Preparation of a New Class of Inner Salts by Formal Addition of Tosyl Nitrene to the Sulfur Atom of Inner Salts, α-Carbeniodithiocarboxylates

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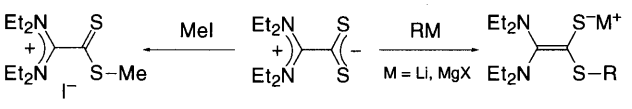
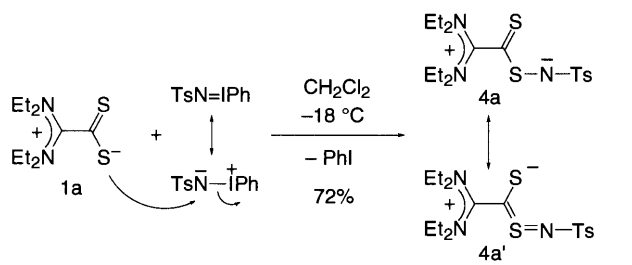
2,2-Bis(diethylamino)-2-ethylium-1-dithiocarboxylate (**1a**) was *S*-iminated by [*N*-(*p*-tolylsulfonyl)imino]phenyliodinane to provide a novel inner salt (**4a**) that formally possesses a thione-*S*-imide structure (>C=S=NR) as one of the canonical structures.

For several years, we have been investigating the synthesis, structure, and reactivities of 2,2-bis(diethylamino)-2-ethylium-1-dithiocarboxylate (**1a**) and the related inner salts.[1] The inner salt **1a** is unique, and its structure and reactivities are of particular interest. The quasi-planes of the carbenium and dithiocarboxylate moieties of **1a** are nearly perpendicular to each other.[1b,k] Its sulfur atom reacts not only with MeI to give the carbenium iodide (**2**)[1a,b] but also with RMgX (RLi) to provide the thiolates (**3**) in high yields,[1e] thus revealing a unique ability to serve both as a nucleophile and as an electrophile. In the extension of these studies, we have investigated the formal addition of an electrophilic species, tosyl nitrene, to the sulfur atom of **1a** and the related salts. Here we report that the expected reaction took place to furnish novel inner salts (**4**), which formally possess a thione-*S*-imide structure (>C=S=NR) as one of the canonical structures.



2 1a 3

The reaction of **1a** with [*N*-(*p*-tolylsulfonyl)imino]phenyliodinane (PhI=NTs)[2] took place smoothly at –18 °C in CH_2Cl_2 without use of any metallic catalyst. Purification of the mixture by column chromatography on Florisil gave the inner salt (**4a**)[3,4] in 72% yield as a red crystalline solid. The reaction probably involves an S_N2 type of nucleophilic substitution on the nitrogen atom, the sulfur atom of **1a** acting as a nucleophile and PhI as a leaving group; the free tosyl nitrene would not participate in the reaction.



1a 4a 4a'

In the ^{13}C NMR spectrum, the carbenium and thiocarbonyl carbons of **4a** resonated at δ 167 and 230, respectively, comparable positions with the corresponding carbon peaks of **1a**.[5] The UV/Vis spectrum exhibited the longest absorption maximum at 422 nm (ε 8450).[5] A molecular structure of **4a**, determined by X-ray crystallographic analysis, is given in Figure 1.[6] The quasi-planes around the carbenium ion part and that around the dithioester part are twisted by a torsion angle of 73°,[7] indicating that conjugative interactions do not take place between these two moieties, at least, in the solid state. The non-bonded distance between the nitrogen and carbenium carbon atoms, 3.01 Å, is smaller than the sum of van der Waals radii, 3.21 Å, indicating the presence of attractive interactions, depicted in the structure (**5**). The bond length data, which show that the carbon–sulfur bond of the C–S–NTs unit, 1.701(5) Å, is longer than that of the other carbon–sulfur bond, 1.644(5) Å, would indicate that the canonical structure **4a** is a greater contributor than the other one (**4a'**), which has a thione-*S*-imide unit.

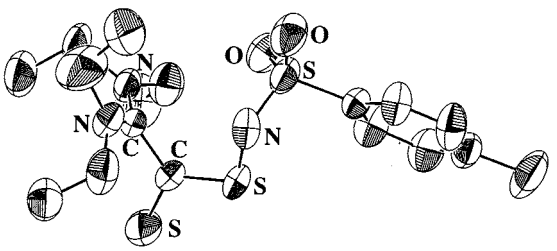
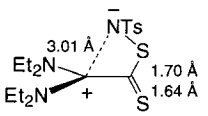


Figure 1. A molecular structure of **4a**.



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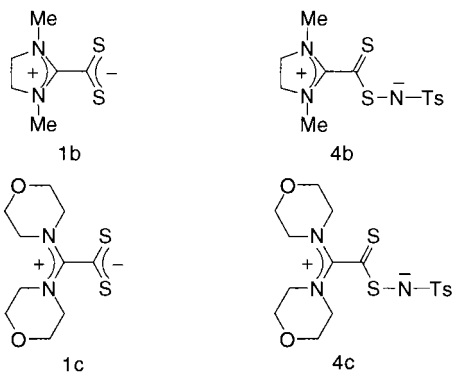
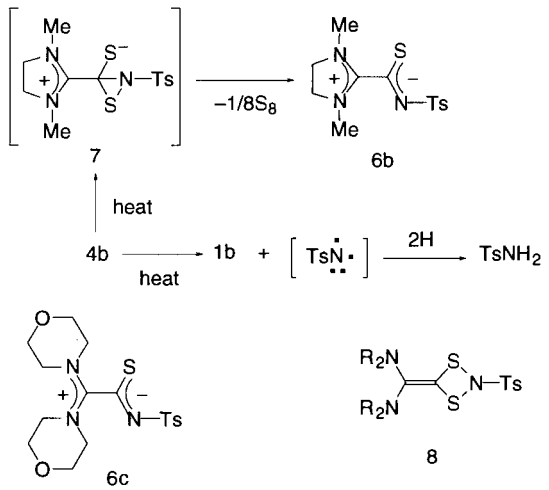
The inner salts (**4b**)[3] and (**4c**)[3] were also prepared by reactions of (**1b**)[1g] and (**1c**)[1g] with PhI=NTs in 82 and 90% yields, respectively.[8]



1b 4b 1c 4c

The inner salt **4b**, which is highly labile in solutions, was not isolated in analytically pure form.[3,8] Thus, it decomposed during purification procedure to give another class of the inner salt (**6b**)[9] in 36% yield, in addition to **1b** and *p*-toluenesulfonamide in 32 and 37% yields, respectively, as the principal products. Furthermore, stirring of a 1:1 mixture of **1b** and PhI=NTs in CH_2Cl_2 for 12 h at room temperature furnished the inner salt **6b** directly in 72% yield, thus providing a better synthesis of **6b**. The formation of **6b** is explained as a result of loss of a sulfur atom from **4b**, which would proceed through a probable intermediate (**7**) as in the case of other thione-*S*-imides.[10]



Another decomposition pathway would produce the inner salt **1b** and the tosyl nitrene; the latter abstracts hydrogen atoms from the solvent to yield *p*-toluenesulfonamide. The inner salt **4c** also decomposed, when heated in refluxing CH_3CN, to give **6c**, **1c**, and *p*-toluenesulfonamide in 15, 20, and 30% yields, respectively. Throughout the decomposition study, cyclization of **4** to four-membered ring compounds (**8**) was not observed.

References and Notes

1 a) J. Nakayama and I. Akiyama, *J. Chem. Soc., Chem. Commun*., **1992**, 1522. b) A. Nagasawa, I. Akiyama, S. Mashima, and J. Nakayama, *Heteroat. Chem*., **6**, 45 (1995). c) J. Nakayama, T. Otani, Y. Sugihara, and A. Ishii, *Tetrahedron Lett*., **38**, 5013 (1997). d) K. Akimoto and J. Nakayama, *Heteroat. Chem*., **8**, 505 (1997). e) J. Nakayama, T. Otani, Y. Sugihara, and A. Ishii, *Chem. Lett*., **1998**, 321. f) J. Nakayama, K. Akimoto, and Y. Sugihara, *Tetrahedron Lett*., **39**, 5587 (1998). g) J. Nakayama, T. Kitahara, Y. Sugihara, T. Otani, and A. Ishii, *Chem. Lett*., **1998**, 887. h) T. Otani, Y. Sugihara, A. Ishii, and J. Nakayama, *Heteroat. Chem*., **9**, 703 (1998). i) J. Nakayama, I. Akiyama, Y. Sugihara, and T. Nishio, *J. Am. Chem. Soc*., **120**, 10027 (1998). j) J. Nakayama, T. Kitahara, Y. Sugihara, and A. Ishii, *Chem. Lett.*, **1999**, 187. k) J. Nakayama, T. Kitahara, Y. Sugihara, A. Sakamoto, and A. Ishii, *J. Am. Chem. Soc*., accepted.

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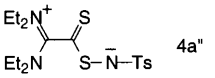
3 **4a**: mp 97.5–99.0 °C (dec); red needles; ^{1}H NMR (400 MHz, $CDCl_3$) δ 1.38 (12H, t, J = 7.1 Hz), 2.37 (3H, s), 3.58–3.68 (4H, m), 3.70–3.81 (4H, m), 7.21 (2H, d, J = 8.1 Hz), 7.74 (2H, d, J = 8.1 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 12.8, 21.3, 47.6, 126.3, 129.0, 140.8, 142.0, 166.7, 229.8. Anal. Calcd for $C_{17}H_{27}N_3O_2S_3$: C, 50.84; H, 6.78; N, 10.46. Found: C, 50.68; H, 6.79; N, 10.29. **4b**: mp > 100 °C (dec); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.38 (3H, s), 3.21 (6H, s), 3.84–3.96 (2H, m), 4.14–4.25 (2H, m), 7.22 (2H, d, J = 8.1 Hz), 7.74 (2H, d, J = 8.1 Hz); ^{13}C NMR (100.6 MHz, CD_2Cl_2, –40 °C) δ 21.7, 34.4, 50.4, 127.9, 129.6, 140.9, 142.1, 164.4, 222.1; **4b** decomposed to a certain extent during the determination of the ^{13}C NMR spectrum in CD_3CN at –20 °C. **4c**: mp > 145 °C (dec); red needles; ^{1}H NMR (400 MHz, CD_2Cl_2) δ 2.38 (3H, s), 3.66–3.68 (8H, m), 3.93–3.99 (8H, m), 7.24 (2H, d, J = 7.6 Hz), 7.67 (2H, d, J = 7.6 Hz); ^{13}C NMR (100.6 MHz, CD_2Cl_2) δ 21.5, 52.2, 66.1, 126.7, 129.5, 141.8, 142.3, 166.5, 229.3.

4 IUPAC name of the compound as the structure **4a"**; *N*-[2-diethylamino-2-(diethylimino)(thioacetyl)thio)]-*p*-toluenesulfonamidate. We thank Dr. N. Inamoto of the Chemical Society of Japan for this naming.



5 The ^{13}C NMR spectrum of **1a** exhibits the corresponding carbon peaks at δ 167 and 236, respectively. The UV/Vis spectrum of **1a** shows absorption maxima at λ_{max} 435 (ε 260) and 368 nm (10800).[1b]

6 Crystal structure data for **4a**: $C_{17}H_{27}N_3O_2S_3$, M_r = 401.63, triclinic, $P1$, a = 8.423(1) Å, b = 14.143(2) Å, c = 17.523(3) Å, α = 91.314(8)°, β = 86.958(9)°, γ = 83.331(9)°, V = 2069.5(6) Å^3, Z = 4, D_x = 1.289 Mg·m^{-3}, λ (Mo Kα) = 0.71073 Å, μ = 3.579 mm^{-1}, T = 295 K, R = 0.064, wR = 0.068, S = 1.834.

7 The corresponding torsion angle for **1a** is 82°.[1b]

8 The yield of **4b** is based on a crude product that was obtained by flush column chromatography on Florisil.

9 **6b**: mp 184.0–184.5 °C (dec); yellow needles; ^{1}H NMR (200 MHz, CD_2Cl_2) δ 2.40 (3H, s), 3.00 (6H, s), 3.83 (4H, s), 7.25 (2H, d, J = 8.1 Hz), 7.92 (2H, d, J = 8.1 Hz); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 21.5, 33.7, 49.9, 128.1, 128.6, 137.7, 142.6, 162.4, 182.5. **6c**: mp 263.0–264.5 °C (dec); yellow needles; ^{1}H NMR (400 MHz, CD_3CN) δ 2.40 (3H, s), 3.44–3.51 (8H, m), 3.69–3.76 (8H, m), 7.30 (2H, d, J = 8.0 Hz), 7.79 (2H, d, J = 8.0 Hz); ^{13}C NMR (100.6 MHz, CD_3CN) δ 21.6, 51.3, 67.0, 128.9, 129.7, 139.8, 143.9, 164.5, 190.2.

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