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CHEMISTRY LETTERS, pp. 1851-1852, 1987.

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A Simple Method for Generation of Thiocarbonyl Ylides and Their Regioselective 1,3-Cycloadditions¹⁾

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Thioketone S-methylides were generated from thioketones and (trimethylsilyl)methyl triflate, and underwent 1,3-cycloaddition with thioketones to give 1,3-dithiolanes.

The production of reactive 1,3-dipole intermediates from organosilicon compounds has been of increasing interest in recent years.²⁾ However, there were few reports on simple generation of thiocarbonyl ylides. Recently, we have reported the novel methods for generation of thiocarbonyl ylides(2) from the organosilicon compounds.³⁾ The methods involve the formation of silylmethyl sulfonium and the subsequent cleavage of the silicon-carbon bond by attacking of the counter anion as shown below.

$$Me_{3}SiCH_{2}SCH_{2}SCH_{3}Me_{3}$$

$$Me_{3}SiCH_{2}SCH_{2}SiMe_{3}$$

$$Me_{3}SiCH_{2}SCH_{2}SiMe_{3}$$

$$Me_{3}SiCH_{2}SCH_{2}SiMe_{3}$$

$$Me_{3}SiCH_{2}SCH_{2}SiMe_{3}$$

$$Me_{3}SiCH_{2}SCH_{2}SiMe_{3}$$

$$Me_{3}SiCH_{2}SCH_{2}SiMe_{3}$$

$$Me_{3}SiCH_{2}SCH_{2}SiMe_{3}$$

$$Me_{3}SiCH_{2}SCH_{2}SiMe_{3}$$

$$Me_{3}SiCH_{2}SiMe_{3}$$

This result prompted us to search for more convenient preparation of 2 via such an intermediary sulfonium as 1 by direct reaction of a thiocarbonyl compound and silylmethyl triflate. Treatment of 2 equiv. of thioketone(3) and (trimethyl-silyl)methyl triflate(4) in DME for 12 h at room temperature gave only 4,4,5,5-tetrasubstituted 1,3-dithiolane(7) in a moderate yield(7a: 54%; 7b: 34%; 7c: 47%). The structures of 7 were determined on the basis of the spectral data.⁴⁾



Generation of ylides(6) proceeded via the silylmethyl sulfonium salts(5) from one equiv. of 3 and 4, and the successive reaction of 6 with dipolarophiles(3) gave the corresponding cycloadducts(7).

In a previous paper, we have correctly rationalized the regioselectivity of thiocarbonyl ylide cycloadditions using the frontier molecular orbital theory.⁵⁾ So we carried out the molecular orbital calculation of a dipole(**6a**) and a dipolar-ophile(**3a**) by means of the MNDO method from the same viewpoint. Figure 1 shows the interaction between **6a** and **3a**, which proves successfully the experimental fact that the product in 1,3-dipolar cycloaddition of **6a** with **3a** was 4,4,5,5-tetrasubstituted 1,3-dithiolane.



a) Optimization of geometry was performed by the MNDO method. b) The frontier orbital energies c) The frontier electron densities

Fig. 1. HOMO-LUMO correlation diagram and the frontier orbital interaction between dipole and dipolarophile in 1,3-dipolar cycloaddition.^{a)}

Thus we have provided a new method for generation of thiocarbonyl ylides from thioketones and silylmethyl triflate. This method is one of the simplest generation of thiocarbonyl ylides.

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- 4) **7a**: mp 199 °C, ¹H-NMR $\delta(CDC1_3)$, 3.73(2H, s, SCH₂S), 6.89-7.38(20H, m, 4xC₆H₅), ¹³C-NMR $\delta(CDC1_3)$, 30.12(t), 77.63(s), 126.29(d), 126.51(d), 131.66(d), 143.09(s), [cf. T. Kalwinsh, Li Xingya, J. Gottstein, and R. Huisgen, J. Am. Chem. Soc., <u>103</u>, 7032(1986).]; **7b**: ¹H-NMR $\delta(CDC1_3)$, 2.56(12H, s, 4xCH₃), 3.69(2H, s, SCH₂S), 6.86-7.21(16H, m, 4xC₆H₄), ¹³C-NMR $\delta(CDC1_3)$, 20.85(q), 29.96(t), 77.15(s), 126.89 (d), 131.60(d), 135.93(s), 140.27(s); **7c**: ¹H-NMR $\delta(CDC1_3)$, 3.72(2H, s, SCH₂S), 6.96-7.41(16H, m, 4xC₆H₄), ¹³C-NMR $\delta(CDC1_3)$, 30.07(t), 76.34(s), 126.84(d), 132.80(d), 133.23(s), 140.65(s).
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(Received June 13, 1987)