, 938, 922, 878 cm^{-1}; MS *m*/*z* 290 (M^+, 8.5), 292 (M^+ + 2, 8.8), 250 (100). Anal. Calcd for $C_{10}H_{11}BrO_3S$: C, 41.25; H, 3.81; S, 11.01. Found: C, 41.28; H, 3.95; S, 11.39.

General Procedure for the Reactions of 5-[3-Halo-4-(methoxy)phenyl]thianthreniumyl Perchlorates (1b−e) with Potassium *tert*-Butoxide in the Presence of 2,5-Dimethylfuran. To a mixture of 2,5-dimethylfuran and *t*-BuOK in dried THF (20 mL) at reflux under nitrogen atmosphere was dropwise added a suspension of **1b**−**e** in THF (10 mL), prepared by using a sonicator, for 2.5 h. The mixture was heated for 30 min at reflux. After removal of the solvent in vacuo, the residue was chromatographed (3 × 10 cm). Elution with *n*-hexane gave **3**. Elution with a mixture of EtOAc and *n*-hexane (1:9) gave 1,4-dimethyl-1,4-epoxy-5-halo-6-methoxy-1,4-dihydronaphthalenes (**12a**−**d**). Elution with acetone gave a mixture of unreacted **1b**-**e** and unknown mixtures.

(i) Reaction with 1b. A mixture of **1b** (200 mg, 0.40 mmol), *t*-BuOK (120 mg, 1.07 mmol), and 2,5-dimethylfuran (1,920 mg, 20.0 mmol) in THF was heated for 3 h at reflux. From the reaction mixture were obtained **3** (82 mg, 95%), 5-bromo-1,4-dimethyl-1,4-epoxy-6-methoxy-1,4-dihydronaphthalene (**12a**) (85 mg, 75%), and a mixture of unreacted **1b** and an unknown (14 mg). Compound **12a** was recrystallized from a mixture of EtOAc and *n*-hexane to give white crystals: mp 126−128 °C; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.78 (s, 3H), 1.99 (s, 3H), 3.75 (s, 3H), 6.31 (d, J = 7.67 Hz, 1H) 6.68 (d, J = 5.33 Hz, 1H), 6.74 (d, J = 5.32 Hz, 1H), 6.83 (d, J = 7.64 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 15.17, 17.70, 56.68, 88.00, 91.22, 106.21, 106.58, 116.89, 145.87, 146.76, 147.40, 152.73, 153.55; IR (KBr) 2928, 1450, 1420, 1376, 1334, 1293, 1251, 1126, 1043 cm^{-1}; MS *m*/*z* 280 (M^+, 26.3), 282 (M^+ + 2, 25.6), 254 (61.0), 239 (100). Anal. Calcd for $C_{13}H_{13}BrO_2$: C, 55.54; H, 4.66. Found: C, 55.52; H, 5.30.

(ii) Reaction with 5-[3-Fluoro-4-(methoxy)phenyl]thianthreniumyl Perchlorate (1c). A mixture of **1c** (176 mg, 0.40 mmol), *t*-BuOK (135 mg, 1.20 mmol), and 2,5-dimethylfuran (961 mg, 10.0 mmol) in THF was heated for 4 h at reflux. From the reaction mixture were obtained **3** (83 mg, 96%), 1,4-dimethyl-1,4-epoxy-5-fluoro-6-methoxy-1,4-dihydronaphthalene (**12b**) (78 mg, 88%), and unreacted **1c** (4 mg, 2%). **12b**: oily liquid; ^1H NMR ($CDCl_3$, 300 MHz) δ 1.78 (s, 3H), 1.95 (d, J = 10 Hz, 3H), 3.74 (s, 3H), 6.38 (t, J = 7.36 Hz, 1H), 6.73−6.67 (m, 3H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 15.19, 16.65, 56.55, 88.67 (d, J = 1.60 Hz), 88.75, 108.30, 113.41 (d, J = 3.45 Hz), 137.38 (d, J = 15.3 Hz), 145.95, 146.59 (d, J = 12.0 Hz), 146.73 (d, J = 249 Hz), 146.92 (d, J = 2.80 Hz), 147.06; IR (neat) 2977, 2936, 1490, 1440, 1384, 1360, 1303, 1264, 1237, 1149, 1080, 1049, 858, 807, 729 cm^{-1}; MS *m*/*z* 220 (M^+, 43.5), 205 (12.1), 194 (64.3), 177 (100).

Anal. Calcd for $C_{13}H_{13}FO_2$: C, 70.90; H, 5.95. Found: C, 70.88; H, 6.05.

(iii) Reaction with 5-[3-Chloro-4-(methoxy)phenyl]thianthreniumyl Perchlorate (1d). A mixture of **1d** (183 mg, 0.40 mmol), *t*-BuOK (135 mg, 1.20 mmol), and 2,5-dimethylfuran (961 mg, 10.0 mmol) in THF was heated for 4 h at reflux. From the reaction mixture were obtained **3** (82 mg, 95%). 5-chloro-1,4-dimethyl-1,4-epoxy-6-methoxy-1,4-dihydronaphthalene (**12c**) (69 mg, 73%), and unreacted **1d** (26 mg, 14%). Compound **12c** was recrystallized from petroleum ether (bp 35−60 °C): mp 96−98 °C; ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.78 (s, 3H), 1.99 (s, 3H), 3.77 (s, 3H), 6.36 (d, J = 7.67 Hz, 1H), 6.72 (dd, J = 14, 5.34 Hz, 2H), 6.81 (d, J = 7.53 Hz, 1H); ^{13}C NMR ($CDCl_3$, 75 MHz) δ 15.17, 17.40, 56.59, 88.19, 90.51, 106.79, 116.21 (two carbons), 145.95, 146.51, 147.35, 150.40, 153.06; IR (neat) 2976, 2936, 1584, 1460, 1430, 1383, 1345, 1301, 1261, 1228, 1136, 1066, 1046, 886, 861, 807, 722, 662, 608 cm^{-1}; MS *m*/*z* 236 (M^+, 33), 210 (78.5), 193 (100). Anal. Calcd for $C_{13}H_{13}FO_2$: C, 65.97; H, 5.54. Found: C, 65.88; H, 5.65.

(iv) Reaction with 5-[3-Iodo-4-(methoxy)phenyl]thianthreniumyl Perchlorate (1e). A mixture of **1e** (220 mg, 0.40 mmol), *t*-BuOK (135 mg, 1.20 mmol), and 2,5-dimethylfuran (960 mg, 10.0 mmol) in THF was heated for 4 h at reflux. From the reaction mixture were obtained **3** (70 mg, 81%), 1,4-dimethyl-1,4-epoxy-5-iodo-6-methoxy-1,4-dihydronaphthalene (**12d**) (76 mg, 58%), and a mixture of unreacted **1e** and unknown mixtures (21 mg). Compound **12d** is an unstable solid. Purification of **12d** by recrystallization has been unsuccessful: ^{1}H NMR ($CDCl_3$, 300 MHz) δ 1.77 (s, 3H), 1.96 (s, 3H), 3.81 (s, 3H), 6.24 (d, J = 7.69 Hz, 1H), 6.73−6.66 (m, 2H), 6.85 (d, J = 7.69 Hz, 1H); MS *m*/*z* 328 (M^+, 27), 302 (94.5), 285 (100).

Acknowledgment. The authors are grateful to CBM for financial support of this work.

Supporting Information Available: Copies of ^{1}H NMR, IR, and elemental analyses of **1b**−**e** and characteristic ^{1}H (300 MHz) and ^{13}C (75 MHz) NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

JO990322P