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Oxidation and Reduction of 2,2-Bis(diethylamino)-2-ethylium-1-dithioate

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ABSTRACT: *Oxidation of the titled inner salt* **1** *with a typical one-electron oxidizing reagent, $NOPF_6$, produced the radical cation* **5a**, *whose dimerization, followed by loss of a sulfur atom, led to the formation of the bis-carbenium salt* **4a** *in 95% yield. Moreover, reduction of* **1** *with a typical one-electron reducing reagent, lithium naphthalenide, produced the ethene-1,1-dithiolate* **16**, *which was converted to the ethene* **17** *in 73% yield by treatment with methyl iodide. Also reported are synthetic applications of the oxidation of* **1** *with bromine and the reduction with $LiEt_3BH$.* © 1998 John Wiley & Sons, Inc. Heteroatom Chem 9: 703–707, 1998

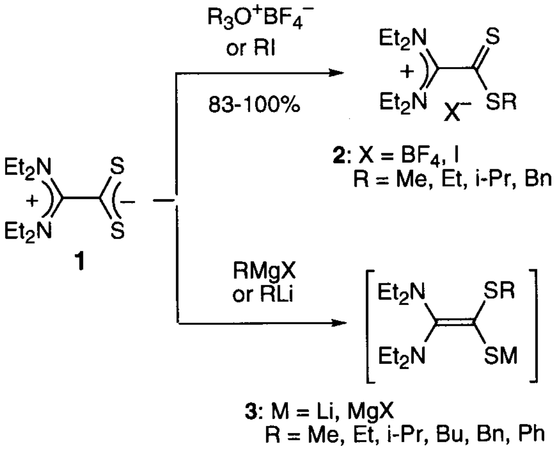
INTRODUCTION

2,2-Bis(dialkylamino)-2-ethylium-1-dithioates are a structurally interesting, unique class of inner salts. However, information on their reactivities is still limited; 1,3-dipolar cycloaddition with alkynic dipolarophiles and *S*-methylation with methyl iodide are typical reactions reported on these inner salts [1]. In recent years, we have been investigating the synthesis, structure, and reactivities of the inner salt, 2,2-bis(diethylamino)-2-ethylium-1-dithioate (**1**), and the related compounds [2–8]; **1** is readily obtainable by reaction of 1-chloro-2,2-bis(diethylamino)ethene with elemental sulfur [2,3]. Quite recently, we have found that **1** reacts with negatively charged nucleophiles, such as Grignard reagents and alkyllithiums, at the negatively charged dithiocarboxylate sulfur atom to afford a range of ethenethiolates **3** [8]. The inner salt **1** is also *S*-alkylated by alkyl iodides and other reagents to give carbenium salts **2** (Scheme 1). Therefore, the sulfur atom of **1** has the unique capability of reacting with both electrophiles and nucleophiles. Inspired with these findings, we have become interested in the redox reactivities of **1** and report here an oxidation and reduction study on **1**.

RESULTS AND DISCUSSION

Oxidation of the Inner Salt 1

Oxidation of the inner salt **1** by $NOPF_6$, a typical one-electron oxidizing reagent, took place smoothly in



SCHEME 1

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Dedicated to Prof. Robert R. Holmes on the occasion of his seventieth birthday.

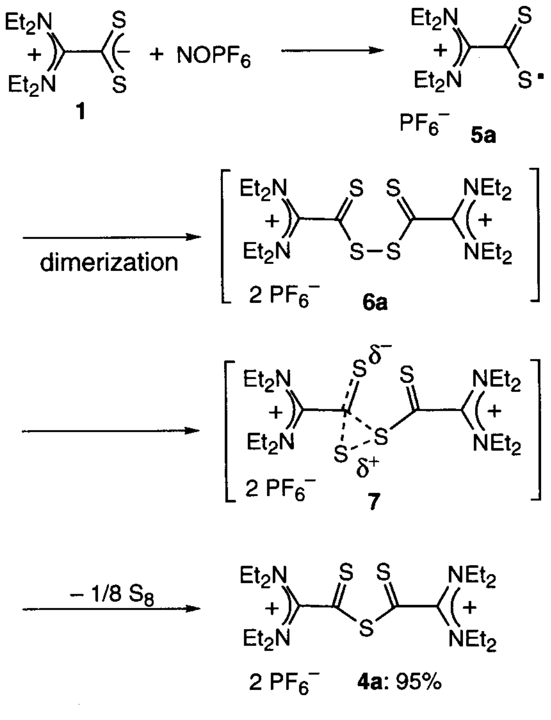
CH_2Cl_2 at 0°C. The original red solution turned dark immediately upon the addition of $NOPF_6$ with evolution of a gas (NO) and turned reddish-purple after 1 hour. Workup of the mixture gave a 95% yield of the bis-carbenium salt **4a** that possesses a dithioic acid anhydride moiety. The structure of **4a** was determined based on ^1H- and ^{13}C-NMR spectroscopy and elemental analyses. A probable mechanism for the formation of **4a** is given in Scheme 2. The single-electron transfer from **1** to $NOPF_6$ would produce the radical cation **5a**, which, in turn, dimerizes to give the disulfide **6a**. Finally, sulfur extrusion in **6a** through a transition state such as **7** would produce **4a** as the final product. The same results were also obtained by oxidation of **1** with $NOBF_4$.

The reaction of **1** with more than 1.5 molar amounts of bromine also afforded the bis-carbenium salt **4b** in 95% yield (Scheme 3). The initial electrophilic addition of bromine to the sulfur atom of **1** would produce the carbenium salt **10**, which further reacts with **1** to give the disulfide **6b**. Finally, **6b** extrudes a sulfur atom to give the final product **4b** as in the case of **6a**. Incidentally, the inner salt **1** was inert to reaction with iodine.

Recently, we have found that the reaction of sodium sulfide with 2 molar amounts of the carbenium salt **2** (R = Me, X = I) produces the trisulfide **11** nearly quantitatively [4]. In analogy with this reaction, **4b** was expected to yield the tetrathiane derivative **12** on reaction with sodium sulfide. The reaction gave the inner salt **1** in 83% yield, however, probably because **12** is thermally labile and decomposed to two molecules of **1**. The decomposition might involve concomitant S–S and C–S bond cleavage to give **12** and the thioketene-*S*-sulfide **13**. The latter may isomerize, through the dithiirane **14**, to give **12** (Scheme 4).

Reduction of the Inner Salt 1

The reduction of **1** with more than 2 molar amounts of lithium naphthalenide (LiNaph), a typical one-



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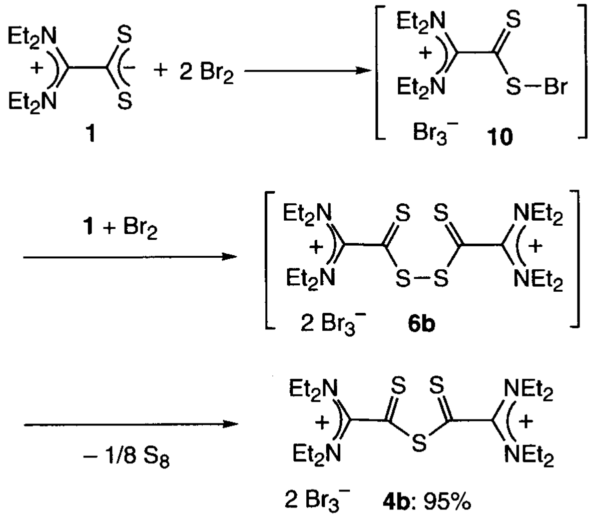

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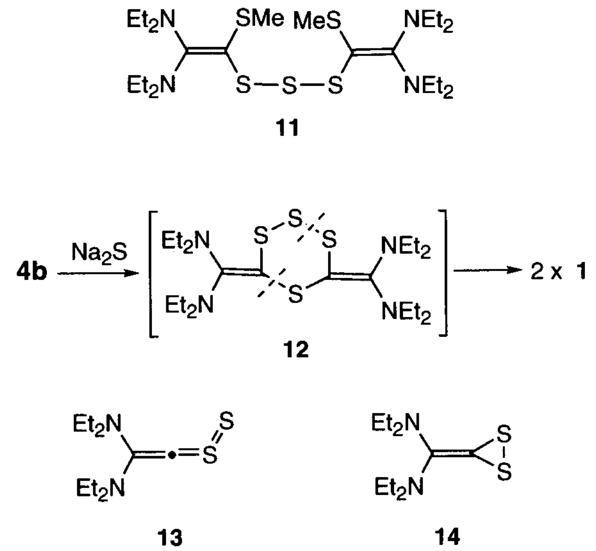


SCHEME 4

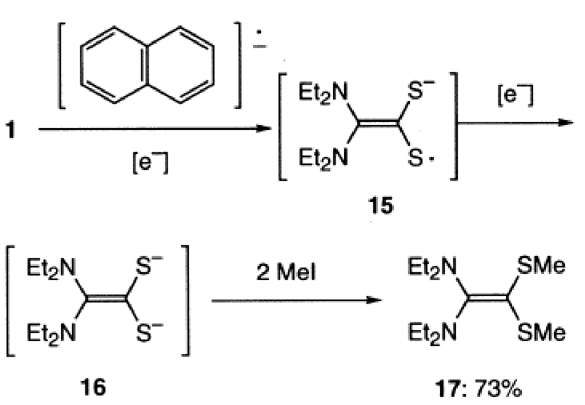
electron reducing reagent [9], produced the ethene-1,1-dithiolate **16**, which was converted to 1,1-bis(diethylamino)-2,2-bis(methylthio)ethene (**17**) in 73% yield on treatment with methyl iodide. In this case, the single-electron transfer from LiNaph to **1** would give rise to the radical anion **15**, which accepts one more electron from LiNaph to give **16**. The evidence for the susceptibility of **15** as a single-electron acceptor is provided by the cyclic voltamogram of **1**; upon scanning anodically between 0 and -2.4 V, only one large reduction peak ($E_{p,c} = -1.80$ V vs. Ag/Ag$^+$) was observed, because the reduction of **1** to **15** is immediately followed by reduction of **15** to **16** due to a small potential gap between **15** and **16** (Scheme 5).

The inner salt **1** was also reduced by 2 molar amounts of LiEt$_3$BH to give the ethene-1,1-dithioate **16** again (Scheme 6). The resulting **16** was converted to the ethene **17** in 85% yield by treatment with methyl iodide. Although attempted alkylation of **16** with diiodomethane failed to give the expected 1,3-dithietane **19**, the reaction with 1,2-dibromoethane satisfactorily gave the 1,3-dithiolane **20** in 77% yield [10]. Treatment of **16** with carbon disulfide also failed to give the expected 1,3-dithietane **22** [11]. In this case, two molecules of carbon disulfide added to **16** to yield **23**. Therefore, treatment of the reaction mixture with methyl iodide gave the trithiocarbonate derivative **21** in 92% yield.

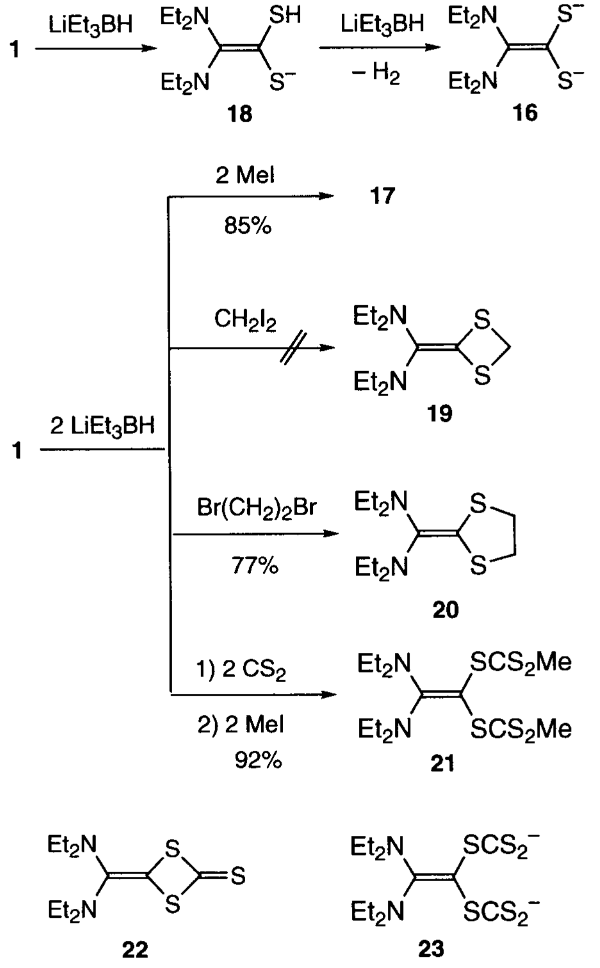
EXPERIMENTAL

Melting points were determined on a Mel-Temp capillary tube apparatus and are uncorrected. ^{1}H- and ^{13}C-NMR spectra were determined on a Bruker AM400 (400 MHz for ^{1}H NMR and 100.6 MHz for ^{13}C), a Bruker AC300P (300 MHz for ^{1}H and 75.5 MHz for ^{13}C), and a Bruker AC200 (200 MHz for ^{1}H and 50 MHz for ^{13}C) spectrometers with TMS as the internal standard. Mass spectra were obtained on a JEOL JMS-DX303 spectrometer operating at 70 eV in the EI mode. Elemental analyses were performed by the Chemical Analysis Center of Saitama University. The cyclic voltammogram was obtained on a BAS 100B/W (CV-50W) system: scan rate, 100 mV/sec; reference electrode, Ag/Ag$^+$; counter electrode, Pt; working electrode, Pt; 0.05 M Bu$_4$NClO$_4$ in CH$_3$CN under N$_2$ at room temperature.

Formation of the Bis-carbenium Salt **4a** *by Oxidation of* **1** *with NOPF$_6$.* To a stirred solution of 234 mg (1.0 mmol) of the inner salt **1** in 10 mL of CH$_2$Cl$_2$ was added 192 mg (1.1 mmol) of NOPF$_6$ in small portions at 0°C. The mixture was stirred for 1 hour at 0°C and warmed to room temperature. A small amount of insoluble material was removed by filtration. The filtrate was evaporated under reduced pressure to leave the crystalline residue. Recrystallization of the crude material from CH$_3$CN/ether gave 342 mg (95%) of **4a** as a dark-purple crystalline pow-



SCHEME 5



SCHEME 6

der: mp > 134°C (dec); ^{1}H NMR (300 MHz, CD_3CN) δ 1.29 (24H, t, $J = 7.0$ Hz), 3.69 (16H, q, $J = 7.0$ Hz); ^{13}C NMR (100 MHz, CD_3CN) δ 13.6, 49.1, 163.2 (C^+), 210.2 (broad, C=S). Anal. calcd for $C_{20}H_{40}F_{12}N_4P_2S_3$: C, 33.23; H, 5.58; N, 7.75. Found: C, 33.40; H, 5.51; N, 7.66.

Formation of the Bis-carbenium Salt **4b** *by Treatment of* **1** *with* Br_2. To a stirred solution of 234 mg (1.0 mmol) of **1** in 10 mL of CH_2Cl_2 was added dropwise a solution of 240 mg (1.5 mmol) of Br_2 in 5 mL of CCl_4 at room temperature. The original red solution of **1** turned dark-red upon the addition of Br_2. The mixture was evaporated under reduced pressure to leave an oily residue. The residue solidified on trituration with carbon disulfide. The solid was recrystallized from CH_3CN/ether to give 420 mg (95%) of the bis-carbenium salt **4b** as a dark-red crystalline powder: mp 82–84°C; ^{1}H NMR (300 MHz, CD_3CN) δ 1.31 (24H, t, $J = 7.0$ Hz, Me), 3.70 (16H, q, $J = 7.0$ Hz, CH_2); ^{13}C NMR (75.5 MHz, CD_3CN) δ 13.7, 49.0, 163.4 (C^+), 207.0 (broad, C=S). Anal. calcd for $C_{20}H_{40}Br_{12}N_4S_3$: C, 26.33; H, 4.42; N, 6.14. Found: C, 26.09; H, 4.34; N, 5.84.

Reaction of the Carbenium Salt **4b** *with* Na_2S. To a stirred suspension of 275 mg (0.30 mmol) of **4b** in 10 mL of water was added 144 mg (0.60 mmol) of $Na_2S\bullet 9H_2O$ at 0°C. The original red suspension turned brown upon the addition. The mixture was stirred for 5 hours, warmed to room temperature, and extracted with CH_2Cl_2 (3 × 10 mL). The combined extracts were dried over $MgSO_4$ and evaporated. The residue was recrystallized from CH_2Cl_2/hexane to give 116 mg (83%) of the inner salt I as red needles, mp 98.0–98.5°C [3].

Reduction of the Inner Salt **1** *with Lithium Naphthalenide; 1,1-Bis(diethylamino)-2,2-bis(methylthio)ethene (***17***).* A mixture of 513 mg (4 mmol) of naphthalene and 28 mg (4 mmol) of lithium in 5 mL of THF was stirred for 6 hours under argon [12]. The resulting deep-green mixture was cooled to −78°C. To this mixture was added a solution of 234 mg (1 mmol) of **1** in 5 mL of THF. After having been stirred for 0.5 hour at −78°C, the mixture was warmed to −20°C and stirred for an additional 0.5 hour. Methyl iodide (568 mg, 4 mmol) was added, and the mixture was warmed slowly to room temperature. After water (30 mL) was added, the mixture was extracted with ether (3 × 30 mL), and the combined extracts were dried over $MgSO_4$ and evaporated. After the naphthalene had been removed from the residue by sublimation, the resulting oil was distilled to afford 193 mg (73%) of **17**, bp 70°C/0.1 mmHg (bulb-to-bulb distillation) [4].

Reduction of the Inner Salt **1** *with* $LiEt_3BH$. *Ethene* **17**. To a solution of 234 mg (1.0 mmol) of the inner salt **1** in 5 mL of THF was added dropwise 2.2 mL (2.2 mmol) of a 1.0 M THF solution of $LiBEt_3H$ at 0°C under argon. After the mixture had been stirred for 0.5 hour at this temperature, 312 mg (2.2 mmol) of methyl iodide was added. Workup of the mixture after 0.5 hour, followed by bulb-to-bulb distillation (bp 70°C/0.1 mmHg), gave 234 mg (85%) of **17** [4].

1,3-Dithiolane **20**. To a mixture containing **16,** prepared from 234 mg (1.0 mmol) of **1** in the same manner as previously described, was added dropwise 262 mg (1.4 mmol) of 1,2-dibromoethane at 0°C. Workup of the mixture after 3 hours, followed by bulb-to-bulb distillation, gave 202 mg (77%) of **20:** bp 75°C/0.15 mmHg; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.01 (12H, t, $J = 7.0$ Hz), 2.95 (8H, q, $J = 7.0$ Hz), 3.19 (4H, s); ^{13}C NMR (50 MHz, $CDCl_3$) δ 14.0, 37.1, 44.0, 73.5, 141.4; MS *m/z* 260 (M^+); HRMS calcd for $C_{12}H_{24}N_2S_2$ *m/z* 260.1380 (M^+); found, 260.1367. Anal. calcd for $C_{12}H_{24}N_2S_2$: C, 55.33; H, 9.29; N, 10.76. Found: C, 55.09; H, 9.40; N, 10.41.

Bis-trithiocarbonate **21**. To a mixture containing **16,** prepared from 234 mg (1.0 mmol) of **1** in the same manner as previously described, was added dropwise 228 mg (3 mmol) of carbon disulfide at 0°C. After being stirred for 0.5 hour, 312 mg (2.2 mmol) of methyl iodide was added to the mixture. Purification of the mixture by column chromatography on silica gel (CH_2Cl_2 as the eluent) gave 382 mg (92%) of **21:** orange crystals; mp 124.0–124.5°C; ^{1}H NMR (300 MHz, $CDCl_3$) δ 1.06 (12H, t, $J = 7.0$ Hz), 2.66 (6H, s), 3.12–3.37 (4H, m), 3.37–3.61 (4H, m); ^{13}C NMR (75.5 MHz, $CDCl_3$) δ 13.3, 20.1, 43.8, 67.6, 171.0, 233.0. Anal. calcd for $C_{14}H_{26}N_2S_6$: C, 40.54; H, 6.32; N, 6.75; Found: C, 40.83; H, 6.35; N, 6.66.

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