Ambident Reactivities of Carbenium Salts Possessing a Thiocarbonyl Group at the *β*-Position

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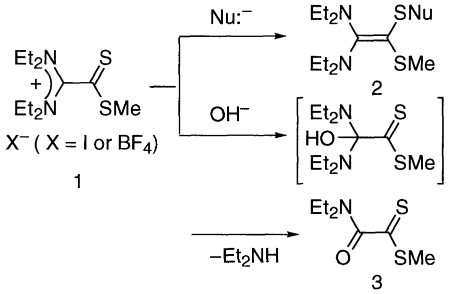
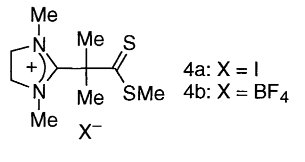
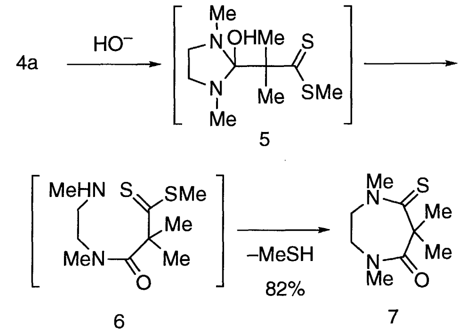
A stable, crystalline carbenium iodide, which possesses a thiocarbonyl group at the β-position, shows ambident reactivities, thereby reacting with a hard nucleophile OH⁻ at the carbenium carbon atom and with a soft nucleophile RLi at the thiocarbonyl sulfur atom. Thermal dissociation of the MeLi adduct to a carbene and a ketene dithioacetal is also presented.

Recently we have reported that carbenium salts (**1**), which carry a dithioester thiocarbonyl group at the α-position of the carbenium ion center, show ambident reactivities toward a series of nucleophiles.[1] They thus smoothly reacted with soft nucleophiles, such as carbon, nitrogen, sulfur, and phosphorus ones, at the thiocarbonyl sulfur atom to give enediamines (**2**) or related compounds, whereas they reacted with a typically hard nucleophile OH⁻ at the carbenium carbon atom to afford an amide (**3**) as the final product. More recently we have succeeded in the preparation of a thermally stable, crystalline carbenium iodide (**4a**), a homolog of **1**, where the carbenium carbon atom and the thiocarbonyl group is insulated by an sp^3 carbon atom.[2] The tetrafluoroborate salt (**4b**)[3,4] was readily derived from **4a** by treatment with $AgBF_4$. Here we report that these carbenium salts **4** also show ambident reactivities toward nucleophiles. Thermal dissociation of the adduct of **4a** with MeLi to a carbene and a ketene dithioacetal is also presented.

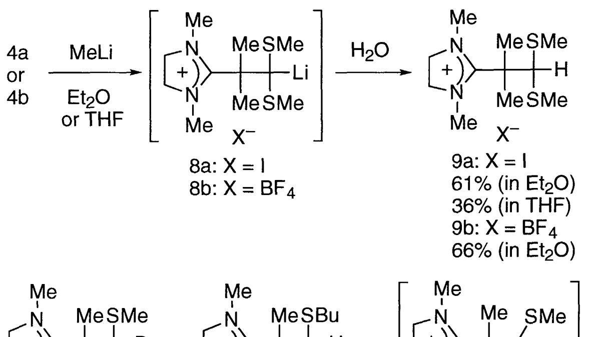


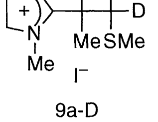


A two-phase mixture of ether and an aqueous solution of **4a** and NaOH was stirred for 8 h at room temperature. Work-up of the ether layer gave a seven-membered ring heterocycle (**7**)[3,4] in 82% yield. The formation of **7** suggests that OH⁻ addition took place at the carbenium carbon atom, that is, the addition of OH⁻ to the carbenium carbon atom, ring-opening of the resulting adduct (**5**) to (**6**), and intramolecular condensation of **6** explain the formation of **7**.

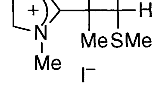


Meanwhile, addition of RLi takes place at the thiocarbonyl sulfur atom. Thus, treatment of a yellow suspension of **4a** or **4b** in ether or THF with MeLi (1.04 M ether solution, 1 equiv) at room temperature for 1 h produced a colorless suspension, which, on quenching with water, afforded carbenium salt (**9a**) or (**9b**)[3,4] in reasonable yields. When the reaction of **4a** with MeLi in ether was quenched with D_2O, the D-incorporated iodide salt (**9a-D**, D content > 95%) was produced. Treatment of **4a** with BuLi in ether also gave the carbenium iodide (**10**)[3,4] in 47% yield. The formation of these products can best be explained by the initial addition of RLi to the thiocarbonyl sulfur atom of **4**, which produces intermediates (**8**) as exemplified in the case of MeLi. The structure of **8** might be alternatively expressed as the 1,3-dipolar structure (**11**). Attempted trapping of **8a** with reagents[5] other than water all failed probably because of steric hindrance.





9a-D



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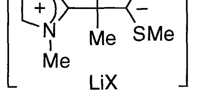

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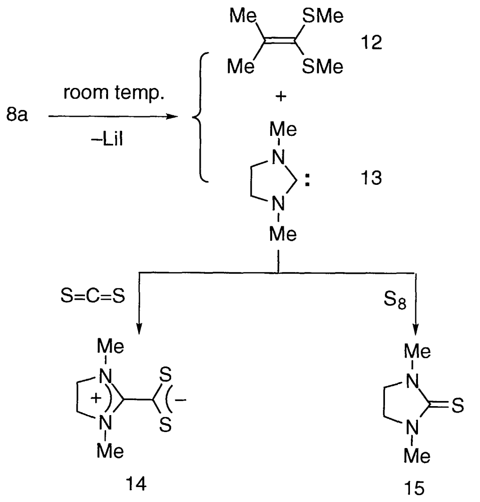
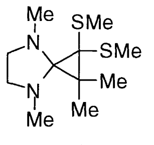
Interestingly, **8a** splits into a ketene dithoacetal (**12**) and a carbene (**13**) at room temperature. No expected intramolecular cyclization to (**16**) took place probably owing to steric reasons. Thus, when the reaction of **4a** with MeLi was quenched with water after 10 h, the yield of **9a** decreased to only 9% with formation of **12** in 75% yield. The carbene **13**, generated above, could be trapped by carbon disulfide and elemental sulfur. Thus, addition of carbon disulfide to the reaction mixture of **4a** with MeLi after 10 h gave the inner salt (**14**)[6] in 55% yield, whereas the addition of carbon disulfide after 1 h provided **14** only in 10% yield. Similarly, addition of elemental sulfur after 10 h gave 2-thioxo-1,3-dimethylimidazolidine (**15**)[7] in 62% yield. However, we cannot rule out the possibility that the actual species that was involved in the above reactions might be the carbene dimer (**18**),[8] and not the free carbene **13**, although this type of carbenes is known to be persistent.[9] The thermal dissociation of **8a** to **12** and **13** is irreversible, thus addition of the ketene dithioacetal (**17**) (4 equiv)[3,4,10] to the reaction mixture of **4a** and MeLi did not give any carbenium salt **10** on quenching with water. The same is also true for the addition of the ketene dithioacetal **12** to the reaction mixture of **4a** with BuLi.





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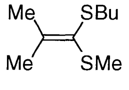

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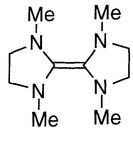

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In summary, the carbenium salts **4** show ambident reactivities, thereby reacting with a typically hard nucleophile OH^- at the carbenium carbon atom and with a soft nucleophile RLi at the soft thiocarbonyl sulfur atom despite the positively charged carbenium carbon atom in existence.

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References and Notes

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

2 J. Nakayama, K. Akimoto, and Y. Sugihara, *Tetrahedron Lett.*, **39**, 5587 (1998).

3 Satisfactory elemental analyses were obtained for all new compounds.

4 **4b**: mp 81-82 °C; yellow crystals; ^1H NMR (400 MHz, $CDCl_3$) δ 1.96 (s, 6H, Me), 2.72 (s, 3H, SMe), 3.18 (s, 6H, NMe), 3.96 (s, 4H, CH_2); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 19.9, 28.9, 35.0, 51.9, 59.6, 168.1, 238.6. **7**: mp 40-41 °C; colorless crystals; ^1H NMR (300 MHz, $CDCl_3$) δ 1.72 (s, 6H, Me), 2.87 (s, 3H, NMe), 3.45 (m, 2H, CH_2), 3.48 (s, 3H, NMe), 3.88 (m, 2H, CH_2); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 31.9, 38.0, 47.4, 50.4, 53.9, 57.8, 175.3 (C=O), 208.9 (C=S); IR (KBr) 1652 cm^{-1} (C=O). **9a:** mp 192-193 °C; colorless crystals; ^1H NMR (400 MHz, $CDCl_3$) δ 1.76 (s, 6H, Me), 2.32 (s, 6H, SMe), 3.44 (s, 6H, NMe), 4.07 (s, 1H, CH), 4.13 (s, 4H, CH_2); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 16.8, 25.9, 39.3, 47.5, 53.0, 63.3, 169.9. **9b:** mp 155-156 °C; colorless crystals; ^1H NMR (400 MHz, $CDCl_3$) δ 1.67 (s, 6H, Me), 2.31 (s, 6H, SMe), 3.37 (s, 6H, NMe), 3.96 (s, 4H, CH_2), 4.11 (s, 1H, CH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 16.6, 25.1, 38.4, 47.6, 52.4, 63.6, 169.9. **10:** mp 150-152 °C; colorless crystals; ^1H NMR (400 MHz, $CDCl_3$) δ 0.95 (t, 3H, J = 7.3 Hz, Me), 1.45 (m, 2H, CH_2), 1.60 (m, 2H, CH_2), 1.74 (s, 3H, Me), 1.76 (s, 3H, Me), 2.33 (s, 3H, SMe), 2.69 (m, 1H, CH_2), 2.79 (m, 1H, CH_2), 3.44 (s, 6H, NMe), 4.13 (s, 4H, CH_2), 4.14 (s, 1H, CH); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 13.6, 16.8, 21.9, 25.8, 25.9, 31.3, 33.3, 39.2, 47.5, 53.0, 61.7, 170.0. **17**: bp 95-100 °C/15 mmHg (bulb-to-bulb distillation; ^1H NMR (400 MHz, $CDCl_3$) δ 0.91 (t, 3H, Me), 1.38-1.54 (m, 4H, CH_2), 2.05 (s, 3H, Me), 2.06 (s, 3H, Me), 2.24 (s, 3H, SMe), 2.68 (t, 2H, CH_2); ^{13}C NMR (100.6 MHz, $CDCl_3$) δ 13.7, 17.1, 21.9, 23.6, 23.9, 31.7, 33.0, 124.5, 144.4.

5 Attempted trapping reagents include MeI, Me_3SiI, PhSH, 1,3-diketones, and $PhSO_2CH{=}CH_2$.

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10 The dithioacetal **17** was obtained by thermal dissociation of the adduct of **4a** with BuLi.