Pergamon

Tetrahedron Letters, Vol. 38, No. 28, pp. 5013-5016, 1997

0040-4039/97 $17.00 + 0.00

PII: S0040-4039(97)01073-3

Ambident Reactivities of Bis(diethylamino)[(methylthio)thiocarbonyl]carbenium Salts; Reactions at the Carbenium Carbon Atom vs. Thiocarbonyl Sulfur Atom

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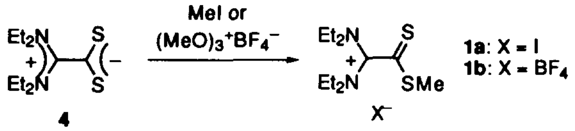
Abstract: Bis(diethylamino)[(methylthio)thiocarbonyl]carbenium salts (**1**), a carbenium ion carrying an α-thiocarbonyl group, show ambident reactivities toward a series of nucleophiles. Thus, they reacted with a typically hard nucleophile, hydroxide, at the carbenium carbon atom, whereas they smoothly reacted with soft nucleophiles, such as carbon, nitrogen, sulfur, and phosphorus nucleophiles, at the thiocarbonyl sulfur atom.

A calculation study on isodesmic reactions showed that the α-thioformylmethylcarbenium ion (**2a**) is significantly stabilized by contribution of the canonical structure (**2b**), and that its isomeric cyclized ion (**3**) is much stabler than (**2**).[1,2] The rate and product analysis study of solvolysis also provided some experimental evidences for the resonance stabilization of α-thioacylcarbenium ions and the intermediary formation of the cyclized ions.[3] Bis(diethylamino)carbeniumdithiocarboxylate (**4**), readily obtainable by reaction of 1,1-bis(diethylamino)-2-chloroethene with elemental sulfur, is methylated with methyl iodide to give the carbenium iodide (**1a**) quantitatively.[4] The tetrafluoroborate salt (**1b**) is also prepared quantitatively by treatment of **4** with trimethyloxonium tetrafluoroborate. These carbenium salts, which possess a thiocarbonyl group at the α-position, would provide a good model to examine the contribution of the foregoing resonance stabilization and the participation of the cyclized ion structure.



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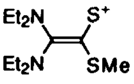
1a: X = I
1b: X = BF_4



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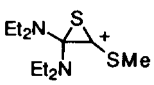

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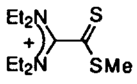

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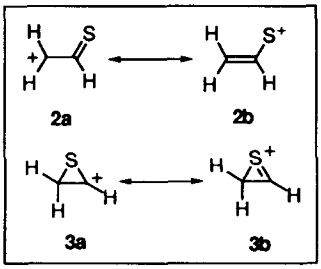


Keeping this in mind, an X-ray single crystal structure analysis of **1a** was carried out (Fig. 1).[5] The most characteristic and unexpected structural feature of **1a** is that the quasi-plane of $(Et_2N)_2C^+$-C unit and the plane of C-C(=S)SMe unit are twisted with a very large torsion angle of 72.6°. The bond length of the carbenium carbon-dithioester carbon bond (1.51 Å) is longer than those of $C(sp^2)-CO_2R$ single bonds (1.49 Å),[6] whereas the mean bond length value of the carbenium carbon-nitrogen bonds (1.32 Å) is equal to those of $C(sp^2)$-N(planar) bonds (1.32 Å).[6] These data reveal that the sulfenium ion structure **5** is a minor contributor of the carbenium ion at least in the crystalline state, and the participation of the cyclized ion structure **6** is also equally eliminated, though coulombic interactions may exist between the carbenium carbon and the thiocarbonyl sulfur atom.[7] Thus, the carbenium ion would be best represented as the canonical structure **7**, where the carbenium ion is stabilized by conjugation with two nitrogen atoms.

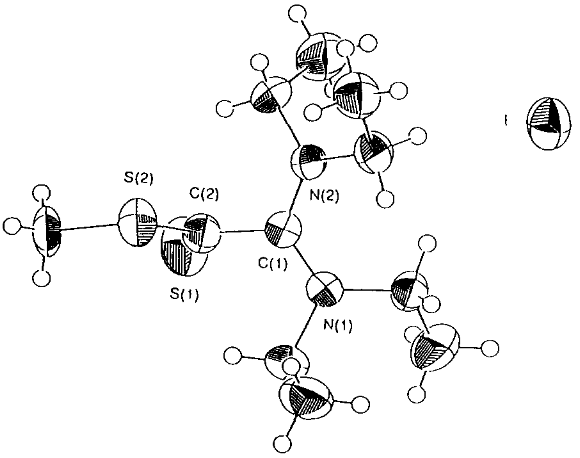
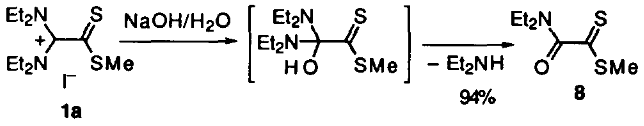


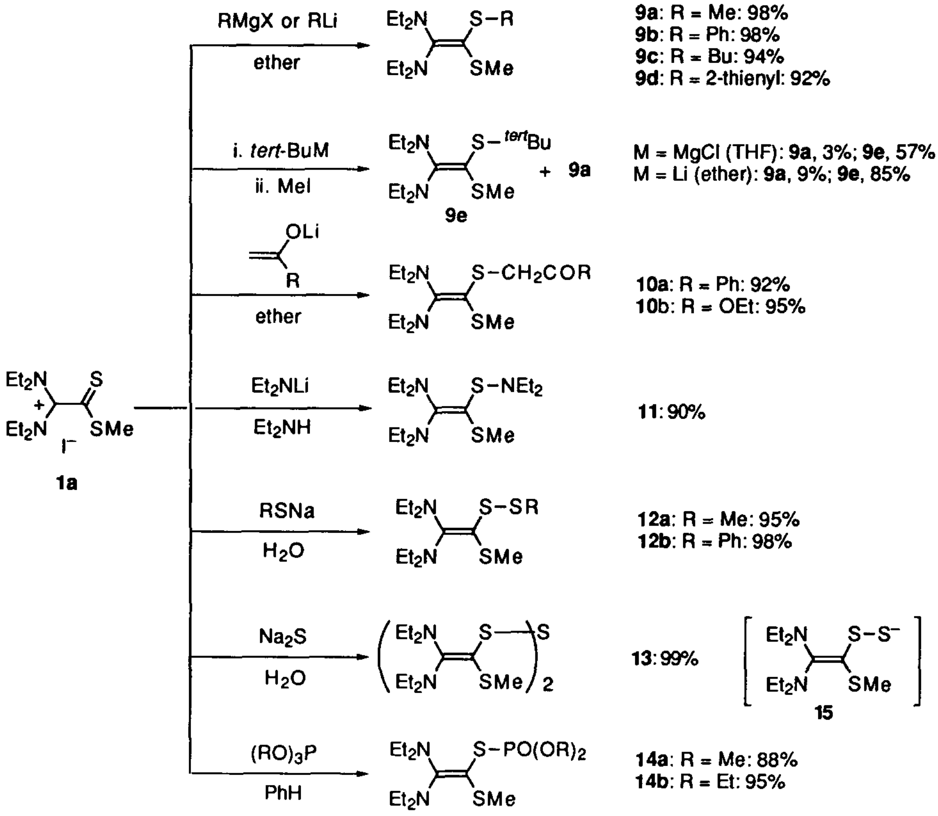
Figure 1. X-Ray structure of **1a**, $C_{11}H_{23}IN_2S_2$ (50% thermal ellipsoids).
Selected bond lengths (Å) and angles (deg): C(1)-C(2), 1.512(16); C(1)-N(1), 1.304(14); C(1)-N(2), 1.345(14); C(2)-S(1), 1.608(14); C(2)-S(2), 1.714(13): N(1)-C(1)-N(2), 124.7(10); N(1)-C(1)-C(2), 119.3(10); N(2)-C(1)-C(2), 116.2(9); C(1)-C(2)-S(1), 119.8(9); C(1)-C(2)-S(2), 116.9(9); S(1)-C(2)-S(2), 128.5(8).

However, reactivities of **1a** toward nucleophiles greatly differed from those expected by the above results. Alkaline hydrolysis of **1a** gave the dithioester **8**[8] in 94% yield. This is the result of the expected addition of HO^- to the carbenium carbon atom followed by elimination of diethylamine.[9] Hydrolysis of **1b** under the same conditions also gave **8** in 80% yield. On the other hand, carbon nucleophiles, MeMgI and PhMgBr, unexpectedly added to the thiocarbonyl sulfur atom, but not the expected carbenium carbon atom, to give enediamines **9a** and **9b**, respectively, nearly quantitatively. The reaction of **1b** with PhMgBr also gave **9b** in 85% yield. Similarly, BuLi and 2-thienyllithium added to the sulfur atom of **1a** to give **9c** and **9d**, respectively, in excellent yields. The reaction of **1a** with *tert*-BuMgCl is of particular interest from a mechanistic point of view. Since the reaction gave the expected product **9e** in lower yield than we had expected from the above results, the reaction mixture was treated with MeI because of the reasons discussed later. This resulted in the formation of **9e** and **9a** in 57 and 33% yields, respectively. Similar treatment of the reaction mixture of **1a** and *tert*-BuLi with MeI also gave **9e** and **9a** in 85 and 9% yields, respectively. Even enolates of acetophenone and ethyl acetate, prepared by treatment of acetophenone and ethyl acetate with lithium diisopropylamide, also reacted with **1a** cleanly to give **10a** and **10b**, respectively, in high yields. In these two cases, no bond formation took place between the carbenium carbon atom of **1a** and the oxygen or carbon atom of the enolates.

Even a nitrogen nucleophile, lithium diethylamide, added to the sulfur atom to produce the structurally interesting sulfenamide **11** in 90% yield. Sulfur nucleophiles, MeSNa and PhSNa, also quickly reacted with

1a in water to give disulfides **12a** and **12b**, respectively, nearly quantitatively. The reaction with sodium sulfide in water produced a rather rare class of compound, divinyl trisulfide **13**, quantitatively. In this case, even the use of an equimolar amount of sodium sulfide and **1a** afforded **13** in nearly 50% yield because a probable intermediate **15** is much more reactive toward **1a** than sodium sulfide. Phosphorus nucleophiles also add to the sulfur atom of **1a**. Thus, trimethyl and triethyl phosphites underwent an Arbusov type reaction to produce the phosphates **14a** and **14b** in 88 and 95% yields, respectively.





9a: R = Me: 98%
9b: R = Ph: 98%
9c: R = Bu: 94%
9d: R = 2-thienyl: 92%

M = MgCl (THF): **9a**, 3%; **9e**, 57%
M = Li (ether): **9a**, 9%; **9e**, 85%

10a: R = Ph: 92%
10b: R = OEt: 95%

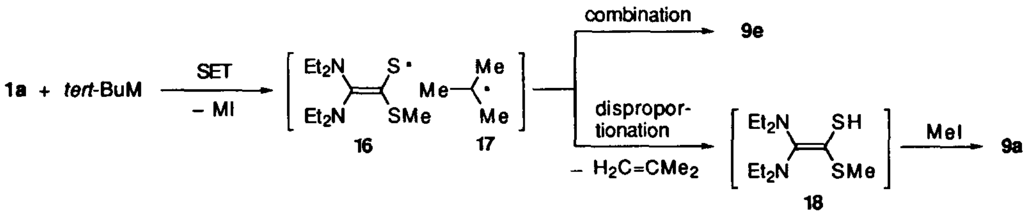
11: 90%

12a: R = Me: 95%
12b: R = Ph: 98%

13: 99%

14a: R = Me: 88%
14b: R = Et: 95%

The above results lead to the conclusion that the present carbenium ion shows ambident reactivities, thereby reacting with a hard nucleophile HO⁻ at the carbenium carbon atom and reacting with softer carbon, nitrogen, sulfur, and phosphorus nucleophiles at the thiocarbonyl sulfur atom. Two mechanisms emerge for the explanation of these results. One involves direct addition of nucleophiles to **1**, where regioselectivity is controlled by hard-soft acid base theory.[10] The other mechanism involves a single-electron-transfer (SET) process.[11] In the latter mechanism, softer and less electronegative nucleophiles transfer one electron to **1** to give a pair of radicals which effecitively combine, probably in a cage, to give the final products, whereas the hard nucleophile HO⁻ directly adds to the carbon atom. This mechanism is in harmony with the results with *tert*-BuMgCl and *tert*-BuLi. Thus, a pair of radicals **16** and **17**, formed by an SET process, either combine to give **9e** or disproportionate to give **18** and isobutene in competitive pathways. The thiol **18** should be easily converted to **9a** on treamtment with MeI.



In conclusion, we have found that the stable carbenium iodide **1a**, carrying a thiocarbonyl group at the α-position, behaves as the ambident electrophile and reacts surprisingly smoothly not only with carbon nucleophiles but also with nitrogen, sulfur, and phosphorus nucleophiles on the sulfur atom to give a wide variety of enediamine derivatives in high yields.

References and Notes

1. For a review on the electronegatively substituted carbocations, see: Creary X. *Chem. Rev.* **1991**, *91*, 1625-1678.
2. a) Lien, M. H.; Hopkinson, A. C. *J. Am. Chem. Soc.* **1988**, *110*, 3788-3792. b) Rodriquez, C. F.; Hopkinson, A. C. *Org. Mass Spectrom.* **1985**, *20*, 691.
3. a) Creary, X.; Mehrsheikh-Mohammadi, M.E. *J. Org. Chem.* **1986**, *51*, 7-15. b) Ablenas, F. J.; George, B. E.; Maleki, M.; Jain, R.; Hopkinson, A. C.; Lee-Ruff, E. *Can. J. Chem.* **1987**, *65*, 1800-1803. c) Creary, X.; Aldridge, T, E. *J. Org. Chem.* **1988**, *53*, 3888-3890. d) Creary, X: Aldridge, T. *J. Org. Chem.* **1991**, *56*, 4280-4285. e) Tokunaga, K.; Ohga, Y.; Takeuchi, K. *Tetrahedron Lett.* **1996**, *37*, 2241-2244.
4. a) Nakayama, J.; Akiyama, I. *J. Chem. Soc., Chem. Commun.* **1992**, 1522. b) Nagasawa, A.; Mashima, S.; Akiyama, I.; Nakayama, J. *Heteroatom. Chem.* **1995**, *6*, 45-49. c) Winberg, H. E.; Coffman, D. D. *J. Am. Chem. Soc.* **1965**, *87*, 2776-2777. d) Schössler, W.; Regitz, M. *Chem. Ber.* **1974**, *107*, 1931-1948.
5. Crystal data for **1a**: $C_{11}H_{23}IN_2S_2$, monoclinic, $P2_1$ (No. 4), a = 6.599(4) Å, b = 15.636(7) Å, c = 8.379(9) Å, β = 106.73(4)°, V = 828.0(8) Å^3, Z = 2, Dc = 1.52 g cm^{-3}. The structure was solved by a direct method using CRYSTAN. Full matrix least-squares refinement yielded the final R value of 0.0421 (R_w = 0.0679) for 1288 independent reflections ($I > 3.00\sigma(I)$) using Mac Science DIP3000 spectrometers.
6. Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G. *J. Chem. Soc. Perkin Trans. II* **1987**, S1.
7. The plane of $(Et_2N)_2C^+$-C unit and that of C-CS_2^- of **4** is nearly perpendicular (82°) to each other.[4b] By adopting this geometry, the vacant p-orbital of the carbenium carbon and the negatively charged sulfur atoms come nearer to make coulombic interactions between them maximum. Also in **1a**, the present geometry makes coulombic interactions between the carbenium carbon and thiocarbonyl sulfur atoms more favorable (non-bonded distance between the carbenium carbon and the thiocarbonyl sulfur atom is 2.70 Å and much smaller than the sum of van der Waals radii, 3.50 Å; Bondi, A. *J. Phys. Chem.* **1964**, 68, 441-451), and an extreme end of this geometry is the cyclized ion structure **6**.
8. Thiel, W.; Mayer, R. *J. Prakt. Chem.* **1989**, *331*, 243-262.
9. Although the reactions of **1a** with sodium methoxide and ethoxide were examined under a variety of conditions, they always gave complex mixtures. For example, the reaction with sodium ethoxide in ethanol gave a complex mixture containing a 30% yield of the inner salt **1**, while the reaction in ether gave one containing a 25% yield of the endiamine **9a**.
10. Pearson, R. G. *Survey of Progress in Chemistry* **1969**, *5*, 1-52.
11. For SET mechanism on reactions of thiocarbonyl compounds with organometallic reagents and for reactions involving radical intermediates, see: a) Ohno, A.; Nakamura, K.; Uohama, M.; Oka, S.; Yamabe, T.; Nagata, S. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 3718-3722. b) Ohno, A.; Nakamura, K.; Shizume, Y.; Oka, S. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 1003-1004. c) Dagonneau, M.; Hemidy, J.-F.; Cornet, D.; Vialle, J. *Tetrahedron Lett.* **1972**, 3003-3006. d) Dagonneau, M.; Vialle, J. *Tetrahedron Lett.* **1973**, 3017-3020. e) Dagonneau, M.; Metzner, P.; Vialle, J. *Tetrahedron Lett.* **1973**, 3675-3678. f) Dagonneau, M.; Vialle, J. *Tetrahedron* **1974**, *30*, 3119-3126.

(*Received in Japan* 9 *May* 1997; *accepted* 30 *May* 1997)