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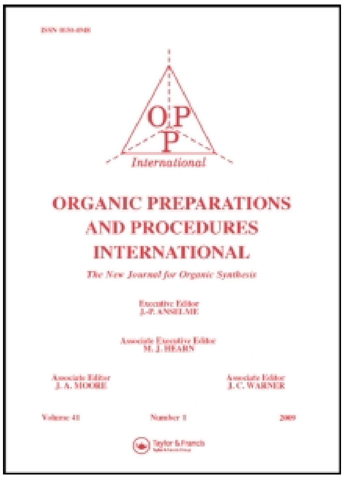

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A RAPID PREPARATION OF 2,2'-DIMERCAPTOBIPHENYL

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A RAPID PREPARATION OF 2,2'-DIMERCAPTOBIPHENYL

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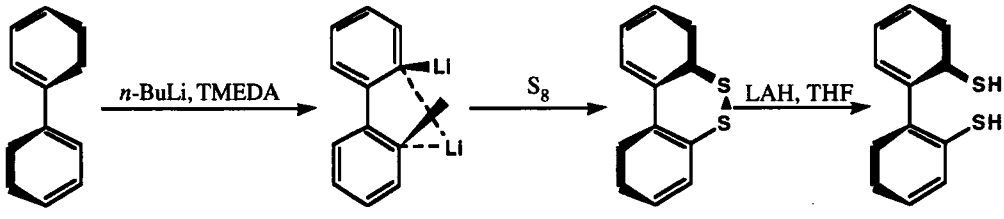
The several methods of preparation of 2,2'-dimercaptobiphenyl (**1**) reported in the literature,[1] reflect its widespread utilization as a substrate for redox[2] and thermodynamic[3] studies, as a ligand and as an atropisomeric chiral reagent.[4] Dithiol **1** is available *via* the Ullman coupling of appropriate precursors,[1b,d] Newman-Kwart rearrangement of thioesters,[5] lithium reduction of dibenzothiophene,[6] and other routes.[7] We now report the experimental details for its preparation from the dianion **3**, which was generated directly *via* *n*-butyllithium (*n*-BuLi)-N,N,N',N'-tetramethylethylenediamine (TMEDA) deprotonation of biphenyl by a known procedure.[8]

Biphenyl was treated under various conditions; the best results were obtained when *n*-BuLi was treated with TMEDA at 25° before the addition of biphenyl. Metallation of biphenyl with 1:1 *n*-BuLi-TMEDA at -15° for *ca* 15 hrs provided optimum conversion to its dianion.[9] Treatment of the dilithio intermediate **3** with 1.1 eq. of elemental sulfur at -35° gave the disulfide **2** in higher yield

(50%) than when a large excess of elemental sulfur or using higher temperatures (0° and 25°) were employed. There was no evidence for the formation of tri-, tetra- or pentasulfides. The only by-product of the metallation was the starting biphenyl. The present method affords comparable yields to the recently reported procedure for the synthesis of disulfide **2** through metallation of dibenzothiophene,[6] which is more expensive.



3 2 1

Lithium aluminium hydride reduction of **2** provided pure **1** in good yield and purity. The availability of this rapid and easy method of preparation of **1** is of interest for the synthesis of other useful reagents. The overall yield (43%) of **1** by our two-step synthesis from biphenyl compares favorably with that reported (52%) by Sorrell by a three-step process from the more expensive 2,2'-biphenol.

EXPERIMENTAL SECTION

Diphenyl and all other reagents were purchased from Aldrich. ^{1}H NMR spectra were recorded using a Varian VXR 300 spectrometer operating at 300 MHz, with TMS as internal standard. IR spectra were recorded on a Perkin-Elmer 298 spectrophotometer. Flash-chromatography was carried out with Merck Kieselgel (230-400 mesh) silica gel. TMEDA was distilled from calcium hydride and tetrahydrofuran from sodium benzophenone ketyl.

Dibenzo[c,e]-1,2-dithiin (**2**).- Biphenyl (5 g, 32.4 mmol) was added in small portions at -15° to a well stirred yellow solution of TMEDA (9.72 mL, 64.85 mmol) in *n*-butyllithium (1.6 M, 0.5 mL, 64.85 mmol). The mixture was allowed to warm to 25° overnight and elemental sulfur (2.28 g, 71.28 mmol) was added with vigorous stirring over *ca.* 3 hrs. The mixture was poured into water (300 mL) and the organic layer was extracted with CH_2Cl_2 (3 x 20 mL), dried (Na_2SO_4) and concentrated *in vacuo*. Flash chromatography using petroleum ether (40-60°) as eluent gave disulfide **2** (3.50 g, 50% yield) as a yellow solid, mp. 111° (CH_2Cl_2-petroleum ether), lit.[1a] mp. 113°. IR (KBr): 3000 (w), 1580 (s), 1550 (s), 780 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 7.23 (td, J = 1.5 and 7.6 Hz, 2H), 7.33 (td, J = 1.5 and 7.6 Hz, 2H), 7.47 (dd, J = 1.2 and 7.6 Hz, 2H), 7.6 (dd, J = 1.2 and 7.6 Hz, 2H).

2,2'-Dimercaptobiphenyl (**1**).- A solution of dibenzo[c,e]-1,2-dithiin (**2**, 2 g, 9.25 mmol) in dry THF (30 mL) was added dropwise at 0° to a suspension of $LiAlH_4$ (0.83 g, 22.3 mmol) in THF (30 mL). The mixture was refluxed for 17 hrs. Water (50 mL) was added at 0° and the solution was acidified with 10% hydrochloric acid (20 mL). The organic layer was extracted with ether (3 x 50 mL), dried (Na_2SO_4) and concentrated *in vacuo* to give 2,2'-dimercaptobiphenyl (1.84 g, 86% yield) as

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white crystals, mp. 76-78° (CH_2Cl_2-petroleum ether), lit.[1a] mp. 78-79°. IR (KBr): 2556 (m), 1451 (w), 1423 (w), 1382 (w), 752 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 3.36 (s, 2H), 7.12-7.28 (m, 6H), 7.35-7.40 (m, 2H).

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