Electrochemical Activation of Dimethyl Disulfide for Electrophilic Aromatic Substitution

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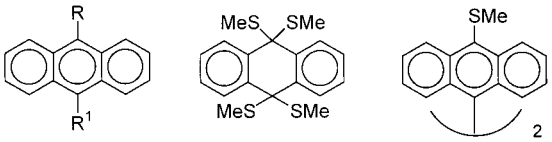
Introduction

To effect electrophilic aromatic substitution, disulfides need to be activated with Lewis or Bronsted acids.[1−3] However, electrochemical oxidation of disulfides should also activate disulfides for electrophilic aromatic substitution by forming the corresponding radical cations, dications, or species with electrophilic sulfur derived from these intermediates.[4,5] The potential advantages of electrochemical activation are the avoidance of heavy metals and acidic conditions. Do et al.[6] reported the exhaustive electrooxidation of disulfides in CH_2Cl_2 to give formally sulfenium cations RS^+. The sulfur electrophile produced could effect substitution with highly activated phenols in 26−77% yield but with the less activated anisoles the yields were only 11−35%. Glass and Jouikov[7] reported that electrooxidation of Me_2S_2 in liquid SO_2 gave a potent methylthiating agent that reacted with a large range of arenes, from strongly activated to weakly activated, in good to excellent yields. In both of these methods, an electrophilic thiating agent is prepared electrochemically, and then, in a subsequent step, it is added to the arene of interest. Alkylthioarenes have been used as pesticidal and pharmaceutical intermediates, as antioxidants[2,6] and as precursors to conducting materials.[8] This procedure requires that the electrophilic sulfur species persist until added to the arene. Since disulfide radical cations and dications are unstable intermediates, it was deemed advantageous to have the reacting arene present as these species are generated. This paper reports our studies of the electrochemical oxidation of Me_2S_2 in the presence of arenes. Since methylthiation of arenes generates products that are easier to oxidize than the starting arene, overoxidation of the product has been observed. Consequently, a strategy to avoid this problem was investigated and the successful strategy is reported here.

Results

In acetonitrile Me_2S_2 shows an irreversible first oxidation peak at 1.05 V vs Ag/0.1M $AgNO_3$ in MeCN reference electrode using the technique of cyclic voltammetry up to a scan rate of 500 mV/s. The oxidation peak of anthracene is about 400 mV more positive than that for Me_2S_2. Consequently, Me_2S_2 may be selectively oxidized in the presence of anthracene. Controlled potential electrolysis of Me_2S_2 in MeCN containing anthracene, in a divided cell, produced 9-methylthioanthracene **1a** in 74% yield and 9,10-di(methylthio)anthracene **1b** in 8% yield. The structures of both of these compounds were unequivocally assigned by comparison with authentic samples.[9,10] However, in addition to these products small amounts of 9,10-anthraquinone, its bis(dimethylthio)-ketal **2** and a dimer tentatively identified as **3** were



1a, R=MeS; R^I=H **2** **3**
b, R=R^I=SMe
c, R=1-pyridinium, R^I=H

found. Structure **2** was assigned on the basis of its spectra and hydrolysis to 9,10-anthraquinone. Structure **3** was assigned on the basis of its spectra and in analogy with the reported dimerization of 9-methoxyanthracene on 2e$^-$ oxidation.[11] The formation of 9,10-anthraquinone, **2**,[12] and **3** result from overoxidation of the methylthiation products. Overoxidation occurred despite the fact that the potential of the working electrode was maintained at the foot of the oxidation peak of Me_2S_2 to avoid oxidation of the reaction products. To avoid this problem the strategy outlined below was investigated.

Anodic oxidation of anthracene[13] and 9,10-diphenylanthracene[14] in the presence of pyridine produces adducts **4a** and **4b**, respectively. These products form by nucleophilic addition of pyridine to dication **5a** and **5b**, respectively. Furthermore, treatment of **4a** with 1 mol of cold

4a, R=H; R^I=R^{II}=1-pyridinium
b, R=Ph; R^I=R^{II}=1-pyridinium
c, R=H; R^I=SMe, R^{II}=1-pyridinium

5a, R=H; R^I=1-pyridinium
b, R=Ph; R^I=1-pyridinium
c, R=H; R^I=SMe

base affords the rearomatized anthracene derivative **1c**.[13] By analogy, electrophilic methylthiation of anthracene generates **5c**, which on nucleophilic attack by pyridine gives adduct **4c**. Adduct **4c** should be difficult to oxidize in comparison with **1a** and **1b** because the anthracene

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(12) Alternatively **2** may result from attack by a MeS^+ donor on **1b** and trapping of the resulting cation by Me_2S_2.
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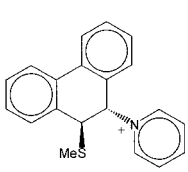
ring is replaced by two benzene rings and the methylthio group is not attached to the aromatic moieties. Elimination of $PyrH^+$ from **4c** produces **1a**.

Controlled potential electrolysis of Me_2S_2 in the presence of anthracene and pyridine did not give any pyridinium adduct but only products derived from electrophilic substitution. However, phenanthrene, acenaphthylene,[15] and cyclohexene all produce the corresponding adducts **6**−**8**, respectively, when a solution of these compounds, Me_2S_2, and pyridine is electrooxidized. These



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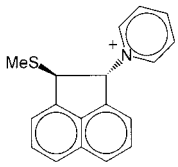

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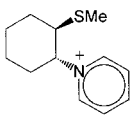

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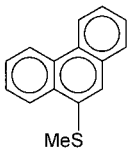
adducts can also be prepared in good yields by the reaction of $[(MeS)_2SMe]SbCl_6$[16] and pyridine with phenanthrene, acenaphthylene, and cyclohexene in CH_2Cl_2. The structures of these adducts including stereochemistry,[17−21] were determined spectroscopically. In addition, the structure of **(7)**$SbCl_6$ was unequivocally established by X-ray crystallographic analysis. Treatment of **6** with sodium methoxide in anhydrous methanol produced 9-methylthiophenanthrene, **9**,[22] in 61% isolated yield. Reaction of **7** with DBU formed **10** in 76% isolated yield.



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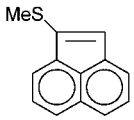

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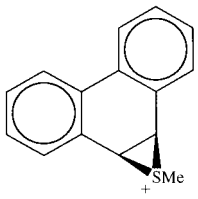
Discussion

While the electrophile which effects electrophilic aromatic substitution on anthracene in acetonitrile on oxidation of Me_2S_2 is not clear, 9-methylthioanthracene **1a** is formed in good yield along with some of the bis-substituted product **1b**. However, products resulting from further oxidation of **1a** and **1b** are formed as well. The strategy of forming adducts by electrophilic addition of MeS^+ followed by nucleophilic addition of pyridine[23] to prevent overoxidation and subsequent rearomatization proved successful for phenanthrene and acenaphthylene. Surprisingly anthracene does not form an adduct under these conditions. However, this may be explained by the formation of thiiranium salts **11** and **12**, respectively, on reaction of phenanthrene and acenaphthylene with the



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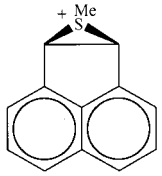

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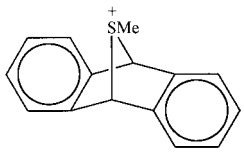

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MeS^+ donor species which is not feasible for anthracene (and formation of **13** from anthracene and MeS^+ is apparently also unfavorable). The formation of thiiranium salts **11** and **12** also accounts for the formation of trans-products **6** and **7**, respectively, since backside displacement by pyridine on the thiiranium salts would preferentially produce these products. It has been reported [24,25] that anodic oxidation of Me_2S_2 in acetonitrile in the presence of alkenes gives products resulting from anti addition owing to the intermediacy of thiiranium salts which undergo backside nucleophilic displacement by acetonitrile. Similarly we have also found that oxidation of Me_2S_2 in acetonitrile in the presence of cyclohexene and pyridine affords trans adduct **8** apparently by nucleophilic attack of pyridine on the corresponding thiiranium salt.

Experimental Section

^1H and ^{13}C NMR spectra were recorded in the solvent indicated with 0.5% TMS as internal standard at 250.13 and 62.9 MHz, respectively. Thick-layer chromatography was done using silica gel plates. Column chromatography was accomplished with silica gel (75−125 μm). Electrochemical experiments were done using three electrodes in a two-compartment cell with a potentiostat. A Pt gauze (3 × 5 cm) was used as the anode and Al foil (5 × 10 cm) as the cathode.

Electrolysis of Me_2S_2 in the Presence of Anthracene. A solution of Me_2S_2 (310 mg, 3.3 mmol) and anthracene (534 mg, 3.0 mmol) dissolved in anhydrous acetonitrile (25 mL) containing $NaClO_4$ (850 mg, 7 mmol) was electrooxidized at +0.85V vs Ag/0.1 M $AgNO_3$ in acetonitrile. After an amount of electricity corresponding to 2 F/mol of Me_2S_2 was passed, the current dropped to approximately 10% of its initial value and the electrolysis was stopped. The solvent was removed by evaporation in vacuo, and the residue was extracted with cold distilled water to remove $NaClO_4$. The organic residue was then chromatographed on silica gel plates using hexanes:CH_2Cl_2 (1:1) as eluent. The fractions collected were the following: **1a**, 494 mg (74% yield), mp 63−64 °C (identical with authentic compound by ^1H NMR and mass spectroscopy and mmp); **1b**, 85.9 mg (11% yield), mp 161−162 °C (identical with authentic compound by ^1H NMR and mass spectroscopy and mmp); **3**, 60 mg (5% yield): ^1H NMR ($CDCl_3$) δ 2.39 (s, 6H), 7.45 (m, 4H), 7.62 (m, 4H), 8.0 (m, 4H), 8.9 (d, 4H, J = 8.9 Hz); MS (EI) 446, 431, 384, 352, 286, 271, 209, 175, 166, 111; **2**, *ca.* 13 mg of crude product (1−3% yield): ^1H NMR ($CDCl_3$) δ 2.18 (s, 12H), 7.68 (m, 4H); 8.58 (m, 4H); MS (EI) 364, 349, 334, 317, 270, 240, 176, 111, 104; anthraquinone, 59 mg (10% yield), mp 284−285 °C (identical with authentic compound).

Electrolysis of Me_2S_2 in the Presence of Phenanthrene, Acenaphthylene, or Cyclohexene and Pyridine. All electrolyses were carried out in a two compartment cell of 30 mL volume separated by a sintered glass diaphragm. The working electrode was a Pt gauze cylinder (1.2 cm diameter, 4 cm length), the counter electrode Al foil (30 cm^2 area) and the reference electrode Ag/0.1M $AgNO_3$ in acetonitrile. A typical solution contained phenanthrene, acenaphthylene or cyclohexene (6.5

(15) Anodic oxidation of Me_2S_2 and acenaphthylene in the absence of pyridine resulted in the apparent acid-catalyzed polymerization of acenaphthylene after the passage of a small amount of electricity.

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mmol), Me_2S_2 (0.30 g, 3.2 mmol), pyridine (1.2 g, 15 mmol), and $NaClO_4$ (1.5 g, 10 mmol) dissolved in acetonitrile (30 mL). The electrolyses were carried out at an applied potential of 1.0−1.2 V until the amount of electricity corresponding to 2 F/mol was passed. The analyte was rotary evaporated and the residue extracted with hexane to leave a solid which was extracted with CH_2Cl_2. The organic extracts were combined, washed with 0.1 M aqueous HCl solution, dried, and rotary evaporated, and the residue was purified by column chromatography when necessary.

6, 46% yield: ^{1}H NMR,^{13} C NMR, and FAB MS are the same as those for **6** obtained by reaction of phenanthrene with [$(MeS)_2$ SMe] $SbCl_6$ and pyridine.

7, 72% yield: ^{1}H NMR,^{13} C NMR, and FAB MS are the same as those for **7** prepared by reaction of acenaphthylene with $[(MeS)_2SMe]SbCl_6$ and pyridine.

8, 92% yield: ^{1}H NMR,^{13} C NMR, and FAB MS are the same as those for **8** obtained by reaction of cyclohexene with $[(MeS)_2SMe]SbCl_6$ and pyridine.

Reaction of Phenanthrene with $[(MeS)_2SMe]SbCl_6$ and Pyridine. A solution of phenanthrene (546 mg, 3.07 mmol) dissolved in anhydrous CH_2Cl_2 (1.0 mL) was added to a solution of $[(MeS)_2SMe]SbCl_6$ (1.38 g, 2.90 mmol) dissolved in anhydrous CH_2Cl_2 (18 mL) with stirring. The color of the solution changed to deep purple. A solution of pyridine (246 mg, 3.11 mmol) in CH_2Cl_2 (1.0 mL) was added after 1 min whereupon the purple color disappeared and a yellow precipitate formed. The mixture was stirred at room temperature for 23 h. The mixture was then filtered and the orange precipitate washed with CH_2Cl_2. After being dried in vacuo, **6** was obtained as orange crystals (1.1 g, 59% yield): mp 124−125 °C (dec); IR (KBr) 3121, 3073, 2917, 1702, 1623, 1477, 1434, 1358, 1249, 1219, 1165, 1123, 1053, 1024, 961, 749, 706, 673, 626, cm^{-1}; ^{1}H NMR [$(CD_3)_2CO$] δ 2.20 (s, 3H), 4.94 (d, 1H, J = 1.3 Hz), 6.69 (d, 1H, J = 1.3 Hz), 7.36 (m, 2H), 7.54 (m, 2H), 7.77 (m,2H), 8.15 (m,3H), 8.25 (d, 1H, J = 7.6 Hz), 8.65 (t, 1H, J = 7.7 Hz), 8.89 (d, 2H, J = 5.8 Hz); ^{13}C NMR [$(CD_3)_2CO$] δ 15.0, 50.8, 72.3, 125.7, 125.9, 127.2, 129.6, 130.2, 130.4, 130.5, 131.1, 131.5, 132.6, 132.8, 133.0, 135.6, 144.3, 147.6; HRMS (FAB) Calcd for $C_{20}H_{18}NS$: 304.1160. Found: 304.1150.

Reaction of Acenaphthylene with $[(MeS)_2SMe]SbCl_6$ and Pyridine. The reaction was carried out as above except using acenaphthylene (146 mg, 0.96 mmol) and anhydrous pyridine (164 mg, 2.08 mmol) dissolved in CH_2Cl_2 (2 mL) added to $[(MeS)_2SMe]SbCl_6$ (446 g, 0.935 mmol) dissolved in CH_2Cl_2 (8 mL). After 20 h at room temperature, the mixture was concentrated on a rotary evaporator and analyzed by ^{1}H NMR spectroscopy showing acenaphthylene (0.5 mmol, 48% conversion) and **7** (0.4 mmol, 86% yield). This residue was purified by column chromatography on silica gel eluting with CH_2Cl_2 to give **7** as its $SbCl_6$ salt as a red solid: 162 mg (58% yield): mp 164−166 °C (dec); IR (KBr) 3125, 3078, 2917, 2359, 2336, 1699, 1623, 1484, 1424, 1358, 1259, 1202, 1146, 974, 825, 789, 752, 706, 679; ^{1}H NMR [$(CD_3)_2CO$] δ 2.07 (s, 3H), 5.33 (d, 1H, J = 3.3, Hz), 7.07 (d, 1H, J = 3.3 Hz), 7.6 (d, 1H, J = 6.8 Hz), 7.7 (m, 2H), 7.8 (d, 1H, J = 7.0 Hz), 8.00 (d, 1H, J = 8.2 Hz), 8.09 (d, 1H, J = 8.0 Hz), 8.36 (t, 2H, J = 7.0 Hz), 8.85 (t, 1H, J = 7.7 Hz), 9.18 (m, 2H); ^{13}C NMR[$(CD_3)_2CO$)] δ 12.1, 58.0, 82.3, 122.6, 123.5, 125.9, 128.1, 129.8, 130.2, 130.4, 132.2, 137.7, 138.6, 139.7, 144.7, 148.1; FAB-MS m/z 278. Anal. Calcd for $C_{18}H_{16}Cl_6NSSb$: C, 35.28; H 2.61; Cl, 34.72. Found: C, 35.32; H, 2.62; Cl, 35.54.

Reaction of Cyclohexene with $[(MeS)_2SMe]SbCl_6$ and Pyridine. The reaction was carried as above using $[(MeS)_2SMe]$-$SbCl_6$ (687 mg, 1.45 mmol) dissolved in CH_2Cl_2 (11 mL) and adding cyclohexene (141 mg, 1.72 mmol) and pyridine (422 mg, 5.34 mmol) in CH_2Cl_2 (1 mL). After standing 18 h at room temperature, the mixture was filtered, washed with CH_2Cl_2, and dried to give **8** as yellow crystals (480 mg, 61% yield) which was recrystallized by vapor diffusion of pentane into a THF solution: mp 176−179 °C (dec); IR (KBr) 3126, 3080, 2939, 2859, 1626, 1484, 1441, 1322, 1282, 1211, 1157, 772, 678 cm^{-1}; ^{1}H NMR [$(CD_3)_2CO$] δ 1.61 (m, 2H), 1.73 (m, 1H), 1.89 (m, 1H), 1.91 (s, 3H), 2.00 (m, 1H), 2.32 (m, 2H), 2.51 (m, 1H), 3.33 (dd, 1H, J = 4.0, 11.4 Hz), 4.83 (dd, 1H, J = 4.0 and 11.7 Hz), 8.34 (t, 2H, J = 7.2 Hz), 8.81 (t, 1H, J = 7.7 Hz), 9.26 (d, 2H, J = 6.6 Hz); ^{13}C NMR [$(CD_3)_2CO$] δ 12.3, 25.5, 26.1, 33.6, 34.4, 49.4, 76.1, 129.5, 144.5, 147.6; HR MS (FAB) Calcd for $C_{12}H_{18}NS$: 208.1160. Found: 208.1163.

X-ray Crystallographic Analysis of 7·$SbCl_6$. Crystals of **7**·$SbCl_6$ suitable for X-ray crystallographic analysis were grown by vapor diffusing pentane into a CH_2Cl_2 solution of **7**·$SbCl_6$.

A red, irregular block of $C_{18}H_{16}NSSbCl_6$ having approximate dimensions of 0.119 × 0.340 × 0.374 mm was mounted on a glass fiber in a random orientation with epoxy. Examination of the crystal on a Bruker SMART 1000 CCD detector X-ray diffractometer at 298(2) K and a power setting of 50 kV, 40 mA showed measurable diffraction to at least θ = 27.50°. Data were collected on the SMART1000 system[26] using graphite monochromated Mo Kα radiation (λ = 0.71073 Å).

Initial cell constants were determined from reflections obtained in three orthogonal 5 deg wedges of reciprocal space. Final cell constants and an orientation matrix for integration were determined from reflections obtained throughout the full data set. A total of 1868 frames at 1 detector setting covering 0° < 2θ < 56° were collected, having an omega scan width of 0.3 and an exposure time of 10 s. The frames were integrated using the Bruker SAINT[27] software package's narrow frame algorithm. A total of 39885 reflections were integrated and retained of which 5388 were unique ($\langle$redundancy$\rangle$ = 7.4, R_{int} = 3.9%, R_σ = 3.0%). Of the unique reflections, 3433 (63.7%) were observed >2$\sigma(I)$. The final orthorhombic cell parameters of a = 18.3477(16), b = 13.3296(12), c = 19.1538(15), $\alpha = \beta = \gamma$ = 90, volume = 4684.4-(7) Å^3 are based on the refinement of the *XYZ*-centroids of 8192 reflections with I > 10 $\sigma(I)$ covering the range of 2.17 < θ < 27.50. Empirical absorption and decay corrections were applied using the program SADABS. The absorption coefficient is 1.957 mm^{-1}, T_{min} = 0.775610, and T_{max} = 0.980669. For Z = 8 and FW = 612.83 the calculated density is 1.738 g/cm^3. Systematic absences and intensity statistics indicate the space group to be *Pbcn* (#60) which was consistent with refinement.

The structure was solved using SHELXS in the Bruker SHELXTL (Version 5.0) software package.[28] Refinements were performed using the freely available SHELXL and illustrations were made using XP. Solution was achieved utilizing direct methods followed by Fourier synthesis. Hydrogen atoms were added at idealized positions, constrained to ride on the atom to which they are bonded and given thermal parameters equal to 1.2 or 1.5 times U_{iso} of that bonded atom. The final anisotropic full-matrix least squares refinement based on F^2 of all reflections converged (maximum shift/esd = 0.002) at R_1 = 0.0669, wR_2 = 0.1065 and goodness-of-fit = 1.015. "Conventional" refinement indices using the 3433 reflections with F > 4 σ(F) are R_1 = 0.0370, wR_2 = 0.0953. The model consisted of 245 variable parameters, 64 constraints, and 0 restraints. There were six correlation coefficients greater than 0.50. Three connected the U_{ii} of Sb with the overall scale factor. The highest peak on the final difference map was 0.662 e/Å^3 located 0.19 Å from SB1. The lowest peak on the final difference map was −0.542 e/Å^3 located 0.93 Å from S1. Scattering factors and anomalous dispersion were taken from International Tables.[29]

The larger than normal thermal parameters for atoms C3 through C8 of the naphthalene ring are due to a temperature-dependent packing disorder.

Dehydropyridination of Adduct 6. A solution of NaOMe was prepared by adding sodium metal (18 mg, 0.78 mmol) to anhydrous MeOH (1.0 mL). This solution was added to a solution of adduct **6** (66 mg, 0.10 mmol) dissolved in anhydrous THF (1.0 mL) at room temperature. After 1 h a precipitate formed, the solvents were rotary evaporated, and water (5 mL) was added. The mixture was extracted with CH_2Cl_2 (3 × 10 mL), and the combined extracts washed with 5% aqueous HCl solution and then brine. The organic phase was separated, dried (anhyd $MgSO_4$), filtered, concentrated by rotary evaporation, and chro-

(26) Bruker 1997 SMART Reference Manual Version 5.0, Bruker AXS Inc., Madison, WI.

(27) Bruker 1997 SAINT Reference Manual Version 5.0, Bruker AXS Inc., Madison, WI.

(28) Bruker 1997 SHELXTL Reference Manual Version 5.0, Bruker AXS, Inc., Madison, WI, USA

(29) *International Tables for X-ray Crystallography*; A. J. C. Wilson, Ed.; Kluwer Academic Publishers: Boston, 1992; Vol. C, Tables 4.2.6.8 and 6.1.1.4.

matographed on silica gel (eluting with CH_2Cl_2/pentane) to give pure **9** (14 mg, 61% yield).[22]

Dehydropyridination of Adduct 7. Treatment of adduct **7**·ClO_4 (160 mg, 0.42 mmol) with DBU (109 mg, 0.70 mmol) in anhydrous THF (20.0 mL) resulted in the formation of a deep red color. After 18 h at room temperature, the mixture was rotary evaporated and the residue dissolved in $CHCl_3$ and then chromalographed through a short silica gel column with CH_2Cl_2:pentane (1:10) to give **10** as an orange oil (64 mg, 76% yield): IR (neat) 3035, 2915, 2843, 1596, 1477, 1461, 1427, 1311, 1106, 1034, 928, 825, 769 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.62 (s, 3H), 6.58 (s, 1H), 7.44 (m, 2H), 7.52 (m, 1H), 7.63 (m, 1H), 7.70 (d, 1H, J = 6.8 Hz), 7.80 (d, 1H, J = 8.1 Hz); ^{13}C NMR ($CDCl_3$) δ 15.4, 119.6, 121.0, 121.7, 125.2, 127.3, 127.9, 128.0, 129.1, 138.7, 139.7, 141.1; HR MS (FAB) Calcd for $C_{13}H_{10}S$: 198.0503. Found: 198.0506.

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Supporting Information Available: ORTEP drawing of **7**·$SbCl_6$, tables of crystallographic data, selected bond lengths and bond angles for **7**·$SbCl_6$, ^1H and ^{13}C NMR spectroscopic data for **6**, **7**, and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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