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Generation of Thioketene S-Methylides and Their 1,3-Cycloadditions1)

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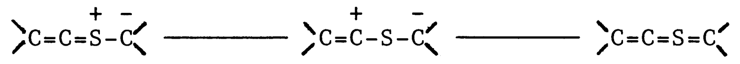
Thioketene S-methylide was found to be generated by release of disiloxane from α-(trimethylsilyl)vinyl (trimethylsilyl)methyl sulfoxide and its 1,3-cycloaddition provided a novel method for synthesis of 2-alkylidenetetrahydrothiophenes.

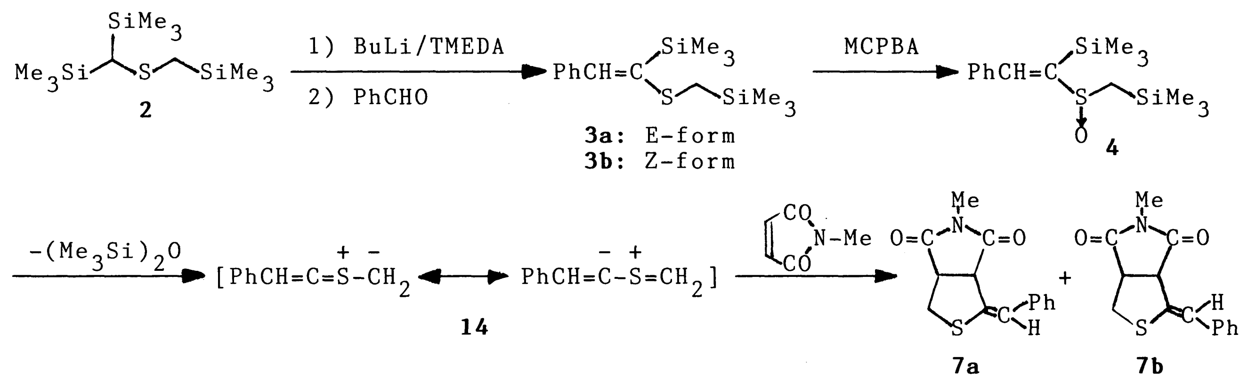
The chemistry of thiocarbonyl ylides has been developed recently by R. M. Kellogg,2) R. Huisgen,3) and us.1,4) A thioketene S-methylide (**1a**) constitutes a new class of thiocarbonyl ylide, the resonance structures of which include a 1,3-dipole species (**1b**) and an interesting heterocumulene skeleton (**1c**) containing a tetravalent sulfur.



1a **1b** **1c**

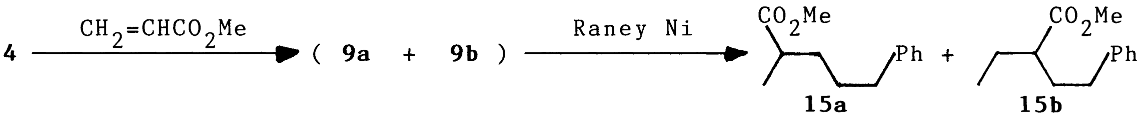
We wish to describe here the first example of generation of thioketene S-methylides and their 1,3-cycloaddition reactions, leading to synthesis of 2-alkylidenetetrahydrothiophene derivatives.

We have already reported new methods for generation of various thiocarbonyl ylides from bromo(trimethylsilyl)methyl (trimethylsilyl)methyl sulfides1,4a) and from bis(trimethylsilylmethyl) sulfoxides.4b) The latter method has been found to be well suited for generation of thioketene S-methylides. Treatment of bis(trimethylsilyl)methyl (trimethylsilyl)methyl sulfide (**2**) with butyllithium and benzaldehyde gave α-(trimethylsilyl)stylyl (trimethylsilyl)methyl sulfide (**3**) in 84% yield. The two geometrical isomers (**3a** and **3b**) were separable by careful column chromatography (silica gel, hexane as an eluent).5) The sulfoxides **4a** and **4b** were prepared by oxidation of **3a** and **3b** with m-chloroperbenzoic acid, respectively. The reaction of **4a** with N-methylmaleimide in HMPA at 100 °C afforded a 1 : 1 mixture of two geometrical isomers (**7a** and **7b**). The sulfoxide **4b** gave also the same mixture of **7a** and **7b** in the same ratio. The structues of the products were determined on the basis of spectral and analytical data.6) ^{13}C-NMR spectra of **7a** and **7b** show characteristic signals in support of tetrahydrothiophene ring system: **7a**, 34.3(t), 47.8(d), 50.1(d), 135.8(s), **7b**, 35.0(t), 46.6(d), 55.2(d), 136.6(s). In ^{1}H-NMR spectrum of **7a**, methine proton at the 3-position resonates at the lower field (4.35 ppm) than that of **7b** (4.06 ppm) by the deshielding effect of near benzene ring, and a proton of benzene ring resonates at the lower field than the others by the deshielding effect of near carbonyl group, which was not observed in the spectrum of **7b**.



These facts suggest that both reactions proceed via the same intermediate, phenylthioketene S-methylide (**14**). Therefore, we carried out the representative experiments of 1,3-cycloaddition without attention to the presence of isomers in the starting materials, and the results are summarized in Table 1.

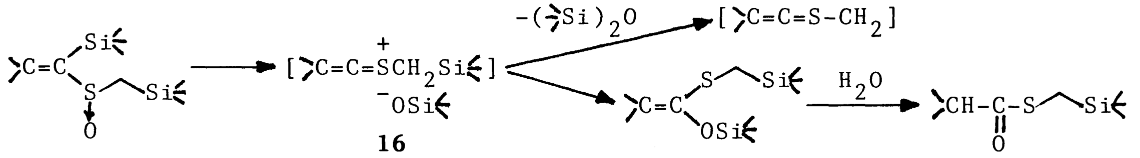
The 1,3-cycloaddition to methyl acrylate afforded a mixture of regioisomers (**9a** and **9b**). For the structure elucidation, **9a** and **9b** were desulfurized quantitatively with Raney Ni to methyl 5-phenyl-2-methylvalerate (**15a**) and its isomer (**15b**). Their ^{1}H-NMR spectra$^{7)}$ established clearly their structures.



The ratio of **9a** and **9b** was determined on the basis of the gas chromatogram (20% SE-30 on Chrom. W, 80-100 mesh) of the mixture of **15a** and **15b** obtained from the crude cycloadduct.

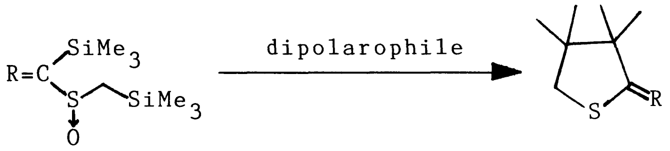
As shown in entries 4 and 5, this method is utilized for generation of alkylthioketene S-methylide leading to the corresponding cycloadducts. The thioketene S-methylide derived from adamantane derivatives underwent 1,3-cycloaddition to give only single cycloadduct as illustrated in entries 6 and 7. These reactions indicate that this method is applied for synthesis of 2-alkylidenetetrahydrothiophenes from ketones.

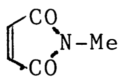
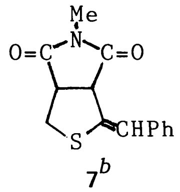
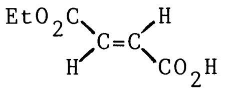
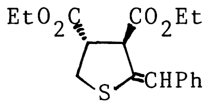
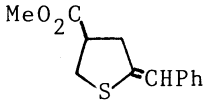
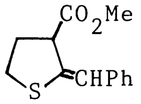
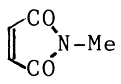
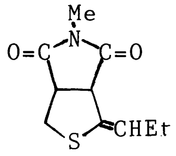
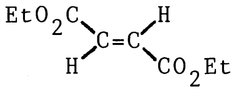
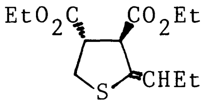
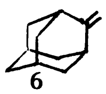
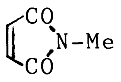
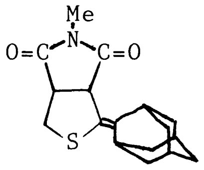
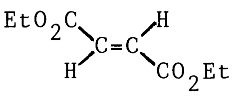
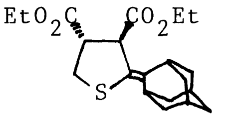
The reaction pathway is considered to involve the release of disiloxane from the same intermediate (**16**) as that of sila-Pummerer rearrangement$^{9)}$ resulting in the formation of thioester.



It seems difficult that thioketene S-methylides are synthesized by the other methods using a thioketene as a starting material, such as thermolysis$^{2,3)}$ of thiadiazolines, because the thioketene is well known$^{8)}$ to be very unstable. Therefore, the present method by employing organosilicon compounds may promise a new development in the chemistry of thiocarbonyl ylides.

Table 1. 1,3-Dipolar Cycloaddition *via* Thioketene S-Methylides



Entry	Substrate (R=)	Dipolarophile	Product (Ratio of isomers)	Yield/%[a]
1	PhCH= **4**		 **7**[b]	78
2	**4**		 **8**[b]	60
3	**4**	$CH_2=CHCO_2Me$	 **9a**[b] (2)  **9b**[b] (1)	45
4	EtCH= **5**		 **10**[b]	36
5	**5**		 **11**[b]	50
6	 **6**		 **12**	65
7	**6**		 **13**	50

a) Isolated yield.

b) A mixture of E- and Z-isomer.

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5) (E)- (**3a**) and (Z)-forms (**3b**) were assigned from the ^{1}H-NMR spectra: A signal due to a trimethylsilyl group adjacent to double bond of **3a** shifts to the lower field than that of **3b**, owing to the deshielding effect of phenyl group. ^{1}H-NMR δ (CDCl$_3$); **3a**(E-isomer), 0.06(9H, s, CH$_2$Si$\underline{(CH_3)}_3$), 0.26(9H, s, =CHSi$\underline{(CH_3)}_3$), 1.89 (2H, s, CH$_2$), 6.90(1H, s, =CH), 7.16-7.54, 7.64-7.78(5H, m, C$_6$H$_5$), **3b**(Z-isomer), 0.05(9H, s, CH$_2$Si$\underline{(CH_3)}_3$), 0.17(9H, s, =CHSi$\underline{(CH_3)}_3$), 1.93(2H, s, CH$_2$), 6.91(1H, s, =CH), 7.17-7.47(5H, m, C$_6$H$_5$).
6) **7a**; mp 126-127 °C, MS (m/e) 259 (M$^+$), ^{1}H-NMR δ (CDCl$_3$), 3.07(3H, s, N-CH$_3$), 3.11-3.65(3H, m, SCH$_2$CH<), 4.35(1H, d, J= 6.8 Hz, =CCH<), 6.95(1H, s, =CH-), 7.14-7.50, 7.70-7.79(5H, m, C$_6$H$_5$), ^{13}C-NMR δ (CDCl$_3$), 25.7(q), 34.4(t), 47.8(d), 50.1(d), 128.0(d), 128.1(d), 128.6(d), 129.7(d), 134.9(s), 135.8(s), 175.8(s), 177.7(s). Found: C, 64.54; H, 5.26; N, 5.17%. Calcd for C$_{14}$H$_{13}$NOS: C, 64.84; H, 5.05; N, 5.40%. **7b**; mp 118-120 °C, MS (m/e) 259 (M$^+$), ^{1}H-NMR δ (CDCl$_3$), 3.03(3H, s, N-CH$_3$), 3.09-3.75(3H, m SCH$_2$CH<), 4.06(1H, dd, J= 7.6, 1.3 Hz, =CCH<), 6.95(1H, d, J= 1.3 Hz, =CH-), 7.14-7.48(5H, m, C$_6$H$_5$), ^{13}C-NMR δ (CDCl$_3$), 25.6(q), 35.0(t), 46.6(d), 55.2(d), 124.7(d), 127.2(d), 128.4(d), 128.5(d), 134.3(s), 136.4(s), 175.4(s), 177.3(s). Found: C, 64.59; H, 5.08; N, 5.29%. Calcd for C$_{14}$H$_{13}$NOS: C, 64.84; H, 5.05; N, 5.40%.
7) ^{1}H-NMR (CDCl$_3$); **15a**, 1.13(3H, d, J= 7.1 Hz, CH$_2\underline{CH_3}$), 1.37-2.88(7H, m, CHCH$_2$-CH$_2$CH$_2$), 3.65(3H, s, OCH$_3$), 7.08-7.41(5H, m, C$_6$H$_5$). **15b**, 0.88(3H, t, J= 7.3 Hz, CH$_2\underline{CH_3}$), 1.37-2.75(7H, m, CH$_2$CHCH$_2$CH$_2$), 3.67(3H, s, OCH$_3$), 6.96-7.66(5H, m, C$_6$H$_5$).
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