Anal. Calcd for $C_{25}H_{23}NS$: C, 81.26; H, 6.27; N, 3.79. Found: C, 81.31; H, 6.20; N, 3.83.

Reaction of *N*-(3,5-Dimethylphenyl)vinylmethylketenimine (1c). Ketenimine **1c** (0.80 g, 4.3 mmol) and thioketone **2** (0.9 g, 4.6 mmol) in 10 mL of CCl_4 were allowed to react at room temperature for 35 h. After evaporation of the solvent, column chromatography of the residue (silica; benzene–*n*-pentane, 7:3) gave the following.

(a) 2-(1-Methyl-1-propenyl)-4,4-diphenyl-5,7-dimethyl-4*H*-3,1-benzothiazine (3c): 0.77 g (2.01 mmol, 45%); mp 135–137 °C (from methanol); IR (CCl_4) 1550 cm^{-1}; ^{1}H NMR δ 1.47 (s, 3 H, CH_3), 1.79 (d, 3 H, CH_3, J = 8.1 Hz), 1.97 (s, 3 H, CH_3), 2.34 (s, 3 H, CH_3), 6.67 (q, 1 H, =CH, J = 8.1 Hz), 6.86 (br, 2 H, arom), 7.20–7.50 (br, 10 H, arom); ^{13}C NMR ($CDCl_3$) δ 13.11, 14.85, 20.61, 23.64 (q, CH_3), 60.90 (s, CPh_2), 136.36, 136.91, 137.28, 142.91, 146.28 (s, arom), 160.8 (s, C=N); mass spectrum, m/e 383 (M^+).

Anal. Calcd for $C_{26}H_{25}NS$: C, 81.42; H, 6.57; N, 3.65. Found: C, 81.53; H, 6.52; N, 3.69.

(b) 3-Methyl-6,6-diphenyl-2-[(3,5-dimethylphenyl)imino]-1-thiacyclohex-3-ene (6c): 0.42 g (1.1 mmol, 24%); mp 186–189 °C (from methanol); IR (CCl_4) 1580 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.95 (d, 3 H, CH_3, J = 1.4 Hz), 2.3 (s, 6 H, CH_3), 3.45 (dd, 2 H, CH_2, J = 5.2, 1.8 Hz), 6.25 (m, 1 H, =CH, J = 5.2, 1.4 Hz), 6.55 (s, 2 H, arom), 6.77 (s, 1 H, arom), 7.32 (m, 10 H, arom); ^{13}C NMR ($CDCl_3$) δ 19.93 (q, CH_3), 21.36 (q, 2 CH_3), 38.14 (t, CH_2), 58.28 (s, CPh_2), 134.55, 138.4, 144.35, 150.57 (s, arom), 183.25 (s, C=N); mass spectrum, m/e 383 (M^+), 220 (M^+ – ArNCS).

Anal. Calcd for $C_{26}H_{25}NS$: C, 81.42; H, 6.57; N, 3.65. Found: C, 81.72; H, 6.47; N, 3.72.

Reaction of *N*-Mesitylvinylmethylketenimine (1d). A solution of crude ketenimine **1d** (1.11 mmol) in 10 mL of CCl_4 prepared in situ from the corresponding imidoyl chloride[9] as described above was reacted with a twofold molar excess of thione **2** (0.4 g, 2.2 mmol) at room temperature for 14 h. From the IR spectrum of the solution the ketenimine **1d** was no longer detectable, whereas from the UV spectrum it appeared that 50% of thioketone **2** had reacted. After evaporation of the solvent, column chromatography of the residue (silica; benzene–*n*-pentane, 1:3) gave 0.20 g (1 mmol) of unreacted **2** and 0.34 g (0.86 mmol, 86%) of **3-methyl-6,6-diphenyl-2-(mesitylimino)-1-thiacyclohex-3-ene (6d)**: mp 126–128 °C (from methanol); IR(CCl_4) 1580 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.01 (br s, 9 H, CH_3), 2.23 (s, 3 H, CH_3), 3.35 (dd, 2 H, CH_2, J = 5.2, 1.8 Hz), 6.30 (m, 1 H, =CH, J = 5.2 Hz), 6.83 (s, 2 H, arom), 7.24 (m, 10 H, arom); ^{13}C NMR ($CDCl_3$) δ 17.60 (q, CH_3), 19.82 (q, 2 CH_3), 20.78 (q, CH_3), 38.31 (t, CH_2), 58.51 (s, CPh_2), 132.59, 134.42, 144.68, 159.43 (s, arom), 188.74 (s, C=N); mass spectrum, m/e 397 (M^+).

Anal. Calcd for $C_{27}H_{27}NS$: C, 81.57; H, 6.85; N, 3.52. Found: C, 81.60; H, 6.81; N, 3.52.

Registry No. **1a**, 82638-89-9; **1b**, 42463-98-9; **1c**, 75340-96-4; **1d**, 82638-90-2; **2**, 1450-31-3; **3a**, 82638-91-3; **3b**, 82638-92-4; **3c**, 82638-93-5; **5**, 82638-94-6; **6c**, 82638-95-7; **6d**, 82638-96-8.

New Synthesis of 1,3-Dithiole and 1,3-Thiazole-2-thiones Promoted by Iron Complexes

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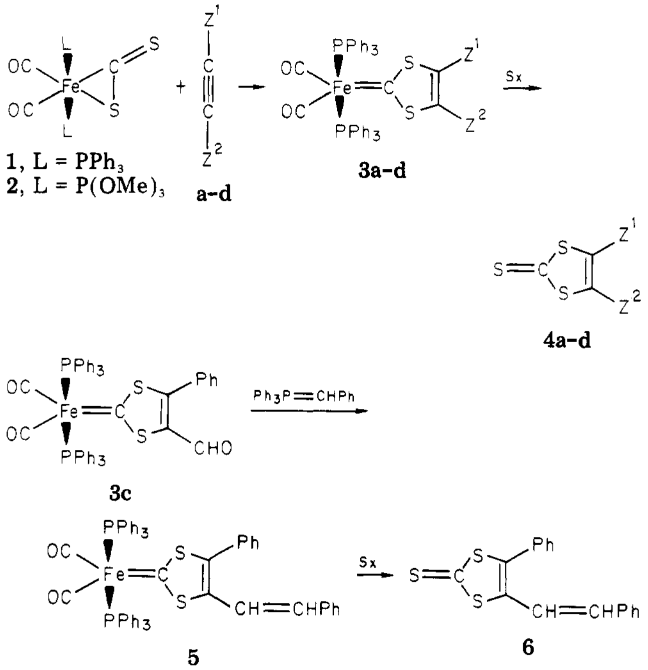
Received January 18, 1982

The discovery of electrical conductance properties of charge-transfer complexes which contain tetrathiafulvalene (TTF) as an electron-donating component[1] has initiated an increasing interest for the development of new syntheses of tetrathiafulvalenes and of their precursors.[2] The methods of formation of TTF derivatives depend markedly on the nature of their substituents. TTF itself is conveniently prepared by coupling of an 1,3-dithiolium salt using a tertiary amine,[3] and substituted TTF can be obtained from the phosphoranes resulting either from the addition of an alkyne to the R_3PCS_2 zwitterion or from the deprotonation of the adduct of a phosphine to an 1,3-dithiolium salt.[4,5] Another efficient method is based on the desulfurization reactions of 1,3-dithiole-2-thiones involving either phosphorus(III) derivatives[2,6,7] or transition-metal complexes.[8] 1,3-Dithiole-2-thiones can also be used as precursors of 1,3-dithiolium salts.[2,3]

Scheme I[a]



[a] **a**, $Z^1 = Z^2 = CO_2Me$; **b**, $Z^1 = Z^2 = CO_2Et$; **c**, Z^1 = Ph, Z^2 = CHO; **d**, Z^1 = Ph, $Z^2 = COCH_3$.

1,3-Dithiole-2-thiones can be prepared by treatment of ethylene trithiocarbonate with alkynes,[9] but this synthesis is limited to electrophilic alkynes. Recently Benitez and Grunwell[10] reported a convenient route, although it was performed under rather drastic conditions (reactor at 140 °C for 24 h) by reacting an excess of substituted acetylenes with bisamine disulfides and carbon disulfide.

We present here a new route to a variety of 1,3-dithiole-2-thiones and 1,3-thiazole-2-thiones containing functional groups in one step from the easily accessible carbon disulfide–iron and isothiocyanate–iron complexes, respectively.

We have shown recently that a variety of alkynes add readily, at room temperature, to the activated carbon disulfide ligand of $Fe(\eta^2\text{-}CS_2)(CO)_2L_2$ complexes **1** (L = PPh_3) and **2** (L = $P(OMe)_3$)[11] to afford the thermally stable

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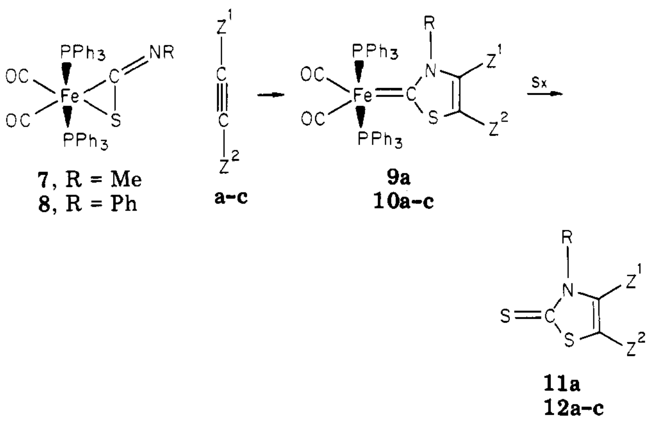
Scheme II[a]



[a] a, $Z^1 = Z^2 = CO_2Me$; b, $Z^1 = Z^2 = CO_2Et$; c, Z^1 = Ph, Z^2 = CHO.

(1,3-dithiol-2-ylidene)iron complexes of type 3[12] (Scheme I) which offer an alternative to the unstable (1,3-dithiol-2-ylidene)phosphoranes.[3,5]

This quantitative reaction can be used for the synthesis of 2-thiones **4** by displacement of the 1,3-dithiol-2-ylidene ligand of compounds **3** by elemental sulfur. Thus the derivatives **3a–d**[12] were prepared by addition of the alkynes **a–d** to complex **1**[11] in toluene, and then the mixture was refluxed with an excess of sulfur for 5 h. The corresponding thiones, containing an ester, a formyl, or an acyl group, were isolated by using silica gel chromatography: **4a**, 64%; **4b**, 40%; **4c**, 22%, **4d**, 31% (Scheme I).

Besides the formation of **4a–d** a small amount of the corresponding tetrathiafulvalene derivative, resulting from the dimerization of the 1,3-dithiol-2-ylidene ligand of precursors **3**, was formed and observed by using chromatography; it could be isolated only from the precursor **3a** and in poor yield (13%).

The formation of thiones **4** is not limited to complex **1** (L = PPh_3). Compound **4a** was obtained from **2** (L = $P(OMe)_3$), via the corresponding carbene–iron complex of type **3**, but in lower yield (25%) than from **1** (64%). This lowering of the reaction yield is likely related to the stability of the Fe–$P(OMe)_3$ bond as compared to the Fe–PPh_3 bond.[11]

A novel synthesis of compound **1**[13] has been performed to make these thiones **4** more accessible. Complex **1** was prepared in one step from iron pentacarbonyl in 80–85% yield by adding to an ethanol solution of $Fe(CO)_5$, in the presence of triphenylphosphine and carbon disulfide, an excess of trimethyl amine oxide, a known carbonyl-displacing reagent.[14]

As the (carbene)carbon–iron bond of complexes **3** is stable toward Wittig reagents, our synthesis of thiones **4** was adapted for the preparation of the 4-alkenyl-1,3-dithiole-2-thione **6** by successive reactions performed in one flask: (i) addition of alkyne **c** to complex **1** in toluene, (ii) treatment with (phenylmethylidene)triphenylphosphorane to afford the intermediate **5**, (iii) reflux with an excess of sulfur. The thione **6** [*m/e* 312.009 (M^+; calcd *m/e* 312.010)] was isolated by using chromatography with an overall yield of 19% from **1** (Scheme I).

The thione synthesis can be generalized to the formation of 1,3-thiazole-2-thiones **11** and **12** (Scheme II).

The addition of alkyne **a** to the (η^2-SCNMe)–iron complex **7** and of alkynes **a–c** to the (η^2-SCNPh)–iron derivative **8** affords the corresponding (1,3-thiazol-2-ylidene)iron complexes **9** and **10**.[15] Further treatment of the reaction mixture with an excess of sulfur in refluxing toluene leads to the formation of thiones **11** and **12** which were isolated by using thick-layer chromatography: **11a**, 32%; **12a**, 25%; **12b**, 21%; **12c**, 18%.

The mechanism of formation of dithiole- and thiazole-2-thiones, which is related to the formation of thioester by the displacement of a Fischer-type carbene ligand from chromium with elemental sulfur,[16] has not been elucidated. However, it can be suggested that the sulfur atom inserts into the iron–carbon bond after dissociation of one phosphorus group for the following reasons: (i) the (carbene)carbon–iron bond is thermally stable under the reaction conditions; (ii) the reaction is easier with **1** than with **2**, dissociation of PPh_3 is easier than that of $P(OMe)_3$, and steric and electronic effects of PPh_3 would disfavor direct nucleophilic addition of sulfur on the carbene carbon; (iii) the treatment of a Fischer-type carbene–chromium derivative has led recently to the isolation of a $(CO)_5W \leftarrow S{=}CR_2$ complex.[17]

In conclusion, the facile access to complexes **1** and **8** makes this one-pot synthesis a convenient route to substituted 1,3-dithiole- and 1,3-thiazole-2-thiones.

Experimental Section

IR spectra were obtained on a Pye-Unicam SP 1100 infrared spectrophotometer. NMR spectra were recorded on Varian EM 360 (^1H) and on Bruker WP 80 (^{13}C) instruments. Mass spectra were obtained at 70 eV with use of a Varian MAT 311 mass spectrometer (Centre de Mesures Physiques, Rennes). Microanalyses were determined by CNRS-Villeurbanne. Alkynes and iron pentacarbonyl were commercial grade (Aldrich).

Synthesis of 1. Into a 500-mL flask were successively introduced a solution of 20 g (0.076 M) of PPh_3 in 175 mL of 95% ethanol, 30 mL of CS_2, and with a syringe 5 mL (0.037 M) of $Fe(CO)_5$. Then to the well-stirred mixture was slowly added a solution of 8.2 g of $Me_3NO{\cdot}2H_2O$ (0.074 M) in 75 mL of 95% ethanol. A gas (CO_2) started to evolved, and the rust-red compound **1** precipitated. When the addition was over, the reaction mixture was treated with a steam bath until the gas evolution had stopped. The rust-red precipitate was recovered by filtration on a frit, washed successively with ether, ethanol, and ether, and finally dried under vacuum: 22 g (83%); mp 147–150 °C dec; IR (THF) ν_{CO} 1999, 1937 cm^{-1}; IR (Nujol) $\nu_{C=S}$ 1140 cm^{-1}; ^{31}P NMR (CD_2Cl_2) δ 56.56 (s). Anal. Calcd for $C_{39}H_{30}FeO_2S_2P_2$: C, 65.64; H, 4.23; P, 8.70; S, 8.98; Fe, 7.86. Found: C, 65.38; H, 4.54; P, 8.69; S, 8.53; Fe, 7.85.

General Procedure for the Synthesis of 1,3-Dithiole-2-thiones 4a–d. To a suspension of complex **1** in toluene (40 mL) under an inert atmosphere was added with a syringe a slight excess of an alkyne, **a–d**. The solution was stirred at room temperature for a period a time depending of the nature of alkyne.[12] An excess of sulfur was then added, and the mixture was refluxed for 5 h. After removal of the solvent the crude products were chromatographed on a silica gel column (with hexane–ether as the eluent) to give the yellow compounds **3a–d**.

4a ($Z^1 = Z^2 = CO_2Me$). Reaction: 0.2 mL of **a**, 0.72 g of **1** (1 mmol), 0.8 g of sulfur. Results: 0.16 g (64%) of **3a**; mp 83–85 °C; mass spectrum, *m/e* 249.9430 (M^+; calcd 249.9428); IR (Nujol) 1760, 1735, 1570 cm^{-1}; ^1H NMR ($CDCl_3$) δ 3.99 (s, CO_2Me) [lit.[3] mp 86–87 °C; ^1H NMR (Me_2SO-d_6) δ 3.83 (s, CO_2Me)].

4b ($Z^1 = Z^2 = CO_2Et$). Reaction: 0.7 mL of **b**, 2.9 g of **1** (4 mmol), 1.0 g of sulfur. Results: 0.46 g (40%) of **3b**; mass spectrum, *m/e* 277.9747 (M^+; calcd 277.9741); IR (Nujol) 1730, 1560 cm^{-1};

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^{1}H NMR (CDCl$_3$) δ 1.37 (t, $^3J_{HH}$ = 7 Hz, CH$_3$), 4.38 (q, $^3J_{HH}$ = 7 Hz, OCH$_2$).

4c ($Z^1 = C_6H_5$, Z^2 = CHO). Reaction: 0.3 mL of **c**, 1.45 g of **1** (2 mmol), 0.6 g of sulfur. Results: 0.10 g (22%) of **3c**; mp 105 °C; mass spectrum, *m/e* 238 (M$^+$; calcd 238); IR (Nujol) 1660, 1530 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 7.73 (m, C$_6$H$_5$), 9.68 (s, CHO).

4d ($Z^1 = C_6H_5$, Z^2 = COCH$_3$). Reaction: 0.3 mL of **d**, 1.45 g of **1** (2 mmol), 1.0 g of sulfur. Results: 0.17 g (31%) of **3d**; mass spectrum, *m/e* 251.9733 (M$^+$; calcd 251.9737); IR (Nujol) 1660, 1545 cm^{-1}; ^{1}H NMR (CDCl$_3$) δ 1.97 (s, CH$_3$), 7.90 (m, C$_6$H$_5$).

1,3-Dithiole-2-thione (6). To a suspension of complex **1** (1.5 g, 2 mmol) in 15 mL of toluene under a nitrogen atmosphere was added 0.25 mL of alkyne **c** with a syringe. The resulting brown solution was stirred at room temperature for 2 h. A solution of 1 equiv of the Ph$_3$PCHPh ylide in toluene was then added, and the mixture was stirred at room temperature for 3 h. An excess of sulfur (1 g) was added, and the reaction mixture was refluxed for 5 h. After removal of the solvent the crude product was chromatographed on silica gel column (with hexane–ether as the eluent) to give 0.14 g (19%) of compound **6**: mass spectrum, *m/e* 312.009 (M$^+$; calcd 312.010); IR (Nujol) 1545, 1075 cm^{-1}; ^{1}H NMR (C$_6$D$_6$) δ 6.61 and 6.70 (dd, HC=CH, J_{HH} = 16.0 Hz), 7.06 (m) and 7.26 (m) (C$_6$H$_5$).

1,3-Thiazole-2-thiones 11a and 12a–c. To a solution of complex **7** or **8** in toluene under a nitrogen atmosphere an excess of alkynes **a**, **b**, or **c** was added with a syringe. The solution was stirred at room temperature for 12 h. An excess of sulfur was then added and the mixture was refluxed for 5 h. After removal of the solvent the crude products were chromatographed on silica gel column (with hexane–ether as the eluent). The yellow compounds **11a** and**12a–c** migrate in front of the column.

11a (R = Me, $Z^1 = Z^2$ = CO$_2$Me). Reaction: 0.4 mL of **a**, 2 g of **7** (2.8 mmol), 0.8 g of sulfur. Results: 0.2 g (32%) of **11a**; mp 78–80 °C; mass spectrum, *m/e* 246.9985 (M$^+$; calcd 246.9972); IR (Nujol) 1745, 1590, 1120 cm^{-1}; ^{1}H NMR (C$_6$D$_6$) δ 3.03 (s), 3.30 (s), 3.43 (s); ^{1}H NMR (CDCl$_3$) δ 3.63 (s), 3.83 (s), 4.00 (s), NMe and two CO$_2$Me groups.

12a (R = Ph, $Z^1 = Z^2$ = CO$_2$Me). Reaction: 0.5 mL of **a**, 2 g of **8** (2.6 mmol), 0.8 g of sulfur. Results: 0.2 g (25%) of **12a**; mass spectrum, *m/e* 309.0128 (M$^+$; calcd 309.0129); IR (Nujol) 1745, 1580, 1120 cm^{-1}; ^{1}H NMR (C$_6$D$_6$) δ 3.23 (s, CO$_2$Me), 3.58 (s, CO$_2$Me), 7.06 (m, C$_6$H$_5$).

12b (R = Ph, $Z^1 = Z^2$ = CO$_2$Et). Reaction: 0.5 mL of **b**, 2 g of **8** (2.6 mmol), 0.8 g of sulfur. Results: 0.18 g (21%) of **12b**; mass spectrum, *m/e* 337.0439 (M$^+$; calcd 337.0442); IR (Nujol) 1745, 1580, 1158 cm^{-1}; ^{1}H NMR (C$_6$D$_6$) δ 1.01 (m, 2 CH$_3$), 4.12 (q, $^3J_{HH}$ = 7 Hz, OCH$_2$), 4.42 (q, $^3J_{HH}$ = 7 Hz, OCH$_2$), 7.27–7.53 (m, C$_6$H$_5$).

12c (R = Ph, Z^1 = Ph, Z^2 = CHO). Reaction: 0.4 mL of **c**, 2 g of **8** (2.6 mmol), 0.8 g of sulfur. Results: 0.14 g (18%) of **12c**; mp 142–144 °C; mass spectrum, *m/e* 297.025 (M$^+$; calcd 297.025).

Registry No. 1, 64424-68-6; **2**, 64424-66-4; **4a**, 7396-41-0; **4b**, 74090-73-6; **4c**, 82679-19-4; **4d**, 82679-20-7; **6**, 82679-21-8; **7**, 82679-17-2; **8**, 82679-18-3; **11a**, 41126-43-6; **12a**, 41126-48-1; **12b**, 41126-49-2; **12c**, 82679-22-9; **a**, 762-42-5; **b**, 762-21-0; **c**, 2579-22-8; **d**, 1817-57-8; Fe(CO)$_5$, 13463-40-6; Ph$_3$PCHPh, 16721-45-2; PPh$_3$, 603-35-0; CS$_2$, 75-15-0.

The 3-(Fluoromethyl)phenyl Group. A Useful Moiety for the Study of Solvolysis Reactions with Large Negative ρ Values

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The use of ρσ linear free-energy[1] relationships has proven to be extremely advantageous for a wide variety of mechanistic studies in organic chemistry. Of particular value to the investigation of the chemistry of carbocations has been the $\rho\sigma^+$ relationships devised by Brown and Okamoto[2] and our use of this relationship in the study of delocalized carbocations through the "tool of increasing electron demand".[3,4] When this concept is applied to systems in which strong electron-withdrawing substituents are attached directly to the incipient positive center,[5] the size of ρ can dramatically increase and, as a result, the rate differences between the commonly used aryl substituents often become very large.[5a,b,f] Since careful examination of systems having a large ρ generally requires a variety of extrapolations, it is important to have available substituents with intermediate σ^+ values in order to minimize the error involved in such extrapolations. As part of our detailed investigation of α-cyanocarbocations, we had need of an aryl substituent that would fall between hydrogen ($\sigma_{meta}{}^+ = 0$) and 3-chloro ($\sigma_{meta}{}^+ = 0.399$). Although 3-phenyl, 3-methylthio, 4-chloro, 4-bromo, 4-iodo, and 4-acetoxy fall within the desired range, they did not fulfill our desire for a group that (a) could not interact in a conjugative manner either through π conjugation or through interaction with nonbonding electrons and (b) were stable to our synthetic and solvolytic conditions. A substituent that appeared to be attractive was the 3-fluoromethyl moiety. If the influence of fluorines on a 3-methyl group were approximately additive, a σ^+ value for a 3-fluoromethyl group would be predicted to be about 0.13.[6] We report in this note the synthesis and kinetic determination of the σ^+ value of the 3-(fluoromethyl)phenyl moiety.

Reduction of commercially available 3-bromobenzaldehyde (**1**) with lithium aluminum hydride gave the known[7] 3-bromobenzyl alcohol (**2**) in 84% yield. When **2** was allowed to react with methanesulfonyl chloride in methylene chloride containing triethylamine at 0 °C, **3** was produced in 75% yield. Treatment of **3** with potassium fluoride and 18-crown-6 in acetonitrile gave 84% of **4**. Attempts to generate a Grignard from **4** resulted in the formation of 1,1′-(1,2-ethanediyl)bis-3-bromobenzene (**5**) as the major product. Fortunately, **4** was readily transmetalated with *n*-butyllithium in tetrahydrofuran at −78

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