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

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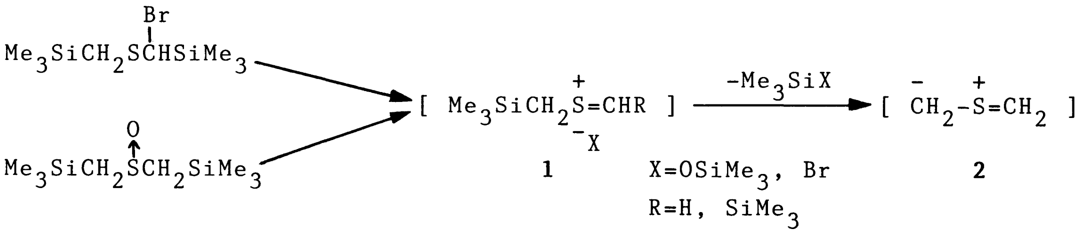
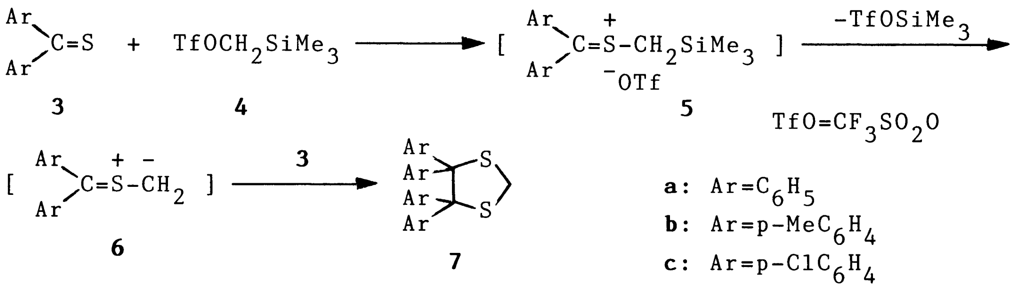
Thioketone S-methylides were generated from thioketones and (trimethylsilyl)methyl triflate, and underwent 1,3-cycloaddition with thioketones to give 1,3-dithiolanes.

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.

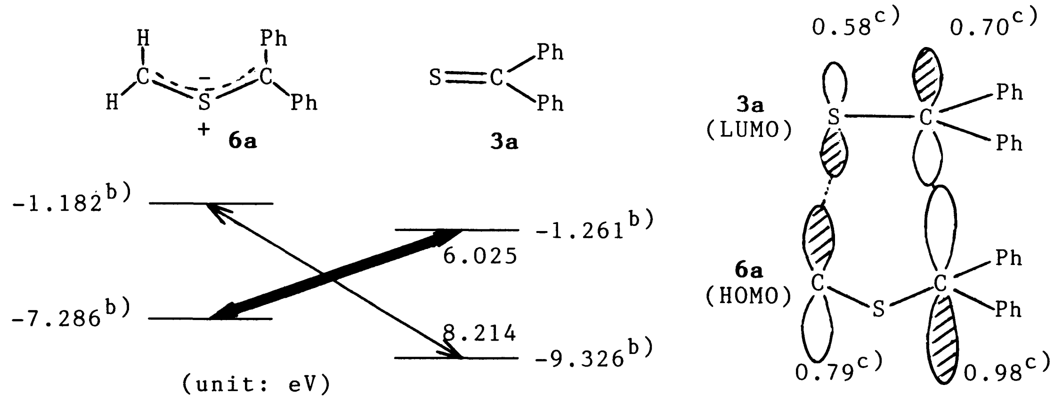


This result prompted us to search for more convenient preparation of **2** via such an intermediary sulfonium as **1** by direct reaction of a thiocarbonyl compound and silylmethyl triflate. Treatment of 2 equiv. of thioketone(**3**) and (trimethylsilyl)methyl triflate(**4**) in DME for 12 h at room 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 dipolarophile(**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.

References

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4) **7a**: mp 199 °C, ^{1}H-NMRδ($CDCl_3$), 3.73(2H, s, SCH_2S), 6.89-7.38(20H, m, 4xC_6H_5), ^{13}C-NMRδ($CDCl_3$), 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., 103, 7032(1986).]; **7b**: ^{1}H-NMRδ($CDCl_3$), 2.56(12H, s, 4xCH_3), 3.69(2H, s, SCH_2S), 6.86-7.21(16H, m, 4xC_6H_4), ^{13}C-NMRδ($CDCl_3$), 20.85(q), 29.96(t), 77.15(s), 126.89(d), 131.60(d), 135.93(s), 140.27(s); **7c**: ^{1}H-NMRδ($CDCl_3$), 3.72(2H, s, SCH_2S), 6.96-7.41(16H, m, 4xC_6H_4), ^{13}C-NMRδ($CDCl_3$), 30.07(t), 76.34(s), 126.84(d), 132.80(d), 133.23(s), 140.65(s).

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