

# Unexpected Formation of an Inner Salt, Bis(*N,N*-diethylamino)carbeniumdithiocarboxylate, from 2-Chloro or 2-Phenoxy Substituted 1,1-Bis(*N,N*-diethylamino)ethylenes and Elemental Sulfur

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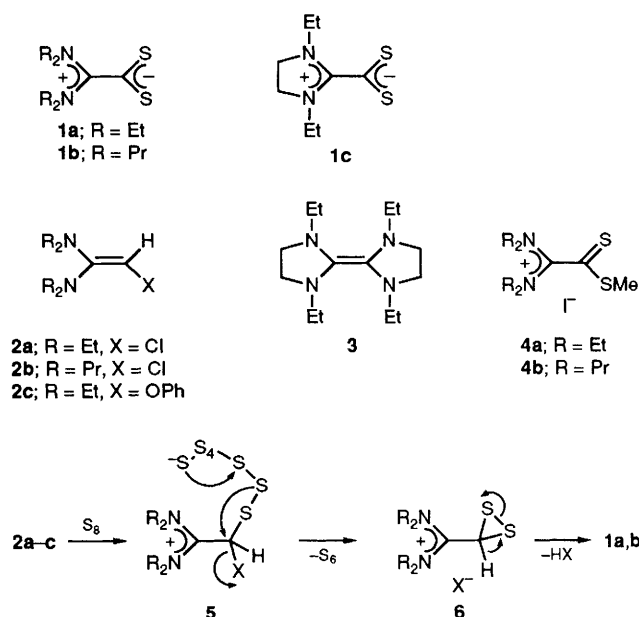
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2-Chloro or 2-phenoxy substituted 1,1-bis(*N,N*-diethylamino)ethylenes **2a** and **c** react with elemental sulfur in benzene at room temperature to give an inner salt, bis(*N,N*-diethylamino)carbeniumdithiocarboxylate **1a**, in excellent yields.

We report here the unexpected formation of an inner salt, bis(*N,N*-diethylamino)carbeniumdithiocarboxylate **1a**, by reaction of 2-chloro or 2-phenoxy substituted 1,1-bis(*N,N*-diethylamino)ethylenes **2a** and **c** with elemental sulfur. This type of the inner salt **1c** was first synthesized in 1965 by reaction of the peraminoethylene **3** with carbon disulfide.<sup>1</sup> Since then, several related compounds have been synthesized and their structures and reactivities investigated in some detail because of their unique intriguing structures.<sup>2</sup> However, their synthesis is still limited to the reaction of peraminoethylenes with carbon disulfide.<sup>1,2</sup>

Stirring a mixture of 1,1-bis(*N,N*-diethylamino)-2-chloroethylene **2a**,<sup>3</sup> elemental sulfur, and triethylamine in benzene for 8 h at room temperature affords the title compound **1a** in 97% yield in addition to triethylamine hydrochloride (94%).<sup>†,‡</sup> The addition of triethylamine is required to scavenge hydrogen chloride liberated; the reaction in the absence of triethylamine gave **1a** only in low yield. In a similar way, 1,1-bis(*N,N*-dipropylamino)-2-chloroethylene **2b**<sup>3</sup> reacts with elemental sulfur in benzene at room temperature for 5 h to give the inner salt **1b**<sup>‡</sup> in 73% yield.

1,1-Bis(*N,N*-diethylamino)-2-phenoxyethylene **2c**<sup>4,5</sup> also reacts smoothly with elemental sulfur at room temperature to give **1a** in 70% yield and phenol in 62% yield. In this case, addition of triethylamine is not required.



Both **1a** and **1b** are soluble in common organic solvents and readily react with methyl iodide to give the stable carbenium salts **4**<sup>‡</sup> quantitatively.

The present reaction must be initiated by electrophilic attack of elemental sulfur ( $S_8$ ) on electron-rich alkenes (enamines) **2a–c** to give betaine intermediates **5**. Then these betaines probably undergo cyclization with elimination of  $S_6$  to give dithirane intermediates **6**, deprotonation of which affords **1a** and **b** with simultaneous ring-opening.

The present reaction provides an unexpected but very convenient synthesis of the inner salts **1a** and **b** since the starting materials **2a** and **b** are easily obtainable from trichloroethylene in one pot.<sup>3</sup>

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<sup>†</sup> A mixture of 3.09 g (15 mmol) of **2a**, 2.09 g of sulfur (8.2 mmol as  $S_8$ ), and 7.78 g of triethylamine (77 mmol) in 200 ml of benzene was stirred at room temp. for 8 h under argon. The resulting suspension was filtered to give 1.93 g (94%) of triethylamine hydrochloride and the dark-red filtrate was evaporated under reduced pressure. The crystalline residue was chromatographed on a column of silica gel. The column was eluted with hexane to give 1.10 g of sulfur and then with  $CH_2Cl_2$ -AcOEt (95:5) to give 3.40 g (97%) of **1a**.

<sup>‡</sup> *Physical and spectroscopic data for 1a*: orange needles; m.p. 98°C;  $^1H$  NMR  $\delta$  ( $CDCl_3$ , 400 MHz) 1.32 (Me, t, 12 H,  $J$  7.2 Hz), 3.59 ( $CH_2$ , q, 8 H,  $J$  7.2 Hz);  $^{13}C$  NMR  $\delta$  ( $CDCl_3$ , 100 MHz) 12.64 (q, Me), 46.49 (t,  $CH_2$ ), 166.65 (s, carbenium carbon), 236.20 (s, dithiocarboxylate); IR (KBr)  $\nu/cm^{-1}$  1050, 1563 (characteristic strong absorptions of this type of inner salt<sup>2b</sup>); MS (EI)  $m/z$  232 ( $M^+$ ); UV-VIS ( $CH_2Cl_2$ ):  $\lambda_{max}/nm$  ( $\epsilon/dm^3 mol^{-1} cm^{-1}$ ) = 226 (17 700), 271 (8910), 368 (12 000). For **1b**: reddish-orange needles; m.p. 104.5–106°C;  $^1H$  NMR  $\delta$  ( $CDCl_3$ , 90 MHz) 0.97 (t, 12 H,  $J$  7.5 Hz), 1.77 (m, 8 H), 3.46 (t, 8 H,  $J$  7.3 Hz);  $^{13}C$  NMR  $\delta$  ( $CDCl_3$ , 22.5 MHz) 11.01 (Me), 20.76 ( $CH_2$ ), 53.68 ( $CH_2$ ), 170.14 (carbenium carbon), 236.29 (dithiocarboxylate); IR (KBr)  $\nu/cm^{-1}$  1054, 1556;<sup>2b</sup> MS (EI)  $m/z$  288 ( $M^+$ ); UV-VIS ( $CH_2Cl_2$ )  $\lambda_{max}/nm$  ( $\epsilon/dm^3 mol^{-1} cm^{-1}$ ) = 225 (12 300), 271 (5860), 369 (7800). For **4a**: dark-red plates; m.p. 112.5–114°C;  $^1H$  NMR  $\delta$  ( $CDCl_3$ , 90 MHz) 1.37 (Me, t, 12 H,  $J$  7.2 Hz), 3.03 (MeS, s, 3 H), 3.75 ( $CH_2$ , q, 8 H,  $J$  7.2 Hz).  $^{13}C$  NMR  $\delta$  ( $CDCl_3$ , 22.5 MHz) 13.13 (Me), 20.36 (MeS), 48.07 ( $CH_2$ ), 163.31 (carbenium carbon), 214.67 (dithioester carbon). Satisfactory elemental analyses were obtained for compounds **1a** and **b** and **4a** and **b**.

<sup>§</sup> Although **2c** can be prepared from **2a** and sodium phenoxide,<sup>4</sup> it is also obtainable in 30% yield by treatment of 2,2,2-trifluoroethyl phenyl ether with lithium diethylamide in a mixture of diethylamine and diethyl ether, under the conditions in which 2,2,2-trifluoroethyl phenyl sulfide and 2,2,2-trifluoroethyl phenyl selenide afford 1-(*N,N*-diethylamino)-2-phenylthioacetylene and 1-(*N,N*-diethylamino)-2-phenylselenoacetylene, respectively.<sup>5</sup>

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