temperature. The mixture was partitioned between H_2O (5 mL) and CH_2Cl_2 (3 × 5 mL). The combined organic extracts were dried over anhydrous $MgSO_4$, filtered, and concentrated to dryness, in vacuo, and the residue was chromatographed via reverse-phase HPLC (MeOH/H_2O 35:65) to afford **18** and **19** (in a ratio of 9:1) in 62% overall yield and **27** in 84% yield.

Hydrolysis of 27 (from 22). A solution of **27** (5 mg) in 6 M HCl (3 mL) was refluxed for 5 h. Additional HCl was added during the course of the reaction to maintain a constant pH. The reaction mixture was concentrated to dryness, in vacuo, and **29** was obtained in 100% yield.

L-Lysine hydrochloride (29): $[\alpha]^{20}_D = +15.7°$ (c = 0.007, D_2O). NMR (D_2O) shifts in ppm from Me_4Si, ^1H δ and J values at 300 MHz: 4.04 (t, J = 6.0 Hz, 1 H); 2.98 (t, J = 7.1 Hz, 2 H); 1.94 (m, 2 H); 1.69 (t, J = 7.2 Hz, 2 H); 1.50 (m, 2 H). LRCIMS (NH_3) m/z: 147 [M^+ + H (3)].

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Supplementary Material Available: Additional NMR data of compounds **7**, **11–13**, **15**, **24**, **27**, **32**; acetylation reactions of compounds **1**, **2**, **5**, **6**, **12–15**, **24**, **30**; the dehydration of **12**; the synthesis of **10** and **11**; ^1H NMR data of compounds **16**, **17**, **20–23**; and the chromatographic operations performed on the solvent-partition fractions (Chart I) (10 pages). Ordering information is given on any current masthead page.

Directed Ortho-Lithiation of Lithium Thiophenolate. New Methodology for the Preparation of Ortho-Substituted Thiophenols and Related Compounds

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Abstract: The directed ortho-lithiation of lithium thiophenolate by reaction with *n*-butyllithium in cyclohexane with *N,N,N',N'*-tetramethylethylenediamine gives almost quantitative conversion to lithium 2-lithiobenzenethiolate (**1**). Reactions of this dilithio derivative with a variety of electrophiles (D_2O, carbon dioxide, acetone, diphenyl disulfide, methyl iodide, and thioxanthone) are described. The adduct to thioxanthone is ring-closed to form a triarylmethyl cation (**9**), and its related carbinol (**8**), with two *o,o'*-sulfide bridges.

Research in the field of ortho-directed aromatic metalations[2] has included studies of ortho-directing substituents that undergo side-chain metalation prior to ring ortho-metalation to give dimetalated species.[3] A method for ortho-lithiation of lithium phenolate has been developed by Posner.[2h] There has been, however, little prior research reported on the ortho-metalation of thiophenol. Gilman reported low-yield dilithiation of monobromothiophenols via halogen–metal exchange.[4b] Work in our laboratories failed to improve these methods.[4c] Related research on the ortho-lithiation of alkylthioarenes has been done.[4e] As a part of our continuing search for new sulfur-containing synthetic intermediates we here report a very efficient and useful method for the direct ortho-lithiation of lithium thiophenolate. Recent work, described in adjacent papers by Eric Block et al.[5a] and Keith Smith et al.,[5b] has established a number of interesting applications of this lithiation and interesting modified versions of this lithiation technique.

Experimental Section

General Procedures. Proton and carbon NMR spectra were obtained from $CDCl_3$ solutions unless otherwise noted and chemical shifts are reported (ppm) downfield from tetramethylsilane internal standard. The COSY NMRs were obtained on a 200.057-MHz Varian instrument.[6]

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(2) For discussions and reviews, see: (a) Gschwend, H. W.; Rodriguez, H. R. *Org. React.* **1979**, *26*, 1. (b) Abicht, H. P.; Issleib, K. *Z. Chem.* **1977**, *17*, 1–9. (c) Slocum, D. W.; Jennings, C. A. *J. Org. Chem.* **1976**, *41*, 3653–3664. (d) Mallan, J. M.; Bebb, R. L. *Chem. Rev.* **1969**, *69*, 693. (e) Wakefield, B. J. *The Chemistry of Organolithium Compounds*; Pergamon Press: New York, 1974; Chapter 3. (f) Beak, P.; Snieckus, V. *Acc. Chem. Res.* **1982**, *15*, 306. (g) Beak, P.; Meyers, A. I. *Ibid.* **1986**, *19*, 356. (h) Posner, G. H.; Canella, K. A. *J. Am. Chem. Soc.* **1985**, *107*, 2571–2573.

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Elemental analyses are within 0.4% of calculated values for the listed elements unless otherwise noted.

Cyclohexane was dried by successive additions of freshly pressed sodium wire until no further hydrogen evolution was seen. The dry cyclohexane was stored with the sodium in a nitrogen atmosphere and was transferred directly to the reaction flask by syringe.

Preparation of Lithium 2-Lithiobenzenethiolate (1). (a) Thiophenol (5.0 g, 0.045 mol) in 10 mL of cyclohexane was slowly added dropwise to *n*-butyllithium (46 mL of a 2.2 M solution in hexane, 0.10 mol) and *N,N,N',N'*-tetramethylethylenediamine (TMEDA; 11.6 g, 0.10 mol) in 100 mL of cyclohexane at 0 °C, under N_2. The reaction mixture was stirred for 30 min at 0 °C and for 22 h at room temperature. (After 3–4 h at room temperature the clear yellow mixture becomes opaquely white and eventually develops the consistency of a viscous slurry). Quenching of a 0.5-mL aliquot with D_2O and comparison of the ^1H NMR spectrum with that of lithium thiophenolate (ortho protons are downfield at δ 7.7) showed 98% conversion to **1**. (b) Thiophenol (5.51 g, 0.050 mol) was slowly added dropwise to *n*-butyllithium (42.0 mL of a 2.38 M solution in hexane, 0.10 mol) and TMEDA (11.6 g, 0.10 mol) in 100 mL of cyclohexane at 0 °C, under N_2. The reaction mixture was stirred for 30 min at 0 °C and for 21 h at room temperature. Quenching of a 0.1-mL aliquot with D_2O and comparison of the ^1H NMR spectrum with that of lithium thiophenolate showed 96% conversion to **1**. (c) Thiophenol (5.51 g, 0.050 mol) was slowly added dropwise to *n*-butyllithium (42.0 mL of a 2.38 M solution in hexane, 0.10 mol) and TMEDA (11.6 g, 0.10 mol) in 100 mL of cyclohexane at room temperature, under N_2. After 19 h, a quenched aliquot showed 97% conversion to **1**. (d) Thiophenol (5.51 g, 0.050 mol) was slowly added dropwise to *n*-butyllithium (42.0 mL of a 2.38 M solution in hexane, 0.10 mol) and TMEDA (11.6 g, 0.10 mol) in 100 mL of cyclohexane at room temperature, under N_2. The reaction mixture was heated to 70 °C for 4 h. The quenched aliquot showed 92% conversion to **1**.

Reactions of Lithio Reagent 1 with Electrophiles. General Procedure. In a typical experiment the desired electrophile in cyclohexane was added to **1** (~10 mmol) at 0 °C. After being stirred for 30 min at 0 °C, the mixture was stirred for 24 h at room temperature. The reaction mixture was quenched with 15% (v/v) aqueous HCl (~50 mL). The resulting water layer was extracted with ether. The ether layer was then dried ($MgSO_4$), and the ether was removed to give the indicated products in parts a–d.

(a) With Carbon Dioxide. Lithio reagent **1** (9.75 mmol) was added to a large excess of finely powdered dry ice. After all of the excess CO_2 had evolved, the reaction mixture was worked up as above and gave 0.914 g (5.94 mmol, 61%) of thiosalicylic acid (**2**) as yellow crystals: mp 165–167 °C (authentic sample 165–168 °C); ^1H NMR ($CDCl_3$–CD_3OD) δ 7.50 (m, Ar*H*, 3), 8.26 (m, 1 *H* ortho to CO_2H); Anal. ($C_7H_6O_2S$) C, H, S.

(b) With Acetone. Acetone (1.00 g, 0.788 mL, 10.8 mmol) was added to lithio reagent **1** (9.75 mmol). Removal of the ether gave slightly impure 2-(1-hydroxy-1-methylethyl)benzenethiol (**3**). Column chromatography on silica gel with CH_2Cl_2 as eluant gave 0.966 g (5.92 mmol, 61%) of pure **3** as a viscous golden oil: ^1H NMR δ 1.75 (s, 6, CH_3), 2.62 (br s, 0.5, O*H*?), 4.23 (s, 0.65, S*H*?), 7.45 (m, 4, Ar*H*); IR ($CHCl_3$) 3680 (vw), 3610 (m), 3460 (br, m, OH), 3100 (w), 3075 (m), 3000 (s), 2945 (m), 2885 (m), 2575 (m, SH), 1915 (vw), 1835 (vw), 1713 (vw), 1595 (m), 1478, (s), 1437 (s), 1390 (s), 1372 (s), 1350 (m), 1283 (m), 1179 (s), 1108 (s), 1060 (m), 1002 (w), 953 (s), 860 (m), 665 (w), 580 (m), 562 cm^{-1} (w); mass spectrum (10 eV) *m/e* (rel intens) 168 (5.80, M^+), 150 (100.00, $M^+ - H_2O$), 149 (89.88), 135 (80.82, $M^+ - H_2O - CH_3$), 110 (15.68, $M^+ - C_3H_6O$), 91 (12.24), 43 (22.46); Anal. ($C_9H_{12}OS$) C, H, S.

(c) With Diphenyl Disulfide. Diphenyl disulfide (2.40 g, 11.0 mmol) was added to lithio reagent **1** (9.75 mmol). Removal of the ether gave 1.39 g of a crude orange solid material which was not positively identified. Recrystallization four times from ethanol–CH_2Cl_2 gave 0.610 g (1.40 mmol, 29%) of 2,2'-bis(phenylthio)diphenyl disulfide (**4**) as colorless needles: mp 125–125.5 °C (lit.[7] mp 121 °C); ^1H NMR δ 7.05–7.63 (m); ^{13}C NMR ($CDCl_3$) 126.654 (CH), 127.063 (CH), 129.174 (CH), 129.252 (CH), 129.415 (CH), 131.936 (CS), 134.898 (CH), 135.873 (CS), 140.461 (CS); IR ($CHCl_3$) 3070 (m), 3020 (m), 1605 (w), 1570 (m), 1480 (m), 1432 (m), 1270 (s), 1238 (m), 1177 (s), 1100 (w), 1080 (m), 1024 (m), 950 (w), 697 (m), 640 cm^{-1} (m); mass spectrum (10 eV) *m/e* (rel intens) 434 (15.69, M^+), 253 (59.98), 218 (24.93, $(C_6H_5S)_2$), 217 (14.95, M^+ – SPhSPh), 216 (5.88), 205 (9.27), 181 (19.42, 91 (100.00); Anal. ($C_{24}H_{18}S_4$) C, H, S.

(d) With Methyl Iodide. Methyl iodide (13.8 g, 97.2 mmol) was added to lithio reagent **1** (48.8 mmol). After the ether was removed the crude product was vacuum distilled and gave 3.25 g (23.6 mmol, 48%) of 2-(methylthio)toluene (**5**) as a colorless oil: bp 96–100 °C (3.0 Torr); ^1H NMR δ 2.35 (s, 3, ArCH_3), 2.45 (s, 3, SCH_3), 7.15 (m, 4, Ar*H*); IR ($CHCl_3$) 3075 (m), 3020 (s), 2970 (s), 2935 (s), 2870 (m), 1990 (w), 1910 (w), 1595 (s), 1475 (s), 1462 (s), 1443 (s), 1384 (m), 1322 (w), 1275 (m), 1110 (m), 1092 (m), 1073 (s), 1052 (m), 1030 (m), 990 (m), 970 (m), 958 (m), 910 (m), 710 (w), 692 (w), 680 (w), 675 cm^{-1} (w); mass spectrum (10 eV) *m/e* (rel intens) 135 (20.44, M^+), 137 (15.07, $M^+ - H$), 124 (100.00, $M^+ - CH_2$), 123 (34.55, $M^+ - CH_3$), 110 (39.01, $M^+ - C_2H_5$); Anal. ($C_8H_{10}S$) C, H, S.

(e) With Thioxanthone. Solid thioxanthone (10.6 g, 50.0 mmol) was added to lithio reagent **1** (45.0 mmol). After the mixture was stirred for 30 min at 0 °C, it was stirred at room temperature for 4 days. It was then quenched with 50% (v/v) aqueous HCl (100 mL) and worked up in the usual manner. Removal of the ether gave 9.6 g (30 mmol, 67%) of crude triarylcarbinol **8**, with small amounts of thioxanthone and other unidentified material present. A portion of this crude material (4.5 g, 14 mmol) was purified by very careful washing of the crude product with hot toluene to give 1.6 g (5.0 mmol, 23% based on starting **1**) of **8** as a light pink solid: mp 200–201 °C dec; ^1H NMR (DMSO-d_6–$CDCl_3$) (see Table I); ^{13}C NMR (DMSO-d_6–$CDCl_3$) (see Table II); IR (Nujol) 3520 (m), 3490 (br, m), 2690 (br, vw), 1960 (br, w), 1805 (w), 1720 (br, w), 1720 (br, w), 1645 (w), 1572 (m), 1535 (w), 1440 (s), 1350 (m), 1301 (m), 1270 (m), 1210 (w), 1125 (m), 1068 (w), 1000 (m), 975 (m), 922 (w), 871 (w), 765 (s), 753 (s), 740 (s), 728 (s), 638 (w), 540 cm^{-1} (vw); mass spectrum (10 eV) *m/e* (rel intens) 320 (14.84, M^+), 304 (68.86, $M^+ - O$), 303 (100.00, $M^+ - OH$), 271 (29.47, $M^+ - OH - S$); Anal. ($C_{19}H_{12}OS_2$) C, H, S.

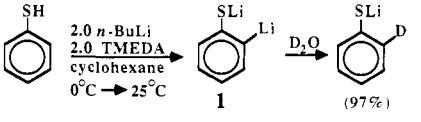
Solvent of crystallization was found in crystals of **8** grown in either acetone, toluene, or ether. Even after heating in vacuum [110 °C (0.1 Torr)] for 24 h solvent was detected by ^1H NMR and analysis in the following ratios. Ether: Anal. Calcd for $C_{19}H_{12}OS_2 \cdot 0.1(CH_3CH_2)_2O$: C, 71.10; H, 3.97; S, 19.55. Found: C, 71.21; H, 4.35; S, 19.77. Acetone–water: Anal. Calcd for $C_{19}H_{12}OS_2 \cdot 0.50H_2O \cdot 0.17$acetone: C, 69.09; H, 4.13; S, 18.90. Found: C, 68.99; H, 4.17; S, 19.14. Toluene: Anal. Calcd for $C_{19}H_{12}OS_2 \cdot 0.2C_6H_5CH_3$: C, 72.34; H, 4.02; S, 18.91. Found: C, 71.94; H, 4.27; S, 18.76.

Preparation of Triaryl Carbocation 9. A sample (35 mg, 0.11 mmol) of triarylcarbinol **8** in trifluoroacetic acid (0.30 mL, excess) gave a deep red solution containing carbocation **9** with approximately 10% of covalent trifluoroacetate **18** evidenced by peaks in the ^1H NMR spectrum very similar to those of **8**, but shifted slightly downfield. Addition of trifluoroacetyl trifluoromethanesulfonate (triflate) (TFAT;[8] 0.2 mL, excess) to the solution caused complete conversion to **9**: ^1H NMR (CF_3CO_2H–TFAT) (see Table I), ^{13}C NMR (CF_3CO_2H–TFAT) δ 128.435, 132.744, 135.263, 138.962, 148.451, 169.159 (a major portion of the spectrum is obscured by solvent peaks).

Attempted Preparation of *S,S'*-Dilithio-2-lithiobenzene-1,3-dithiol. To 40 mL of cyclohexane were added *n*-butyllithium (10.6 mL of a 2.2 M solution in hexane, 23.2 mmol) and TMEDA (3.50 mL, 23.2 mmol). The mixture was stirred for 15 min at room temperature and for 20 min at 0 °C before benzene-1,3-dithiol (1 g, 7 mmol) was added in 10 mL of cyclohexane. After 30 min at 0 °C the mixture was stirred at room temperature for 20 h. An aliquot quenched with CH_3OD showed no evidence for lithiation in the 2-position (^1H NMR). The reaction mixture was then boiled for 4 h, after which an ^1H NMR spectrum of an aliquot quenched with CH_3OD showed ~15% lithiation in the 2-position (normalized to an aliquot quenched with CH_3OH). Additional boiling for up to 96 h did not cause any further lithiation to occur as measured by ^1H NMR.

Results and Discussion

Synthesis. The directed ortho-lithiation proceeds in excellent yield with the use of 2.0 equiv of *n*-butyllithium (*n*-BuLi) and 2.0 equiv of *N,N,N',N'*-tetramethylethylenediamine (TMEDA). The



reagents are mixed at room temperature, and then the reaction mixture is heated to 70 °C. Reaction is essentially complete in

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(7) Killops, S. D.; Knox, S. A. R.; Riding, G. H.; Welch, A. J. *J. Chem. Soc., Chem. Commun.* **1978**, 486.

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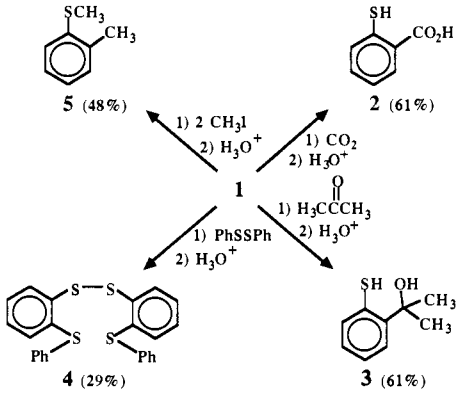
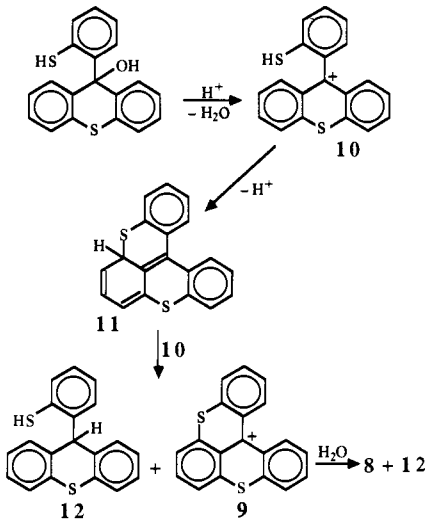
Scheme I



Scheme II

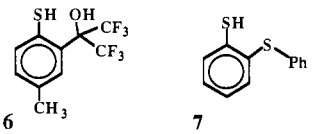


~4 h (92%) as measured by quenching aliquots of the reaction mixture with D_2O and examining the ^1H NMR spectra of the deuteriated products. Lithiation at room temperature for ca. 20 h provides a somewhat better conversion to **1** (97–98%).

Scheme I shows the various reactions that have been carried out with **1**. Reagent **1** provides a very convenient route to thiosalicylic acid (**2**) upon carbonation. This method is much simpler than the more traditional routes to **2**.[9]

Addition of acetone to **1** gives thiol alcohol **3**, a substitution type that has been used in our laboratory[3b] as a precursor to sulfuranes. The analogous fluorinated thiol **6** has proven very useful as an intermediate in the synthesis of a variety of sulfuranes.[10] Air oxidation of **3** to the disulfide is slow enough not to present a problem in isolating the free thiol **3**.

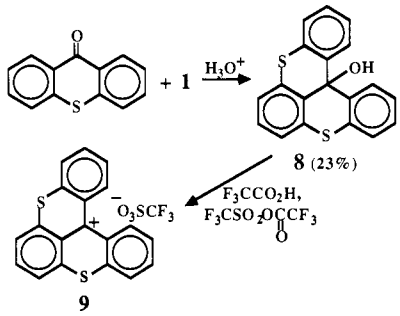
Treatment of **1** with diphenyl disulfide gives disulfide **4** after recrystallization from ethanol–methylene chloride in the presence of oxygen. This product must arise from oxidation of the 2-(phenylthio)benzenethiol (**7**) initially formed. The oxidation may



be by air or by unreacted diphenyl disulfide. We have not optimized the conditions to obtain a maximum yield of **4**. The earlier reported synthesis of **4** was by ultraviolet irradiation of diphenyl disulfide.[7] Even with conditions that are not optimized, we obtain higher yields with shorter reaction times. Compound **4** has been reported to be useful as a chelating agent for transition metals providing metallocycles.[7]

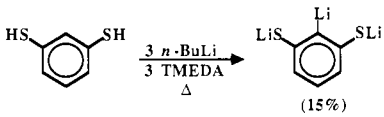
Addition of 2 equiv of methyl iodide to **1** conveniently gives 2-methylthioanisole (**5**).[11]

When thioxanthone is added to **1** triarylcarbinol **8** is produced. The synthesis of **8** marks the climax to many unsuccessful attempts in our laboratory to form this molecule,[4c] the first triarylcarbinol



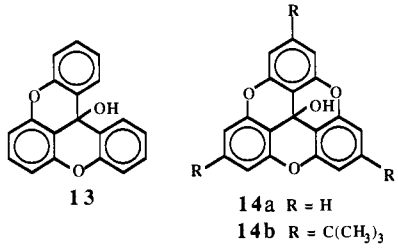
incorporating two sulfur ortho bridges. The formation of **8** may be explained by a mechanism similar to one proposed by Yamaye[4c] for the formation of a similar triarylcarbinol with one sulfur and one oxygen ortho bridge. Scheme II shows the probable route to **8** by quenching the reaction with aqueous hydrochloric acid. Oxidation of intermediate **11** to the corresponding carbocation **9** could proceed by hydride transfer to carbocation **10** from **11** to form triarylmethane **12**. This would provide a 1:1 mixture of carbinol **8** and methane **12** in the product mixture. Triarylmethane **12** was observed by NMR in the reaction mixture. We therefore expect a maximum 0.5 mol of **8** per mol of starting material **1**, plus 0.5 mol of **12**.

An attempt to introduce a third lithium into the 2-position of *S,S'*-dilithiobenzene-1,3-dithiol gave ~15% of the trilithiated species. We were unable to increase the efficiency of this reaction.



The formation of the trilithio derivative of the analogous 1,2-dithiol was found by Block et al.[5] to proceed more effectively, probably because the intermediate lithium salts are more soluble than the dilithium salts of the 1,3-dithiol.

Structure and Basicity of Carbinol 8. Much work has been done on doubly and triply ortho bridged triarylmethyl derivatives **13**,[12] and sesquixanthydrol **14**.[13,4d] Of particular interest is their ability



to form very stable cations and radicals. The stability is in part attributed to the fact that the oxygen ortho bridges make the cations and radicals, particularly those formed from **14**, have an essentially planar geometry.[14] This allows the aromatic π system

(9) Traditional routes to **2** include heating ortho-halogenated benzoic acids with alkaline hydrosulfide in the presence of copper: Ger. Pat. 189,200, 1906; or reduction of dithiosalicylic acid which is prepared from diazotonation of anthranilic acid and subsequent treatment with sodium sulfide: Allen, C. F. H.; MacKay, D. D. *Organic Syntheses*; Wiley: New York, 1943; Collect. Vol. II, p 580.

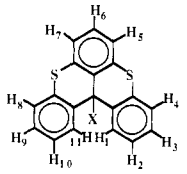
(10) Astrologes, G. W.; Martin, J. C. *J. Am. Chem. Soc.* **1977**, *99*, 4390–4400.

(11) For earlier methods of preparation of *o*-methylthioanisole that involve methylation of *o*-(methylthio)phenol with dimethyl sulfate, see: Leandri, G.; Mangini, A.; Passerini, R. *Gazz. Chim. Ital.* **1954**, *84*, 3. Gasperini, G. M.; Modena, G.; Todesco, P. E. *Ibid.* **1960**, *90*, 12a.

(12) Neunhoeffer, O.; Haase, H. *Chem. Ber.* **1958**, *91*, 1801.

(13) Martin, J. C.; Smith, R. G. *J. Am. Chem. Soc.* **1964**, *86*, 2252–2256; Sabacky, M. J.; Johnson, C. S., Jr.; Smith, R. G.; Gutowsky, H. S.; Martin, J. C. *Ibid.* **1967**, *89*, 2054–2058.

Table I. ^{1}H NMR Chemical Shifts for Triarylcarbinol **8** and Triaryl Carbocation **9** (360 MHz)



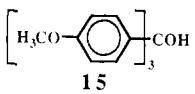
8 X = OH
9 X = +

8		9	
chem shift,[a] δ	proton	chem shift,[b] δ	proton
6.41 (S, 0.85)	O*H*		
6.19 (d, 1, J = 8 Hz)	H_1	7.80 (s, 3)	H_5, H_6, H_7
6.75 (t, 1, J = 8 Hz)	H_2	8.00 (t, 2, J = 8.0 Hz)	H_3, H_9
6.95 (d, 2)	H_{10}, H_{11}	8.13 (t, 2, J = 8.0 Hz)	H_4, H_8
7.05 (t, 2)	H_6, H_9	8.37 (d, 2, J = 8.0 Hz)	H_2, H_{10}
7.16 (m, 1)	H_3	8.75 (d, 2, J = 8.0 Hz)	H_1, H_{11}
7.25 (m, 3)	H_5, H_7, H_8		
8.07 (d, 1, J = 8 Hz)	H_4		

[a] In $CDCl_3$–DMSO–d_6. [b] In CF_3CO_2H–$CF_3SO_3COCF_3$.

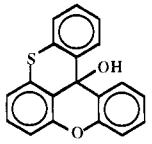
to delocalize the positive charge or odd electron much more effectively than if no such bridges existed.[15] Resonance interactions of the bridging oxygen atoms in the carbocation formed from **14a** are markedly accentuated by its planar geometry. The pK_R^+ of **14a** (9.25),[13] shows it to be a much more basic species than the analogous tris(*p*-methoxyphenyl)methanol (**15**) (pK_R^+ 0.82).[13] This means that at pH 9.25 carbinol **14a** is 50% converted to the cation.

$$pK_R^+ = pH + log\left(\frac{[Ar_3C^+X^-]}{[Ar_3COH]}\right)$$

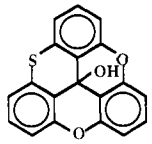


15

Attempts to prepare the sulfur analogues of **13** and **14** have met with only moderate success.[4c,4d] Yamaye[4c] prepared triarylcarbinols **16** and **17** through rather complex synthetic routes



16



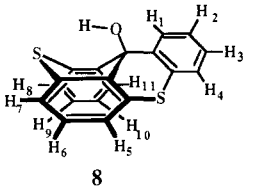
17

initiated by preparation of a substituted thioxanthone derivative, followed by treatment with (2-methoxyphenyl)lithium (leading to **16**) or (2,6-dimethoxyphenyl)lithium (leading to **17**).[4c] Our new methodology provides a more efficient route for direct incorporation of sulfur into both bridges of carbinol **8**, an analogue of **13** and **16**.

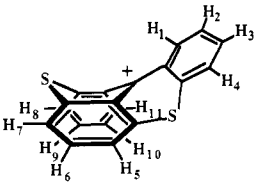
While crystal structure data is not yet available for carbinol **8** or carbocation **9**, ^{1}H NMR evidence strongly suggests the structures shown in Figure 1. Table I shows the proton NMR data based on COSY results. These structures are also suggested by examination of molecular models, with the longer C–S bonds making **9** more nonpolar than the cation formed from **13**.

Table II shows ^{13}C NMR data for **8**. Comparison of the ^{13}C NMR data for **8** and the triply bridged carbinol **14b** shows a significant difference in the chemical shift for C_1 in **8** (δ 74.5) and **14b** (δ 50.5).[4d] The shift for **8** closely resembles the chemical shift for the nonbridged triarylcarbinol precursor to **14b** (δ 75.1)[4d] and is consistent with the bent (or nonplanar) structure proposed for **8**.

Figure 1 shows the proposed structure for carbocation **9**. Examination of molecular models shows that the preferred conformation is a propeller shape which maintains one ortho proton above the other. Steric interactions between H_1 and H_{11} and their adjacent carbons provide less planar geometries because of the long C–S bonds in the bridging rings. A large amount of strain would develop in a planar conformation. The proton NMR spectrum of **9** (Table I) shows downfield shifts relative to **8**, as expected, for all of the protons. The signals for H_5, H_6, and H_7 overlap to form a broad singlet (δ 7.80). Although the lower frequency ^{1}H NMR spectrum available[4c] for the carbocation of **16** is not as well resolved as that for **9**, it does show a multiplet between δ 7.8 and 8.9. This is a similar shift to that of **9**. Work is continuing to provide evidence for the detailed structure of **9**.



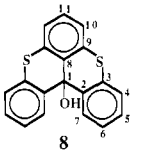
8



9

Figure 1. Proposed structures of triarylcarbinol **8** and triaryl carbocation **9**.

Table II. ^{13}C NMR Chemical Shifts of Triarylcarbinol **8** (in $CDCl_3$–DMSO)

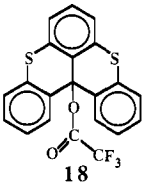


8

chem shift, δ	carbon	chem shift, δ	carbon
74.476	C_1	130.513	C_7 or C_5 or C_{11}
124.789	C_4 or C_6 or C_{10}	130.799	C_5 or C_7 or C_{11}
125.724	C_6 or C_4 or C_{10}	133.683	C_{11} or C_5 or C_7
126.329	C_{10} or C_4 or C_6	135.548	C_3 or C_9
127.511	C_2 or C_8	144.510	C_9 or C_3
127.998	C_8 or C_2		

The ^{13}C NMR chemical shifts for **9** are somewhat obscured by the peaks for the solvent (trifluoroacetic acid–trifluoroacetyl triflate) used to generate **9**; however, downfield peaks at δ 169.2 and 148.4 provide evidence for the existence of carbocation **9**.[4d]

The geometry of **9**, proposed in Figure 1 and supported by NMR data, suggests that the marked distortion from coplanarity of the aromatic rings, caused by the long C–S bonds, should reduce the resonance stabilization of the cation. In accord with this prediction we find carbinol **8** to be appreciably less basic than carbinols **16** or **13**, compounds with C–O bonds shorter than the C–S bonds of **9**. Carbinol **8** is only slightly soluble in hydrochloric acid, whereas the more basic **16** is completely soluble in hydrochloric acid by conversion to the carbocation. Dissolving **8** in trifluoroacetic acid provides approximately 90% conversion to cation **9** in the presence of 10% of the covalent trifluoroacetate **18**. Carbinols **16** and **13** are, however, completely converted to



18

the ionic trifluoroacetate salt of the carbocations in trifluoroacetic

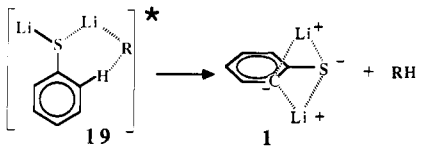
(14) The stability of the radical of **13** results mainly from a steric repulsion between the two neighboring ortho hydrogens. Such unfavorable steric interaction is intensified as the hybridization about the central carbon atom (sp^2) approaches sp^3 during formation of the dimer (See ref 4c.).

(15) Gilman, H.; Arntzen, C. E.; Webb, F. J. *J. Org. Chem.* **1945**, *10*, 374.

acid. Only after a strong acid (e.g., triflic acid, formed by reaction of TFAT with trifluoroacetic acid) is added to the trifluoroacetic acid solution of **8** do we see its complete ionization to form cation **9**. The lower basicity of **8** relative to **16** is, of course, partly attributed to the difference in the π-electron-donating ability of sulfur and oxygen (σ^+ for *p*-SMe is −0.164, while σ^+ for *p*-OMe is −0.648), making **16** the stronger base.

Conclusions on Ortho-Lithiation of Thiophenols. Although dimetalated thiophenols are clearly highly desirable synthetic intermediates, there has been little earlier success in their preparation. Very limited success was experienced by Gilman in preparing dilithiated thiophenol starting with 2-bromothiophenol.[4b]

The success of direct ortho-lithiation of lithium benzenethiolate is partly attributable to the choice of cyclohexane as a solvent. In a variety of other solvents we found lithiation by *n*-butyllithium–TMEDA to be much less effective. The nonpolar, unreactive cyclohexane solvent may favor coordination of the lithium cations, already coordinated to TMEDA, to the benzenethiolate anionic sulfur. The dilithiated species **1** could be formed via a transition state similar to **19**.[2e-g,16] The pictured ion cluster



structure of **1** was suggested by Streitwieser[17] after our personal communication to him concerning the preparation of **1**. The Coulomb interactions of two cations and a dicarbanion are favorable in such a geometry. (The lithium cations are also coordinated to the bidentate TMEDA ligands.)

The weak C–S bond of **1** provides an antibonding σ^* orbital low enough in energy to provide a stabilizing interaction with the adjacent carbanion lone pair of electrons in the plane of the benzene ring.[18,19] This may significantly contribute to the efficiency of this reaction.

Acknowledgment. The experimental aspects of this research were carried out at the University of Illinois with funding support from the U.S. Department of Health and Human Services (Grants CA-13963, GM-36844). We thank Dr. A. J. Arduengo, III for helpful suggestions, Dr. Eric Block for his cooperative interactions with us in his closely related studies, and Dr. Keith Smith for informing us of his related results.

Registry No. **1**, 117526-82-6; **2**, 147-93-3; **3**, 62172-72-9; **4**, 58074-47-8; **5**, 14092-00-3; **8**, 117526-90-6; **9**, 117526-92-8; thiophenol, 108-98-5; diphenyl disulfide, 882-33-7; thioxanthone, 492-22-8; benzene-1,3-dithiol, 626-04-0.

(16) For further examples of species involving suggested chelation of lithium to a sulfide sulfur, see: Eliel, E. L.; Hartmann, A. A.; Abatjoglou, A. G. *J. Am. Chem. Soc.* **1974**, *96*, 1807–1816. Abatjoglou, A. G.; Eliel, E. L.; Kuyper, L. F. *J. Am. Chem. Soc.* **1977**, *99*, 8262–8269.

(17) Streitwieser, A., Jr. *Acc. Chem. Res.* **1984**, *17*, 353. Kost, D.; Klein, J.; Streitwieser, A., Jr.; Schriver, G. W. *Proc. Natl. Acad. Sci. U.S.A.* **1982**, *79*, 3922. Compatible calculations on dilithio derivatives were also published by: Schleyer, P. v. R.; Kos, A. J. *J. Chem. Soc., Chem. Commun.* **1982**, 448.

(18) (a) For a discussion of stabilization of carbanions stabilized by adjacent vacant σ^* S–C bond molecular orbitals, see: Barbarella, G.; Dembech, P.; Garbesi, A.; Bernardi, F.; Bottoni, A.; Fava, A. *J. Am. Chem. Soc.* **1978**, *100*, 200–202. (b) For a discussion that rules out d-orbital effects in the above carbanion stabilization, see: Bernardi, F.; Csizmadia, I. G.; Mangini, A.; Schlegel, H. B.; Whangbo, M. H.; Wolfe, S. *Ibid.* **1975**, *97*, 2209–2218. (c) For a discussion of stabilization of carbanions next to sulfur through a σ^* interaction, see: Streitwieser, A., Jr.; Ewing, S. P. *Ibid.* **1975**, *97*, 190–191. Streitwieser, A., Jr.; Williams, J. E., Jr. *Ibid.* **1975**, *97*, 191–192. Epiotis, N. D.; Yates, R. L.; Bernardi, F.; Wolfe, S. *Ibid.* **1976**, *98*, 5435–5439. Bernardi, F.; Schlegel, H. B.; Whangbo, M. H.; Wolfe, S. *Ibid.* **1977**, *99*, 5633–5636. (d) For other related discussions, see: Eliel, E. L.; Willer, R. L. *Ibid.* **1977**, *99*, 1936–1942. Graham, S. L.; Heathcock, C. H. *Ibid.* **1980**, *102*, 3713–3718, and references therein.

(19) The analogous ortho-lithiation of lithium benzeneselenolate (Loop, C.; Martin, J. C., in preparation) is facile, providing data compatible with suggested explanations for the formation of **1**.

o-Lithiothiophenol Equivalents: Generation, Reactions, and Applications in Synthesis of Hindered Thiolate Ligands[1]

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Contribution from the Department of Chemistry, State University of New York at Albany, Albany, New York 12222. *Received March 14, 1988*

Abstract: Treatment of 2-(phenylthio)tetrahydropyran (**11**) with *tert*-butyllithium in THF–HMPA at −90 °C followed by chlorotrimethylsilane or chlorotriethylsilane and then mercuric chloride–hydrogen sulfide affords 2-(trimethylsilyl)benzenethiol (**13**) or 2-(triethylsilyl)benzenethiol (**14**), respectively. Compounds **13** and **14** can also be obtained directly from thiophenol by conversion of the latter to lithium 2-lithiobenzenethiolate (**16**) followed by quenching of a THF solution of **16** at −78 °C with an equivalent of the appropriate chlorosilane; by this same procedure, 4-*tert*-butylbenzenethiol can be converted into 4-*tert*-butyl-2-(trimethylsilyl)benzenethiol (**18**) via lithium 4-*tert*-butyl-2-lithiobenzenethiolate (**17**) and 2-naphthalenethiol can be transformed into 3-(trimethylsilyl)-2-naphthalenethiol (**31**) via lithium 3-lithio-2-naphthalenethiolate (**30**). Reaction of **13** with *n*-butyllithium in hexane followed by chlorotrimethylsilane gives 2,6-bis(trimethylsilyl)benzenethiol (**15**) together with products derived from lithiation of the silyl methyl groups. Treatment of a solution of **16** in THF with dichlorodimethylsilane, dichlorodiethylsilane, 1,2-dichlorotetramethyldisilane, or 1,2-bis(chlorodimethylsilyl)ethane affords bis(2-mercaptophenyl)-dimethylsilane (**23**), bis(2-mercaptophenyl)diethylsilane (**24**), 1,2-bis(2-mercaptophenyl)tetramethyldisilane (**25a**), or 1,2-bis[(2′-mercaptophenyl)dimethylsilyl]ethane (**25b**), respectively. Oxidation of **23** yields 11,11-dimethyl-11*H*-dibenzo[*c*,*f*]-[1,2,5]dithiasilepin (**26**). Treatment of **17** with diethyldichlorosilane and dichlorodiphenylsilane affords bis(5-*tert*-butyl-2-mercaptophenyl)diethylsilane (**27**) and bis(5-*tert*-butyl-2-mercaptophenyl)diphenylsilane (**28**), respectively. The latter compound upon exposure to air gives **29**, the diphenyl analogue of **26**. Thiophenol can be transformed into 1,2-benzenedithiol (**32a**) by way of **12**; similarly 4-*tert*-butylbenzenethiol can be converted into 4-*tert*-butyl-1,2-benzenedithiol (**32b**). Compound **32a** can be further transformed into 1,2,3-benzenetrithiol (**34**) via a trilithio species **33**. The ^1H and ^{13}C NMR spectra of dilithio salts **16** and **17** were determined.

The intense contemporary interest in metal thiolate chemistry[2] reflects both the biological significance and the structural diversity associated with this fundamental metal–ligand type. In connection with our research on nitrogenase models, we have initiated a

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