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GENERATION OF THIOCARBONYL YLIDES WITH RELEASE OF DISILOXANE FROM BIS(TRIMETHYLSILYLMETHYL) SULFOXIDES[1)]

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Abstract : A novel and general method for generation of thiocarbonyl ylide by release of disiloxane from bis(trimethylsilylmethyl) sulfoxide (**1**) has been found. This method was also demonstrated for generation of aliphatic and aromatic thioaldehyde S-methylide.

Thiocarbonyl ylides have become increasingly attractive for studies on 1,3-dipolar cycloadditions.[2)] Their formation by thermolysis of 1,3,4-thiadiazole was discovered by Kellogg and his co-workers[3)] and has been investigated in detail.[4)] Evidence for the existence of thiocarbonyl ylide was provided by Tamagaki and Oae.[5)] We reported a convenient method for generation of trimethylsilylthioaldehyde S-methylide.[6)] However, it is suprising that the parent ylide, thioformaldehyde S-methylide (**3**) has not been reported. We have now succeeded in the generation of ylide (**3**) under the neutral and mild conditions and 1,3-cycloaddition with conjugated dipolarophiles. Our strategy involved the release of disiloxane from bis(trimethylsilylmethyl) sulfoxide (**1a**)[7)] through a pathway related to the sila-Pummerer rearrangement[8)].

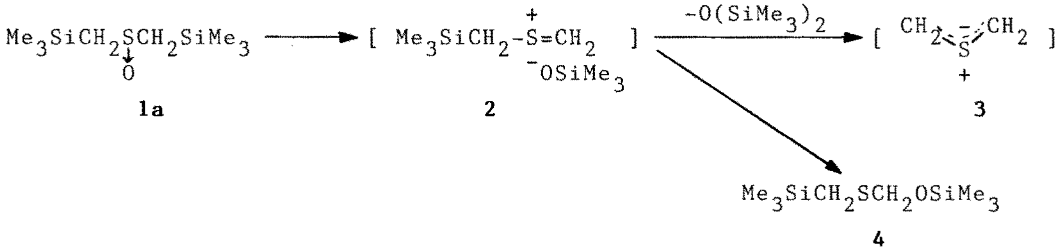
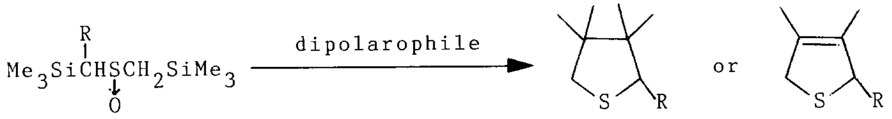
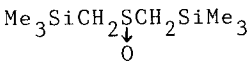
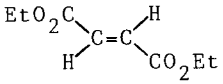
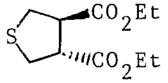
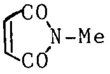
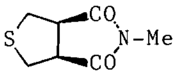
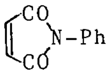
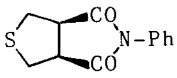
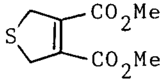
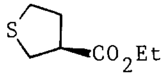
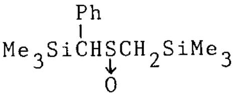
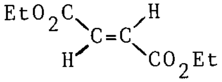
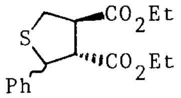
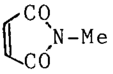
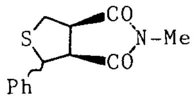
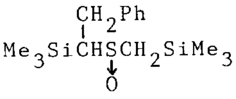
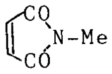
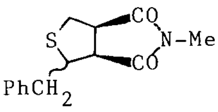


Table I. 1,3-Dipolar Cycloaddition *via* Thiocarbonyl Ylides



1 **5** **6**

Run	Sulfoxide	Dipolarophile	Cycloadduct	Yield[a] (%)
1	 $\mathrm{Me_3SiCH_2\underset{\overset{\downarrow}{O}}{S}CH_2SiMe_3}$ **1a**		 **5a**	80
2	**1a**		 **5b**	81
3	**1a**		 **5c**	70
4	**1a**	$\mathrm{MeO_2C{-}C{\equiv}C{-}CO_2Me}$	 **6a**	61
5	**1a**	$\mathrm{CH_2{=}CHCO_2Et}$	 **5d**	55
6	 $\mathrm{Me_3Si\overset{\overset{Ph}{|}}{C}H\underset{\overset{\downarrow}{O}}{S}CH_2SiMe_3}$ **1b**		 **5e**[b]	50
7	**1b**		 **5f**[c]	65
8	 $\mathrm{Me_3Si\overset{\overset{CH_2Ph}{|}}{C}H\underset{\overset{\downarrow}{O}}{S}CH_2SiMe_3}$ **1c**		 **5g**[d]	65

a Isolated Yield.

b 2,3-*cis* : 2,3-*trans* = 1 : 1.

c A single stereoisomer was obtained.; see ref. 12.

d 2,3-*cis* : 2,3-*trans* = 1 : 5.; see ref. 12.

The required sulfoxide (**1a**) for this reaction was prepared from readily available sulfide by oxidation with m-chloroperbenzoic acid in CH_2Cl_2 at -70°C.[9)] Treatment of 1.5 equiv of **1a** with a dipolarophile in HMPA at 100°C[10)] gave the corresponding cycloadduct. As indicated by the representative example in runs 1-5 (Table I), 1,3-cycloaddition of **1a** proceeded smoothly to give the tetrahydrothiophenes and 2,5-dihydrothiophenes in good to moderate yields.[11)] This method was also utilized for generation of thiobenzaldehyde S-methylide and phenylthioacetaldehyde S-methylide as shown in runs 6-8.[12)]

Treatment of the rearrangement product **4** with a dipolarophile under similar conditions did not give any cycloadduct. This fact suggests that intermediate **2** partitions between the desired ylide **3** and the sila-Pummerer rearrangement product **4**.

Thus we have provided a novel and general method for generation of various thiocarbonyl ylides such as thioformaldehyde S-methylide, and aromatic and aliphatic thioaldehyde S-methylides by employing organosilicon compounds.

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review see: W. P. Weber, "Silicon Reagents for Organic Synthesis" Springer Verlag. Berlin(1983), pp 346-350.

9) Sulfoxide **1** was obtained as a sufficiently pure liquid in practice without distillation after the usual workup. **1a**: IR (neat) 1028 cm^{-1}(νSO). ^{1}H-NMR ($CDCl_3$, 90 MHz) δ 0.22(18H, s), 2.14(2H, d, J=13.7 Hz), 2.45(2H, d, J=13.7 Hz). **1b**: IR (neat) 1035 cm^{-1}(νSO). **1c**: IR (neat) 1030 cm^{-1}(SO).

10) The reaction was completed in 10 min. after addition of a solution of **1a** and a dipolarophile in HMPA to HMPA warmed at 100°C.

11) All products gave satisfactory spectral and analytical data consistent with the structures shown. Their ^{13}C-NMR spectra provided conclusive evidence for cycloadducts. ^{13}C-NMR ($CDCl_3$) δ **5a**: bp 150-151°C (15 mmHg). 14.90(q), 33.33(t), 51.10(t), 61.20(d), 171.80(S). **5b**: mp 90-91°C. 22.25 (q), 36.00(t), 48.68(d), 177.93(S). **5C**: mp 152-153°C. 36.52(t), 48.49(d), 126.45(d), 128.73(d), 129.11(d), 132.51(s), 177.60(S). **5d**: bp 90-91°C (15 mmHg). 14.19(q), 30.66(t), 33.43(t), 33.92(t), 48.33(d), 60.79(t), 169.36 (s). **6a**: bp 95-96 (0.5 mmHg). 39.39(t), 52.45(q), 138.46(s), 164.55(s).

12) **5e**: The ratio of both isomers was determined by gas chromatographic analysis. bp 150-152 (6 mmHg). ^{13}C-NMR ($CDCl_3$, 90 MHz) δ 13.76(q), 14.14 (q), 33.32(t), 33.43(t), 48.65(d), 51.74(d), 52.12(d), 54.72(d), 56.78(d), 59.17(d), 60.63(t), 60.90(t), 62.12(t), 61.22(t), 127.70(d), 127.98(d), 128.08(d), 128.52(d), 128.73(d), 169.48(s), 171.32(s), 171.86(s). **5f**: mp 166-167°C. ^{1}H-NMR ($CDCl_3$) δ 2.96(3H, s), 3.15-3.25(1H, m), 3.45-3.60(3H, m), 4.67-4.77(1H, m), 7.30(5H, s). ^{13}C-NMR ($CDCl_3$) δ 25.08(q), 34.40(t), 50.17(d), 52.23(d), 56.72(d), 128.30(d), 134.69(s), 174.56(s), 177.81(s), Stereochemistry of **5f** is not clear. **5g**: 2,3-*cis* isomer mp 72-72°C. ^{1}H-NMR ($CDCl_3$) δ 2.70-2.92(2H, m), 3.04(3H, s), 3.20-3.76(5H, m), 7.25(5H, s). ^{13}C-NMR ($CDCl_3$) δ 25.14(q), 34.73(t), 35.76(t), 49.14(d), 49.74(d), 54.99 (d), 126.72(d), 128.51(d), 128.62(d), 139.78(s), 177.98(s). 2,3-*trans* isomer mp 84-85°C. ^{1}H-NMR ($CDCl_3$) δ 2.92(2H, d, J=7.2 Hz), 2.96(3H, s), 3.12-3.56(4H, m), 3.92(1H, td, J=7.2 Hz, 1 Hz), 7.28(5H, s). ^{13}C-NMR ($CDCl_3$) δ 25.30(q), 33.86(t), 41.61(t), 48.65(d), 52.71(d), 53.69(d), 127.00(d), 128.62(d), 128.63(d), 129.17(d), 138.51(s), 139.78(s), 177.98 (s).

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