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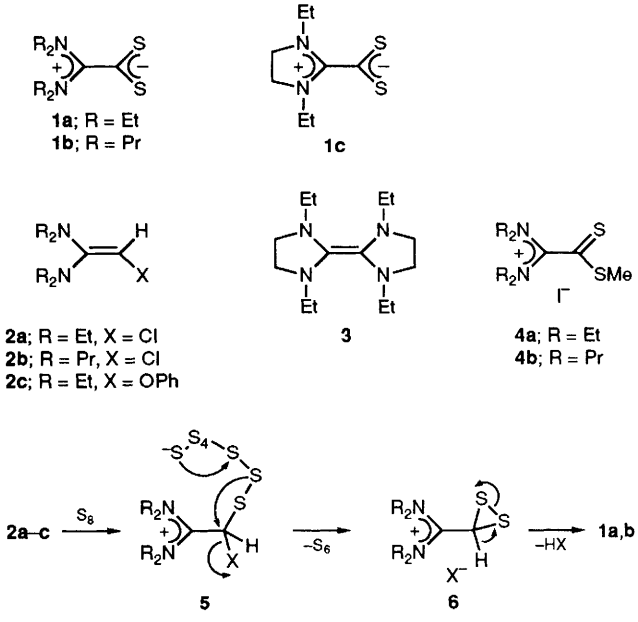
2-Chloro or 2-phenoxy substituted 1,1-bis(*N,N*-diethylamino)ethylenes **2a** and **c** react with elemental sulfur in benzene at room temperature to give an inner salt, bis(*N,N*-diethylamino)carbeniumdithiocarboxylate **1a**, in excellent yields.

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.[1] Since then, several related compounds have been synthesized and their structures and reactivities investigated in some detail because of their unique intriguing structures.[2] However, their synthesis is still limited to the reaction of peraminoethylenes with carbon disulfide.[1,2]

Stirring a mixture of 1,1-bis(*N,N*-diethylamino)-2-chloroethylene **2a**,[3] 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%).†,‡ 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**[3] reacts with elemental sulfur in benzene at room temperature for 5 h to give the inner salt **1b**‡ in 73% yield.

1,1-Bis(*N,N*-diethylamino)-2-phenoxyethylene **2c**§[4,5] 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**‡ 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 dithiirane 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.[3]

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† 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**.

‡ *Physical and spectroscopic data* for **1a**: orange needles; m.p. 98 °C; ^{1}H NMR δ ($CDCl_3$, 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 δ ($CDCl_3$, 100 MHz) 12.64 (q, Me), 46.49 (t, CH_2), 166.65 (s, carbenium carbon), 236.20 (s, dithiocarboxylate); IR (KBr) ν/cm^{-1} 1050, 1563 (characteristic strong absorptions of this type of inner salt[2b]); MS (EI) *m/z* 232 (M^+); UV–VIS (CH_2Cl_2): λ_{max}/nm (ε/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; ^{1}H NMR δ ($CDCl_3$, 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 δ ($CDCl_3$, 22.5 MHz) 11.01 (Me), 20.76 (CH_2), 53.68 (CH_2), 170.14 (carbenium carbon), 236.29 (dithiocarboxylate); IR (KBr) ν/cm^{-1} 1054, 1556;[2b] MS (EI) *m/z* 288 (M^+); UV–VIS (CH_2Cl_2) λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) = 225 (12 300), 271 (5860), 369 (7800). For **4a**: dark-red plates; m.p. 112.5–114 °C; ^{1}H NMR δ ($CDCl_3$, 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 δ ($CDCl_3$, 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**.

§ Although **2c** can be prepared from **2a** and sodium phenoxide,[4] 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.[5]

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