Addition of Grignard and Organolithium Reagents to the Negatively Charged Sulfur Atom of 2,2-Bis(diethylamino)ethan-2-ylium-1-dithioate

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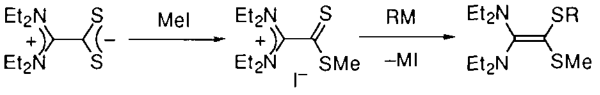
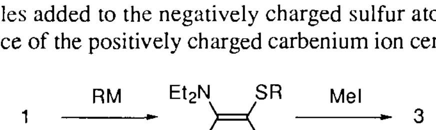
A range of Grignard and organolithium reagents added to the negatively charged sulfur atom of the inner salt **1**, despite the presence of the positively charged carbenium carbon, to give enethiolates **4**, which were methylated by MeI to give dithioacetals **3** as the final product in excellent yields. A mechanism involving a single-electron-transfer process from nucleophiles to **1** is presented for this thiophilic addition.

We have been investigating the synthesis, structure, and reactivities of the inner salt, 2,2-bis(diethylamino)ethan-2-ylium-1-dithioate (**1**), and its related salts.[1-3] Recently, we have reported that the carbenium salt (**2**), which is easily obtainable from **1**, shows ambident reactivities toward a variety of nucleophiles.[3] For example, **2** reacted with soft nucleophiles such as Grignard and organolithium reagents on the sulfur atom of the thiocarbonyl group to give dithioacetals **3** nearly quantitatively, whereas it reacted with a hard nucleophile, hydroxide, on the carbenium carbon atom. In this connection, we have now become interested in the reactivities of **1** toward Grignard and organolithium reagents.



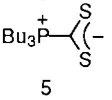
1 2 M = MgX or Li 3

Although the inner salt **1** smoothly reacted with MeMgI in ether at 0 °C with disappearance of the red color due to **1**, quenching of the reaction by water gave an intractable mixture. However, treatment of the reaction mixture with excess MeI gave the dithioacetal **3** (R = Me) in 94% isolated yield. These results reveal that MeMgI added to the dithiocarboxylate sulfur atom, but not the carbenium carbon atom, to give the enethiolate **4** (R = Me, M = MgI), which gave **3** on methylation with MeI. Results summarized in Table 1 demonstrate that the reaction is quite general, and a range of Grignard and organolithium reagents added to the sulfur atom to give **4**, thus affording **3** as the final product in excellent yields by treatment with MeI.[4] The present reaction is of particular interest in that the negatively charged nucleophiles added to the negatively charged sulfur atom despite the presence of the positively charged carbenium ion center.



M = MgX or Li 4

A literature survey revealed that some analogy is found in the reaction of the phosphonium salt **5** with BuLi, which gives **6**.[5]



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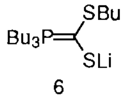

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Table 1. Formation of **3** by reactions of **1** with RM followed by treatment with MeI[a,b]

Entry	Solvent	R	M	Yields (%) of 3
1	THF	Methyl	MgI	92
2	Ether	Ethyl	MgI	94
3	THF	Ethyl	MgI	89
4	Ether	n-Butyl	Li	85
5	Ether	Benzyl	MgCl	88
6	Ether	iso-Propyl	MgCl	84
7	THF	Allyl	MgCl	88
8	THF	Phenyl	MgBr	88
9	THF	2-Thienyl	Li	88

[a] 1.2 Molar amounts of RM was used while MeI was used in excess. [b] All reactions were carried out at 0 °C under argon.

Reactions of **1** with *t*-BuLi and *t*-BuMgCl provide some valuable information on the mechanism of the present reaction (Table 2). The reaction of **1** with 1.2 molar amounts of *t*-BuLi in ether gave a mixture of dithioacetals **7** and **8** in a moderate yield after treatment with MeI. A considerable amount of **1** remained unchanged. Meanwhile, the reaction of **1** with 2 molar amounts of *t*-BuLi also gave a 56:44 mixture of **7** and **8** in a better yield (89%) with complete consumption of **1**. These results can best be explained as follows. The reaction is initiated by a single-electron-transfer process from *t*-BuLi to **1** to produce a pair of radicals **9** (M = Li) and **10**. Combination of **9** and **10** in a solvent cage would give rise to the enethiolate **11**, which is methylated by MeI to afford **7** as one of the final products. Meanwhile, disproportionation of **9** and **10** would produce **12** and isobutene.[6] Then, **12** is lithiated by *t*-BuLi to give **13**, which is dimethylated with MeI to give the other final product **8**. This explains the reasons why **1** was recovered in a considerable amount on reaction with 1.2 molar amounts of *t*-BuLi and why 2 molar amounts of *t*-BuLi was required for the complete comsumption of **1**. The ratio of **7** to **8** is much influenced by the solvent used; in THF, the ratio is reversed (Entries 1 and 2). The ratio is also dependent on the metal ions. Thus, treatment of **1** with *t*-BuMgCl (2 molar amounts) in ether gave no disproportionation product **8**, whereas, in THF, **7** and **8** were formed in the ratio of 82:18 (Entries 3 and 4).[7]

The mechanism presented above should be operative also in the examples given in Table 1. However, for these cases, since steric hindrance is not severe, a pair of radicals combine in a cage to give **4** exclusively.

Although the carbenium salt **2** reacted with a variety of soft nucleophiles such as sulfur, nitrogen, and phosphorus nucleophiles, on the sulfur atom, **1** did not react with these

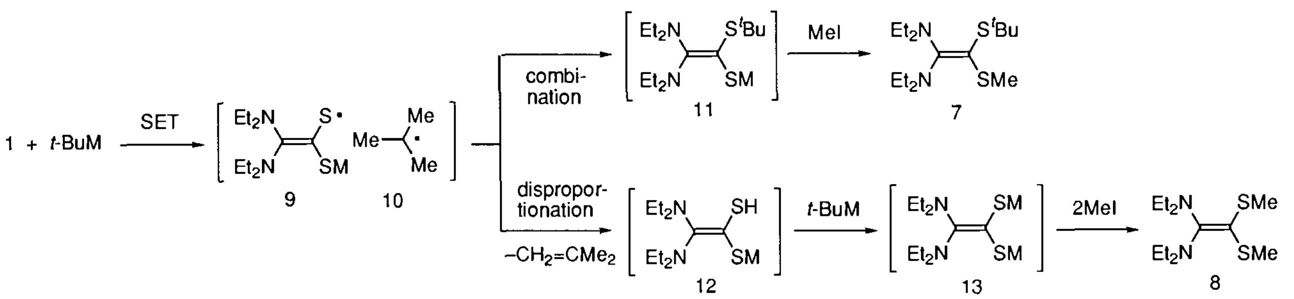
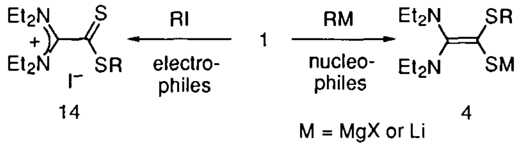


Table 2. Reactions of **1** with *t*-BuM followed by treatment with MeI[a]

Entry	Solvent	M	Yields (%) of **7** + **8**	Relative Ratio **7**:**8**
1	Ether	Li	89	56:44
2	THF	Li	94	38:62
3	Ether	MgCl	89	100:0
4	THF	MgCl	91	82:18

[a] 2 Molar amounts of *t*-BuM was used while MeI was used in excess. [b] All reactions were carried out at 0 °C under argon.

reagents.[3] This can be explained by large difference of the cyclic voltammetric peak potentials between **1** ($E_{p,a}$; −1.99, $E_{p,c}$; −1.80, $E_{1/2}$; −1.89 V) and **2** ($E_{p,a}$; −0.88, $E_{p,c}$; −0.72, $E_{1/2}$; −0.80V).[8] From these values, evidently **1** is much weaker than **2** as a single-electron acceptor and should be less reactive than **2** toward nucleophiles.



In conclusion, the inner salt **1** shows a unique property which enabled it to react with both electrophiles (RI) and nucleophiles (RM) to give **14** and **4**, respectively.[9]

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, *Heteroatom Chem.*, **6**, 45 (1995). c) K. Akimoto and J. Nakayama, *Heteroatom Chem.*, **8**, 505 (1997). d) K. Akimoto, K. Masaki, and J. Nakayama, *Bull. Chem. Soc. Jpn.*, **70**, 471 (1997). e) K. Akimoto, Y. Sugihara, and J. Nakayama, *Bull. Chem. Soc. Jpn.*, **70**, 2555 (1997).

2 For a review, see J. Nakayama, *Sulfur Lett.*, **15**, 239 (1993).

3 J. Nakayama, T. Otani, Y. Sugihara, and A. Ishii, *Tetrahedron Lett.*, **38**, 5013 (1997).

4 Supporting spectral data (^{1}H- and ^{13}C-NMR) and correct elemental analyses were obtained for all new compounds.

5 N. I. Tyryshkin, A. I. Konovalov, V. V. Gavrilov, and N. A. Polezheva, *Phos. Sulf. Sil.*, **109-110**, 553 (1996). See also A. Moradopour and S. Bittner, *Tetrahedron Lett.*, **28**, 3805 (1987).

6 Isobutene was detected as the adduct with Br_2 ($Me_2CBr\text{-}CH_2Br$).

7 The extent of solvation and aggregation of *t*-BuM should be responsible for these effects: J. L. Wardell, in "Comprehensive Organometallic Chemistry," ed by G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon, Oxford (1982), Vol. 1, Chapter 2; W. E. Lindsell, in "Comprehensive Organometallic Chemistry," ed by G. Wilkinson, F. G. A. Stone, and E. W. Abel, Pergamon, Oxford (1982), Vol. 1, Chapter 4.

8 Anodic scanning: scan rate, 100 mV/sec; reference electrode, Ag/Ag$^+$; counter electrode, Pt; working electrode, Pt; 0.05 M Bu_4NClO_4 in CH_3CN under N_2 at room temperature.

9 MeI, EtI, i-PrI, $PhCH_2I$, and CH_2I_2 alkylated **1** to give the corresponding carbenium iodides **14** in good yields.[4]