Heteroatom Chemistry
Volume 8, Number 6, 1997

An Improved Synthesis of Inner Salts, 2,2-Bis(dialkylamino)-2-ethylium-1-dithioates

Keiichi Akimoto and Juzo Nakayama*

Department of Chemistry, Faculty of Science, Saitama University, Urawa, Saitama 338, Japan

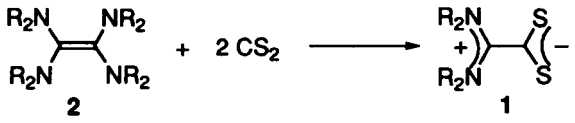
Received 7 March 1997

ABSTRACT

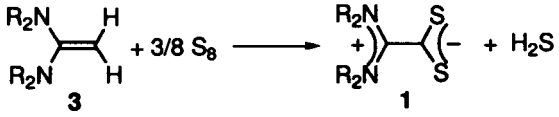
*The reaction of 1,1-bis(dialkylamino)ethenes (***3***) with an equimolar amount of disulfur dichloride in the presence of triethylamine affords the stable inner salts 2,2-bis(dialkylamino)-2-ethylium-1-dithioates (***1***) in good yields.* © 1997 John Wiley & Sons, Inc. Heteroatom Chem 8:505–508, 1997

INTRODUCTION

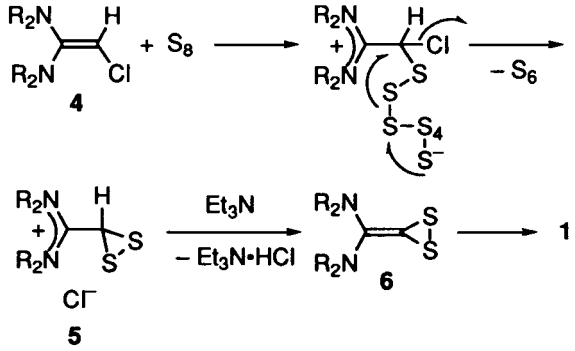
2,2-Bis(dialkylamino)-2-ethylium-1-dithioates (**1**) are a structurally interesting unique class of inner salts [1]. Two methods have been developed for the synthesis of these inner salts. Thus, peraminoethenes (**2**) reacted with carbon disulfide to give the corresponding salts **1** (Scheme 1) [2–5]. The other method involves sulfuration of 1,1-bis(dialkylamino)ethenes by elemental sulfur [6–8]. The sulfuration of 1,1-bis(dialkylamino)ethenes (**3**) with elemental sulfur afforded the salts **1** in about 50% yields for two examples (Scheme 2) [6], while the sulfuration of 1,1-bis(dialkylamino)-2-chloroethenes (**4**) with sulfur in the presence of triethylamine gave **1** in much better yields [7,8]. However, the latter synthesis suffers from the disadvantage that synthesis of the starting materials **4** is more laborious than



SCHEME 1



SCHEME 2



SCHEME 3

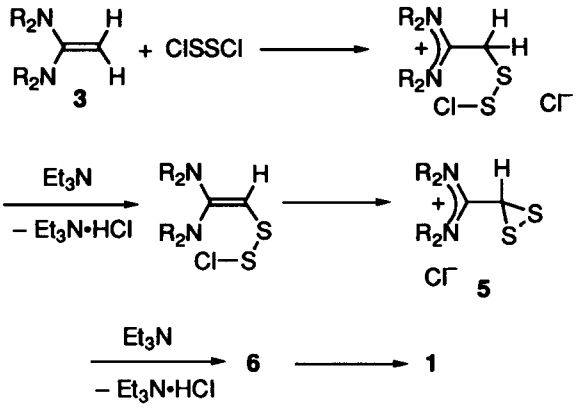
that of **3**. The mechanism shown in Scheme 3 was proposed for the formation of **1** from the ethenes **4**.

If the mechanism proposed above is truly operative, the intermediates (**5**) should be also formed by addition of disulfur dichloride to **3** to afford the salts **1** as the final products (Scheme 4). With this working hypothesis, we have investigated the reaction of **3** with disulfur dichloride and found that the reaction provides another effective synthesis of **1**.

Dedicated to Prof. William E. McEwen on the occasion of his seventy-fifth birthday.

*To whom correspondence should be addressed.

 CCC 1042-7163/97/060505-05



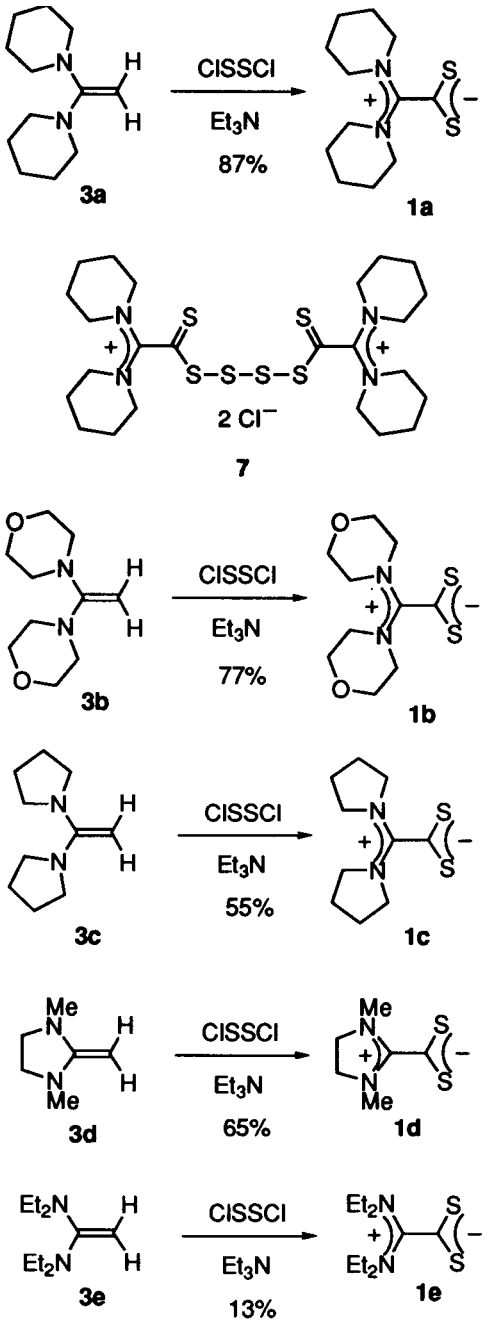
SCHEME 4

RESULTS AND DISCUSSION

The reaction of 1,1-dipiperidinoethene (**3a**) with disulfur dichloride was thus examined under a variety of conditions, which revealed that the optimum yield (87%) of the expected 2,2-dipiperidino-2-ethylium-1-dithioate (**1a**) is obtainable in the following way. A solution of disulfur dichloride in dichloromethane was slowly added to a stirred solution of an equimolar amount of **1a** and triethylamine in dichloromethane below −10°C. The mixture was slowly warmed to room temperature and stirred overnight. Workup of the mixture gave **3a** in 87% yield (Scheme 5). The exact 1:1 molar ratio of **1a** and disulfur dichloride is crucial, and even the use of a slight excess of disulfur dichloride afforded **1a** in a less satisfactory yield. Thus, the use of 1.2 molar amounts of disulfur dichloride gave **1a** in 24% yield. The sulfur atoms of the inner salts **1** are known to be nucleophilic enough to be alkylated by iodomethane [2,6,7,9] and diiodomethane [10]. Therefore, the resulting **1a** should react with electrophilic disulfur dichloride to give the carbenium salt (**7**) to afford **1a** in a decreased yield, although no effort was made to isolate **7.**

In a similar way, the reactions of 1,1-dimorpholinoethene (**3b**), 1,1-dipyrrolidinoethene (**3c**), 2-methylene-1,3-dimethylimidazolidine (**3d**), and 1,1-bis(diethylamino)ethene (**3e**) with disulfur dichloride gave the expected salts **1b, 1c, 1d,** and **1e** in 77%, 55%, 65%, and 13% yields, respectively.

Thus, the method developed here provides a convenient synthesis of the inner salts **1** because of easy accessibility [11–14] of the starting materials **3** (**3b** is even commercially available), satisfactory yields of the desired products except **1e,** and simple workup procedure.



SCHEME 5

EXPERIMENTAL

^{1}H- and ^{13}C-NMR spectra were determined on a JEOL EX-270 (270 MHz for ^{1}H and 67.8 MHz for ^{13}C) spectrometer with TMS as an internal standard. Elemental analyses were performed on a Yanaco MT-3 CHN CORDER. Melting points are uncorrected.

*2,2-Dipiperidino-2-ethylium-1-dithioate (***1a***).* A solution of 810 mg (6 mmol) of disulfur dichloride in 5 mL of dichloromethane was added to a solution of 1.148 g (6 mmol) of freshly distilled 1,1-dipiperidinoethene [11] (**3a**) and 1.67 mL (12 mmol) of triethylamine in 30 mL of dichloromethane over a pe-

riod of 1 hour below −10°C. The mixture turned from colorless to purple, which was slowly warmed to room temperature and stirred overnight. Dichloromethane was added to the mixture until the separated materials completely dissolved. After the resulting mixture was washed with water and dried over sodium sulfate, the solvent was evaporated. The residue was purified by chromatography on a column of silica gel with chloroform as the eluent to give 1.345 g (87%) of **1a:** mp 217–218°C (dec) (mp 234–235°C, dec [6]); dark red plates (from dichloromethane/hexane); ^{1}H NMR ($CDCl_3$) δ 1.71 (4H, quintet, J = 4.9 Hz, CH_2 of the γ position of the piperidine rings), 1.78 (8H, t/t, J = 5.4/4.9 Hz, β position CH_2), 3.56 (8H, t, J = 5.4 Hz, α position CH_2); ^{13}C NMR ($CDCl_3$) δ 23.4 (t), 25.8 (t), 51.8 (t), 169.0 (s, carbenium carbon), 234.9 (s, dithiocarboxylate carbon). Anal. calcd for $C_{12}H_{20}N_2S_2$: C, 56.21; H, 7.86; N, 10.92. Found: C, 56.20; H, 7.80; N, 10.87.

*2,2-Dimorpholino-2-ethylium-1-dithioate (***1b***).* A solution of 810 mg (6 mmol) of disulfur dichloride in 5 mL of dichloromethane was added to a solution of 1.190 g (6 mmol) of freshly distilled 1,1-dimorpholinoethene (**3b**) (purchased from Tokyo Kasei) and 1.67 mL (12 mmol) of triethylamine in 30 mL of dichloromethane over a period of 0.5 hour below −10°C. The mixture turned from colorless to purple, which was slowly warmed to room temperature and stirred for 2 days. The mixture was treated as described above to give the crude product, which was purified by silica-gel column chromatography with dichloromethane as the eluent to give 1.203 g (77%) of **1b:** mp 228.5–229.5°C (dec) (mp 233–236°C, dec [6]); dark red plates (from dichloromethane/hexane); ^{1}H NMR ($CDCl_3$) δ 3.67 (8H, t, J = 4.6 Hz, α position CH_2 of the morpholine rings), 3.88 (8H, t, J = 4.6 Hz, β position CH_2); ^{13}C NMR ($CDCl_3$) δ 50.7 (t), 66.3 (t), 168.8 (s, carbenium carbon), 232.5 (s, dithiocarboxylate carbon). Anal. calcd for $C_{10}H_{16}N_2O_2S_2$: C, 46.13; H, 6.19; N, 10.76. Found: C, 46.06; H, 6.05; N, 10.49.

*2,2-Dipyrrolidino-2-ethylium-1-dithioate (***1c***).* A solution of 815 mg (6.04 mmol) of disulfur dichloride in 5 mL of dichloromethane was added to a solution of 1.004 g (6.04 mmol) of freshly distilled 1,1-dipyrrolidinoethene [12] (**3c**) and 1.69 mL (12.06 mmol) of triethylamine in 30 mL of dichloromethane over a period of 1 hour below −10°C. The mixture turned from colorless to purple, which was slowly warmed to room temperature and stirred for 2 days. The reaction mixture was treated as described above to give the crude product, which was purified by chromatography on a column of silica gel with dichloromethane-ethyl acetate (95:5) as the eluent to give 758 mg (55%) of **1c:** mp 217.5–219.0°C (dec); red plates (from dichloromethane/hexane); ^{1}H NMR (DMSO-d_6) δ 1.98 (8H, broad s, β position CH_2 of the pyrrolidine rings), 3.92 (8H, broad s, α position CH_2); ^{13}C NMR (DMSO-d_6, 67°C) δ 24.3 (t), 50.4 (t), 164.0 (s, carbenium carbon), 236.6 (s, dithiocarboxylate carbon). Anal. calcd for $C_{10}H_{16}N_2S_2$: C, 52.59; H, 7.06; N, 12.27. Found: C, 52.55; H, 6.97; N, 12.24.

*2-(1,3-Dimethylimidazolidinio)dithiocarboxylate (***1d***).* A solution of 840 mg (6.22 mmol) of disulfur dichloride in 5 mL of dichloromethane was added to a solution of 698 mg (6.22 mmol) of freshly distilled 2-methylene-1,3-dimethylimidazolidine [13] (**3d**) and 1.73 mL (12.5 mmol) of triethylamine in 30 mL of dichloromethane over a period of 1 hour below −10°C. The mixture turned from colorless to purple, which was slowly warmed to room temperature and stirred for 2 days. After the resulting mixture was washed with water and dried over sodium sulfate, the solvent was evaporated. The residue was purified by chromatography on a column of silica gel with dichloromethane-ethyl acetate (95:5) as the eluent to give 707 mg (65%) of **1c:** mp 258.6–259.3°C (dec) (mp 263°C [4]); dark red plates (from dichloromethane/hexane); ^{1}H NMR ($CDCl_3$) δ 3.11 (6H, broad s, *N*-methyl hydrogens), 3.86 (4H, broad s, CH_2 of the imidazolidine ring); ^{13}C NMR ($CDCl_3$) δ 33.6 (t), 49.3 (t), 167.2 (s, carbenium carbon), 225.3 (s, dithiocarboxylate carbon). Anal. calcd for $C_6H_{10}N_2S_2$: C, 41.35; H, 5.78; N, 16.07. Found: C, 41.29; H, 5.66; N, 15.98.

*2,2-Bis(diethylamino)-2-ethylium-1-dithioate (***1e***).* A solution of 575 mg (4.26 mmol) of disulfur dichloride in 5 mL of dichloromethane was added to a solution of 762 mg (4.48 mmol) of freshly distilled 1,1-bis(diethylamino)ethene [14] (**3e**) and 1.19 mL (8.52 mmol) of triethylamine in 30 mL of dichloromethane over a period of 1 hour below −10°C. The mixture turned from colorless to purple, which was slowly warmed to room temperature and stirred for 1.5 days. The mixture was purified by silica-gel column chromatography with dichloromethane-ethyl acetate (95:5) as the eluent to give 96 mg (13%) of **1c:** mp 96.0–97.5°C (mp 98°C [8]); red needles (from hexane); ^{1}H NMR ($CDCl_3$) δ 1.32 (12H, t, J = 7.2 Hz, CH_3), 3.59 (8H, q, J = 7.2 Hz, CH_2); ^{13}C NMR ($CDCl_3$) δ 12.6 (q), 46.5 (t), 166.6 (s, carbenium carbon), 236.2 (s, dithiocarboxylate carbon).

REFERENCES

[1] For a review, J. Nakayama, *Sulfur Lett., 15,* 1993, 239.

[2] H. E. Winberg, D. D. Coffman, *J. Am. Chem. Soc., 87,* 1965, 2776.
[3] H. E. Winberg, J. E. Carnhan, D. D. Coffman, M. Brown, *J. Am. Chem. Soc., 87,* 1965, 2055.
[4] W. Krasuski, D. Nikolaus, M. Regitz, *Liebigs Ann. Chem.,* 1982, 1451.
[5] W. S. Sheldrick, A. Schönberg, E. Singer, P. Eckert, *Chem. Ber., 113,* 1980, 3605.
[6] D. Clemens, A. J. Bell, J. L. O'Brien, *Tetrahedron Lett.,* 1965, 3257.
[7] J. Nakayama, I. Akiyama, *J. Chem. Soc., Chem. Commun.,* 1992, 1552.
[8] A. Nagasawa, I. Akiyama, S. Mashima, J. Nakayama, *Heteroatom Chem., 6,* 1995, 45.
[9] W. Schössler, M. Regitz, *Chem. Ber., 107,* 1974, 1931.
[10] J. Nakayama, Y. Nagata, unpublished results
[11] D. H. Clemens, A. J. Bell, J. L. O'Brien, *J. Org. Chem., 29,* 1964, 2932.
[12] G. Opitz, F. Zimmermann, *Chem. Ber., 97,* 1964, 1266.
[13] U. Gruseck, M. Heuschmann, *Chem. Ber., 120,* 1987, 2053.
[14] S. M. McElvain, B. E. Tate, *J. Am. Chem. Soc., 67,* 1945, 202.