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GENERATION AND REACTIVITY OF A SILYLATED THIOCARBONYL *S*-METHYLIDE ¹

Grzegorz Mloston,^{a*} Katarzyna Urbaniak,^a Anthony Linden,^b and Heinz
Heimgartner^{b*}

a: Department of Organic and Applied Chemistry, University of Lodz,
Narutowicza 68, PL-90-136 Lodz, Poland; E-mail: gmloston@uni.lodz.pl

b: Institute of Organic Chemistry, University of Zürich, Winterthurerstrasse 190,
CH-8057 Zürich, Switzerland; E-mail: heimgart@oci.unizh.ch

In memory of Professor *Ivar Ugi*

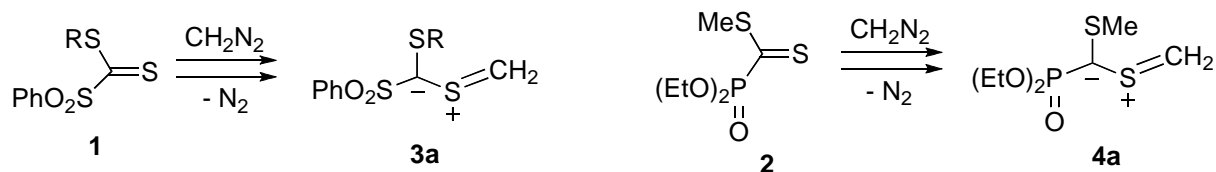
Abstract – The reaction of (trimethylsilyl)diazomethane with methyl (diethoxyphosphonyl)dithioformate (**2**), after elimination of N₂ at –35°C, yields the 4,5-bis(trimethylsilyl)-1,3-dithiolane-2-phosphonate (**8**). This product is the result of the dimerization of the intermediate silylated thiocarbonyl ylide (**4b**) to give the cyclic sulfonium ylide (**7**), followed by the elimination of a disubstituted carbene. Trapping of the intermediate (**4b**) with maleimide (**9**), maleic anhydride (**10**), thiobenzophenone (**11**), and the phosphonylated dithioformate (**2**) yields the corresponding [2+3] cycloadducts (**12**), (**13**), (**14b**), and (**18**), respectively. The crystal structures of **13** and **14b** have been established by X-Ray crystallography.

INTRODUCTION

In the recent two decades, thiocarbonyl ylides, which belong to the class of sulfur-centered 1,3-dipoles, have been studied extensively.^{2,3} They were shown to be relevant models for the mechanistic studies of [2+3] cycloaddition reactions,⁴ as well as versatile building blocks for the synthesis of sulfur heterocycles.⁵

Numerous studies showed that the behavior of thiocarbonyl ylides and their reactivity toward different dipolarophiles strongly depend on the substitution pattern. Despite the fact that several methods for the generation of reactive thiocarbonyl ylides are known, the [2+3] cycloaddition of diazo compounds with

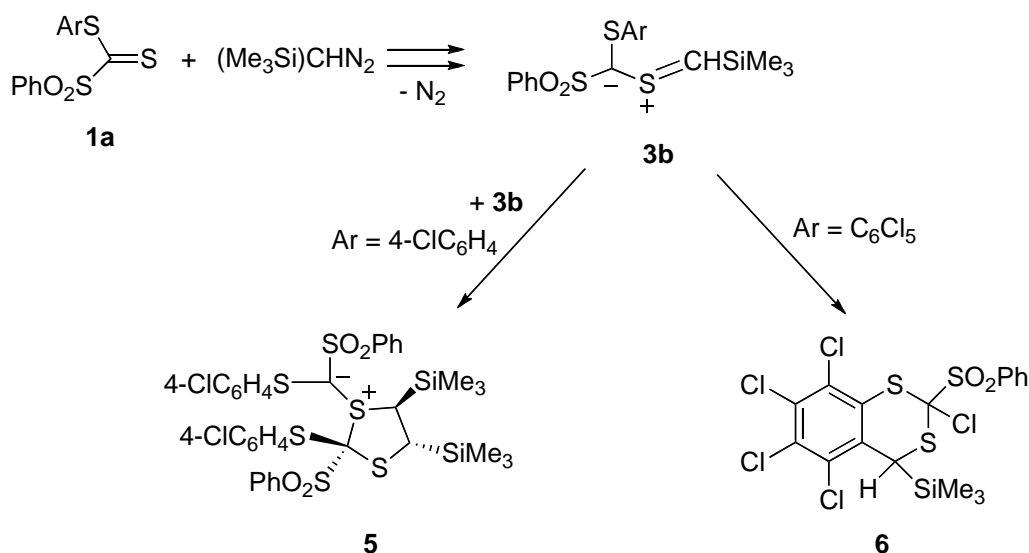
C=S dipolarophiles and subsequent N₂ elimination from the initially formed 2,5-dihydro-1,3,4-thiadiazoles is the most convenient one. Along with thioketones, dithioesters were used to generate thiocarbonyl ylides by this cycloaddition/elimination process. As demonstrated in several recent papers, C-sulfonylated and C-phosphonylated dithioformates (**1** and **2**, resp.), which are prone to react with diazomethane and its derivatives, are of special interest.



It has been shown that *S*-methanides (**3a**) and (**4a**) derived from **1** or **2** are conveniently accessible by treatment of the corresponding dithioformate with diazomethane at ca. -70°C , followed by warming to ca. -40°C in order to eliminate N₂. In the presence of suitable dipolarophiles, the reactive thiocarbonyl ylides (**3a**) and (**4a**) are trapped to yield five-membered heterocycles.^{6,7} In the absence of dipolarophiles, the *S*-methanide (**4a**) undergoes a stepwise dimerization, which finally leads to a 2,2,3,3-tetra-substituted 1,4-dithiane.⁸ In the case of *S*-methanide (**3a**), the formation of a dimer was not observed.^{6,9}

The replacement of diazomethane by (trimethylsilyl)diazomethane results in a significant change of behaviour of the corresponding thiocarbonyl ylide (**3b**) (*Scheme 1*). In the absence of dipolarophiles, it undergoes a 'cycloadditive dimerization', which produces the cyclic sulfonium ylide (**5**).¹¹ This type of dimerization has been described earlier for other 1,3-dipoles (cf. ref. ⁸), but in the series of thiocarbonyl ylides it was observed only in the case of ylide (**3b**).

Scheme 1



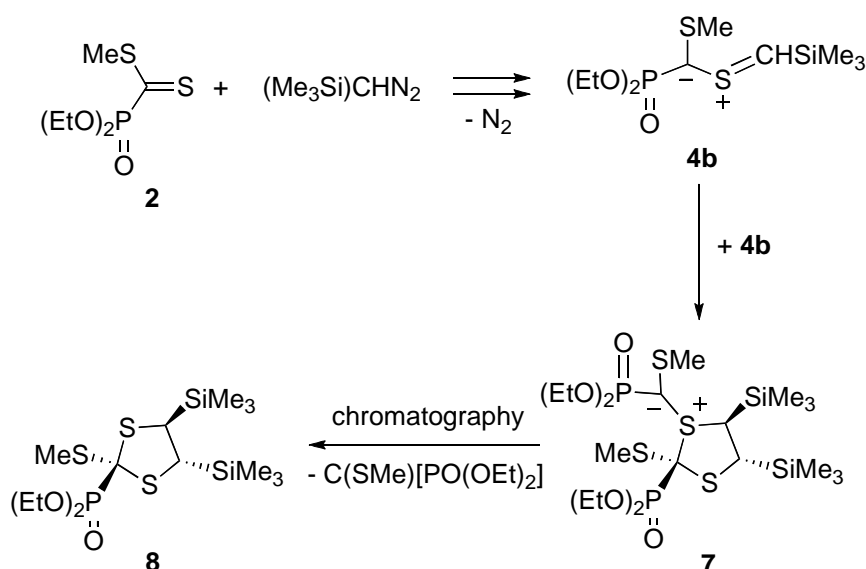
Recently, it has been reported that the pentachlorophenyl derivative of **3b** undergoes a cyclization *via* substitution of a Cl-atom to give the benzo-1,3-dithiine (**6**) (*Scheme 1*).¹⁰ It is worth mentioning that no [2+3]-cycloadditions with **3b** are known.

Due to the current interest in the exploration of phosphonylated dithioformates in [2+3] cycloaddition chemistry, we studied their reaction with (trimethylsilyl)diazomethane to get more insight into the chemistry of the corresponding thiocarbonyl *S*-(trimethylsilyl)methanide (**4b**).

RESULTS AND DISCUSSION

The addition of (trimethylsilyl)diazomethane (TMSCHN₂) to the violet solution of methyl (diethoxyphosphonyl)dithioformate (**2**) in THF at -60°C led to decoloration of the mixture without N₂ elimination. After warming to ca. -35°C, evolution of N₂ was observed. When the reaction was completed, the ¹H-NMR spectrum of the crude product showed the presence of an AB-system at 3.12 and 3.25 ppm with *J*_{AB} = 12.2 Hz for two CH groups and two singlets at 0.21 and 0.23 ppm for two Me₃Si groups. In addition to these signals, characteristic absorptions for EtO groups were located at 1.38 (triplet) and 4.0–4.5 ppm (multiplet). Two signals with comparable intensities at 2.25 and 2.37 ppm were attributed to MeS groups. We propose that these signals belong to the initially formed, unstable compound **7**.

Scheme 2



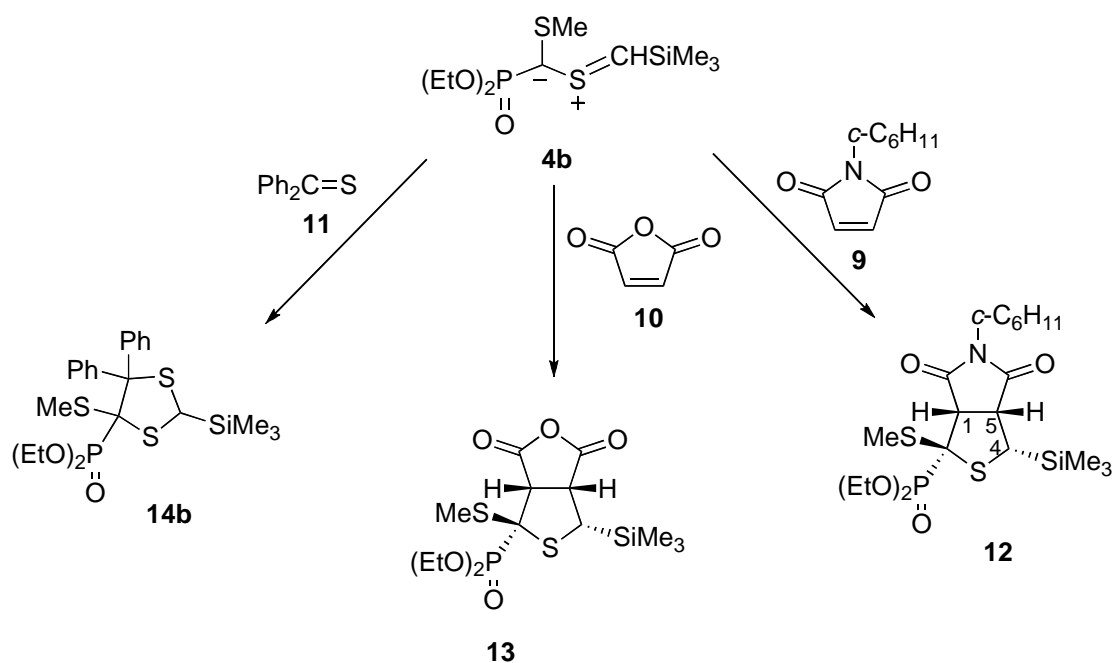
Chromatographic workup gave an oily product, which showed only one MeS signal at 2.39 ppm. Examination of the intensities of the signals of the purified product indicate that the structure of the compound corresponds with the dimer of the expected ylide after elimination of a C(SMe)[PO(OEt)₂]

fragment. In fact, the ESI-MS revealed the $[M+Na]^+$ peak at m/z 455. Based on all spectroscopic data and in comparison with the data reported for compound (**5**) (*Scheme 1*), the isolated product was identified as the 1,3-dithiolane derivative (**8**) (*Scheme 2*). This result confirms that the intermediate ylide (**4b**), in analogy to **3b**, undergoes the 'cycloadditive dimerization' to give the five-membered product (**7**). However, in contrast to the sulfonyl analogue (**5**), it eliminates easily a carbene fragment to give the final product (**8**). The further reaction of the eliminated fragment is not known.

In order to trap the intermediate (**4b**), the decomposition of the initially formed cycloadduct of **2** and $\text{Me}_3\text{SiCHN}_2$ was carried out at -35°C in the presence of selected $\text{C}=\text{S}$ and $\text{C}=\text{C}$ dipolarophiles. In the cases of **9**, **10** and **11**, the formation of the [2+3] cycloadduct competed efficiently with the dimerization process, and **8** was formed as a minor product only (*Scheme 3*).

The most reactive dipolarophile in this series is *N*-(cyclohexyl)maleimide (**9**), as in this case less than 5% of **8**, *i.e.*, the product of the dimerization of the intermediate (**4b**), was detected in the crude mixture. On the other hand, in the trapping reaction with maleic anhydride (**10**), up to 30% of **8** was formed. A similar ratio of cycloadduct (**14b**) and **8** was obtained in the experiment with thiobenzophenone (**11**).

Scheme 3



The isolated [2+3] cycloadducts, which were formed as a single isomer in each case, were characterized on the basis of their spectroscopic data. In the $^1\text{H-NMR}$ spectrum of **12**, the signal of the MeS group appears at 2.29 ppm and the Me_3Si group absorbs at 0.25 ppm. The high-field shifted signal, which appears as *dd* at 3.01 ppm, is attributed to $\text{H-C}(4)$ with $^3J_{\text{H,H}} = 6.2$ Hz and $^4J_{\text{H,P}} = 1.4$ Hz. The signals for

H–C(1) and H–C(5) are located at 3.20 (*dd*, $^3J_{\text{H,H}} = 7.1$, $^3J_{\text{H,P}} = 1.0$ Hz) and 3.55 ppm (*dd*, $^3J_{\text{H,H}} = 6.9$ and 6.3 Hz). In analogy to similar structures obtained in the reaction of thiocarbonyl ylide (**4a**) and *N*-phenylmaleimide,⁷ we first proposed that the phosphonate group of **12** occupies the *exo*-position. The relative configuration at C(4) could not be assigned accurately, but the similarity of the coupling constants between H–C(1)/H–C(5) and H–C(4)/H–C(5) suggests that Me₃Si is *endo* oriented. Based on the similarity of the ¹H-NMR spectra of **12** and **13**, the analogous structure has been attributed to the latter.

Finally, the structure of **13** was determined by X-Ray crystallography (*Figure 1*). The compound in the crystal is enantiomerically pure and the absolute configuration of the molecule has been determined independently by the diffraction experiment. *Figure 1* shows the true absolute configuration. One ethyl group is disordered. The S-containing five-membered ring has a half-chair conformation twisted on S(1)–C(5), while the other five-membered ring has an envelope conformation with C(3) as the envelope flap. Unexpectedly, the bulky P(O)(OEt)₂ and Me₃Si groups are both *endo* oriented.

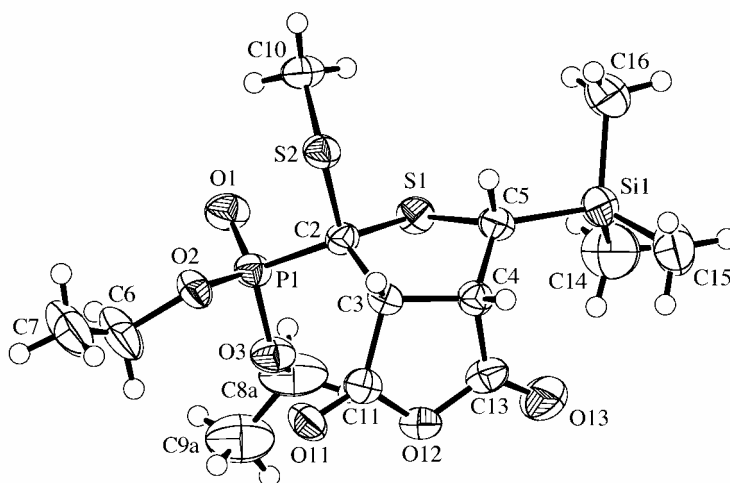
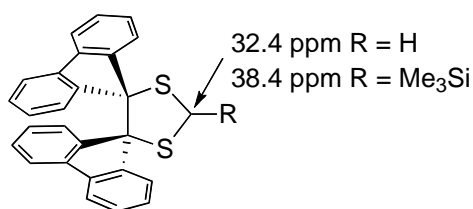


Figure 1. ORTEP plot¹⁴ of the molecular structure of one of the two disordered conformations of **13** (50% probability ellipsoids; arbitrary numbering of the atoms).

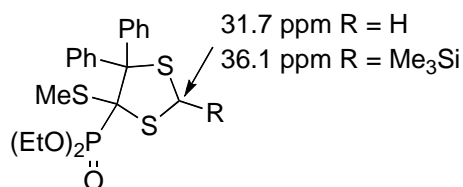
Because of the similarity of the ¹H-NMR spectra mentioned above, we propose that the P(O)(OEt)₂ and Me₃Si groups of **12** are also *endo* configured and that the MeS group is *exo* oriented. This result is in accordance with an *endo* transition state of the 1,3-dipolar cycloaddition of **4b** with (*E,E*)-configured P(O)(OEt)₂ and Me₃Si groups, but is in contrast to the earlier described structure of the cycloadduct of **4a** (R = Me) with *N*-phenylmaleimide, in which the phosphonate group occupies the *exo* and the MeS group the *endo* position.⁷

The trapping of non-symmetrical thiocarbonyl ylides with thiobenzophenone **11** leads in many cases to

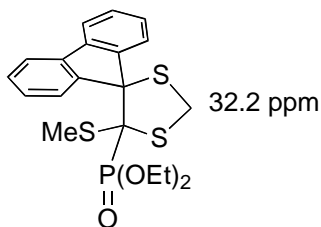
two regioisomeric 1,3-dithiolanes.^{2,3,5b} However, in the case of **4a**, the [2+3] cycloaddition occurs regioselectively to give the sterically more crowded '2-CH₂' isomer.⁷ In the present study, the reaction with **4b** afforded only one 1,3-dithiolane, *i.e.*, the formation of the heterocycle occurs regio- and stereoselectively. The following analysis indicates that the product is a 2-(trimethylsilyl)-1,3-dithiolane (**14b**): the replacement of a H-atom at C(2) of the 1,3-dithiolane ring of **15a**¹⁵ by Me₃Si (*i.e.* **15b**)¹³ results in a low-field shift of the ¹³C-NMR signal of 6 ppm. Furthermore, the comparison of the spectrum of **15a** with those of **16** shows that there is no significant difference in the chemical shifts of ¹³CH₂ in these two 1,3-dithiolanes. On the other hand, the difference in the chemical shifts of ¹³CH₂ in the two regioisomers **16** and **17** is significant (19 ppm) and corresponds with the characteristic values of these two series.¹⁶



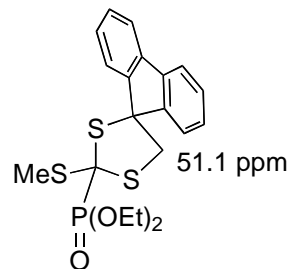
15a R = H (ref. 15)
b R = Me₃Si (ref. 13)



14a R = H (ref. 15)
b R = Me₃Si



16 (ref. 7)



17 (ref. 7)

Because the spectroscopic data do not give convincing arguments for the elucidation of the relative configuration of **14b**, the structure was determined by X-Ray crystallography (*Figure 2*). The compound in the crystal is racemic. The five-membered ring has an envelope conformation with S(1) as the envelope flap. The Me₃Si group is in a pseudo-equatorial position and *cis* to the phosphonate group.

The dithioester (**2**) traps the thiocarbonyl ylide (**4b**) more efficiently than thiobenzophenone (**11**), and the product (**8**) of the dimerization was formed in less than 10% yield. The reaction affords a single [2+3]-cycloadduct (**18**), which was isolated as a yellowish oil in 65% yield. Based on the ¹H- and ¹³C-NMR data, and using an analogous argumentation to that in the case of **14b**, the structure of this product can be formulated as depicted in *Scheme 4*. The *cis*-configuration of the substituents at C(4) and C(5) is supported by the appearance of only one signal for the MeS groups as well as for the MeCH₂O groups in the ¹H- and the ¹³C-NMR spectra. Although the relative configuration at C(2) is unknown, in

analogy to the *cis*-oriented P(O)(OEt)₂ and Me₃Si groups in **13** and **14b**, it seems likely that the Me₃Si group in **18** is in a *cis*-relationship with the phosphonyl groups at C(4) and C(5).

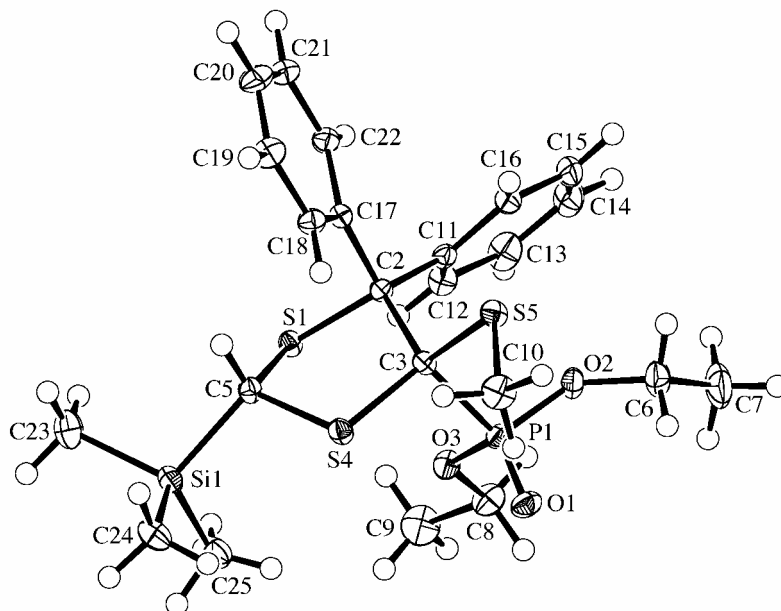
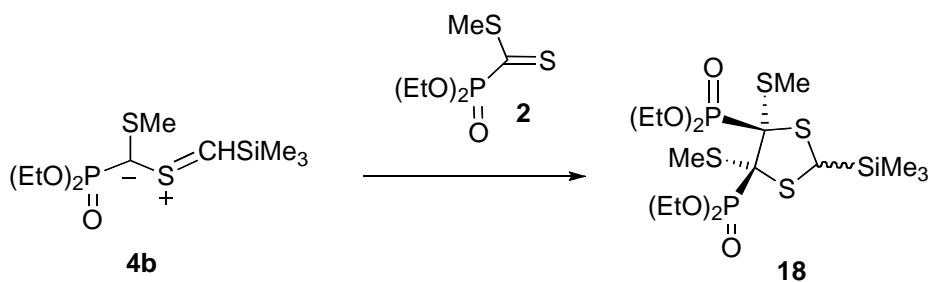


Figure 2. ORTEP plot¹⁴ of the molecular structure of **14b** (50% probability ellipsoids; arbitrary numbering of the atoms).

Scheme 4



In addition to the experiments with **9** and **10**, two other C=C dipolarophiles, namely tetracyanoethylene (TCNE) and fumaronitrile were tested as trapping reagents for **4b**. The formation of the [2+3] cycloadduct with TCNE occurs efficiently, and no traces of **8** could be detected in the crude mixture (¹H-NMR). The absorption of the MeS group of the expected cycloadduct appears at 2.45 ppm, and CH absorbs at 3.48 ppm. However, all attempts to isolate the product were in vain. In contrast to TCNE, the less reactive fumaronitrile¹⁷ did not capture the ylide (**4b**) and, therefore, the only product of the reaction was **8**.

In summary, the present study shows that the silylated thiocarbonyl *S*-methanide (**4b**), in the absence of

dipolarophiles undergoes a dimerization reaction analogous to the corresponding sulfonyl-substituted intermediate **3b**. Neither the 1,3-electrocyclization to give the thiirane nor the head-to-head dimerization to the 1,4-dithiane, which are typical for cycloaliphatic and aromatic thiocarbonyl ylides, respectively, are observed. In comparison with thiobenzophenone *S*-methanide, the dimerization process can be suppressed only with the most reactive dipolarophiles. The application of (trimethylsilyl)diazomethane in reactions with thiocarbonyl compounds is more attractive than that of diazomethane with respect to the safer handling, but the presence of the Me₃Si group reduces the reactivity of the intermediate dipole in terms of [2+3]-cycloaddition processes.

EXPERIMENTAL

General remarks. Melting points were determined in a capillary using a MEL-TEMP II apparatus (*Aldrich*) and are uncorrected. IR spectra were recorded with a FT-IR NEXUS instrument as KBr pellets or as films, and the position of absorption bands are given in cm⁻¹. ¹H-NMR, ¹³C-NMR, and ³¹P-NMR spectra were recorded on a BRUKER-AC-300 (¹H at 300 MHz, ¹³C at 75 MHz, and ³¹P at 121 MHz) instrument in CDCl₃ solutions using TMS ($\delta = 0$ ppm) as an internal standard; chemical shifts (δ) in ppm. MS spectra were recorded on a LKB-2091 spectrometer using chemical ionization (CI-MS; with NH₃) or electrospray (ESI) method; *m/z* (rel. %). Elemental analyses were performed in the Analytical Laboratory of the University of Zürich or in the Laboratory of the Polish Academy of Sciences (CBMiM) in Lodz.

Starting materials. Methyl (diethoxy)phosphonyldithioformate (**2**) was prepared from diethyl phosphite and carbon disulfide following a known protocol.¹⁹ Thiobenzophenone (**11**)²⁰ was prepared by heating commercial benzophenone with *Lawesson's* reagent in boiling toluene and purified by column chromatography over silica gel. *N*-(Cyclohexyl)maleimide (**9**) was synthesized following a literature protocol.²¹ Maleic anhydride (**10**) was purchased from *Sigma-Aldrich* and used without further purification. (Trimethylsilyl)diazomethane was used as a commercially available 2 M solution in Et₂O (*Sigma-Aldrich*). THF was distilled from sodium benzophenone ketyl.

Reaction of methyl (diethoxy)phosphonyldithioformate (2) with (trimethylsilyl)diazomethane. A solution of **2** (228 mg, 1 mmol) in dry THF (1 mL) was placed in a flask equipped with a magnetic stirring bar. The violet solution was cooled in an acetone/dry ice bath to -65°C. While stirring, 0.5 mL of a commercial 2M solution of (trimethylsilyl)diazomethane in Et₂O was added drop-wise until the color of the starting material disappeared completely (step-wise decolorization of the mixture was observed after each drop). The mixture was stirred and allowed to warm to room temperature. Elimination of N₂ was

observed at *ca.* -35°C . The solvent was evaporated and the oily residue was purified on PLC plates coated with SiO_2 using a 3:2 mixture of hexane and AcOEt as the eluent.

Diethyl [(4RS, 5RS)-2-methylsulfanyl-4,5-bis(trimethylsilyl)-1,3-dithiolan-2-yl]phosphonate (8). Yield: 180 mg (42%). Yellowish oil after PLC. IR (neat): 2979*m*, 2962*m*, 2917*m*, 2905*m*, 1441*w*, 1390*w*, 1252*vs* (P=O), 1163*w*, 1055*vs* and 1026*vs* (P–O–C), 970*s*, 857*vs*, 842*vs*, 746*m*. $^1\text{H-NMR}$: 0.21, 0.23 (2*s*, 18H, 2 Me_3Si); 1.37 (*t*, $^3J_{\text{H,H}} = 7.0$ Hz, 6H, 2 MeCH_2O); 2.39 (*d*, $^4J_{\text{H,P}} = 0.5$ Hz, 3H, MeS); 3.16, 3.26 (2*d*, $^3J_{\text{H,H}} = 12.2$ Hz, 2H, 2 CHSi); 4.25–4.33 (*m*, 4H, 2 MeCH_2O). $^{13}\text{C-NMR}$: -0.5 , -0.3 (2 Me_3Si); 16.7 (*d*, $^3J_{\text{C,P}} = 5.5$ Hz, 2 MeCH_2O); 16.9 (MeS); 46.4 (CHSi); 50.0 (*d*, $^3J_{\text{C,P}} = 3.5$ Hz, CHSi); 64.9 (*d*, $^2J_{\text{C,P}} = 6.6$ Hz, 2 MeCH_2); 68.3 (*d*, $^1J_{\text{C,P}} = 163.7$ Hz, C_q). $^{31}\text{P-NMR}$: 17.68. ESI-MS: 455 (100, $[\text{M}+\text{Na}]^+$). Anal. Calcd for $\text{C}_{14}\text{H}_{33}\text{O}_3\text{PS}_3\text{Si}_2$: C, 38.86; H, 7.69; S, 22.23. Found: C, 39.26; H, 7.75; S, 21.90.

Reaction of 4b with thiobenzophenone (11), maleic anhydride (10), *N*-(cyclohexyl)maleimide (9), and 2. To a solution of **2** (228 mg, 1 mmol) in dry THF (1 mL) was added 0.5 mL of a commercial 2M solution of (trimethylsilyl)diazomethane in Et_2O as described in the preceding section. After complete decolorization of the mixture, 1 mmol of the corresponding dipolarophile was added and the mixture was stirred and allowed to warm to room temperature. Elimination of N_2 was observed at -35°C . The solvent was evaporated and the crude mixture was purified either by crystallization or chromatographically on PLC plates coated with silica.

Diethyl (7-cyclohexyl-2-methylsulfanyl-6,8-dioxo-4-(trimethylsilyl)-3-thia-7-azabicyclo[3.3.0]octan-2-yl)phosphonate (12). Yield: 330 mg (67%). Yellowish oil after PLC (hexane/AcOEt 3.5:1.5), which was crystallized from hexane in the refrigerator to give colorless crystals; mp 119–121 $^{\circ}\text{C}$. IR (KBr): 2980*m*, 2926*m*, 2855*m*, 1701*vs* (C=O), 1453*w*, 1398*m*, 1379*s*, 1248*s* (P=O), 1201*m*, 1055*s* and 1026*s* (P–O–C), 971*m*, 846*m*, 570*m*. $^1\text{H-NMR}$: 0.25 (*s*, 9H, Me_3Si); 1.32–1.78 (*m*, 10H, 5 CH_2 cyclohex.); 1.33, 1.39 (2*t*, $^3J_{\text{H,H}} = 7.1$ Hz, 6H, 2 MeCH_2O); 2.29 (*s*, 3H, MeS); 3.01 (*dd*, $^3J_{\text{H,H}} = 6.2$ Hz, $^4J_{\text{H,P}} = 1.4$ Hz, H–C(4)); 3.20 (*dd*, $^3J_{\text{H,H}} = 7.1$ Hz, $^3J_{\text{H,P}} = 1.0$ Hz, H–C(1)); 3.55 (*dd*, $^3J_{\text{H,H}} = 6.9$ and 6.3 Hz, H–C(5)); 3.85–4.05 (*m*, CHN); 4.21–4.32 (*m*, 4H, 2 MeCH_2O). $^{13}\text{C-NMR}$: -0.7 (Me_3Si); 16.2 (MeS); 16.7 (*d*, $^3J_{\text{C,P}} = 5.7$ Hz, 2 MeCH_2O); 25.2, 26.0, 26.1, 28.8, 29.1 (5 CH_2 cyclohex.); 36.2 (*d*, $^3J_{\text{C,P}} = 4.1$ Hz, CH); 52.7 (CH); 53.2 (*d*, $^2J_{\text{C,P}} = 10.6$ Hz, C(1)); 57.7 (CHN); 64.4 (*d*, $^2J_{\text{C,P}} = 7.1$ Hz, 2 MeCH_2O); 69.3 (*d*, $^1J_{\text{C,P}} = 151$ Hz, C_q); 172.3, 176.2 (2 C=O). $^{31}\text{P-NMR}$: 17.91. CI-MS (NH_3): 496 (17), 495 (27), 494 (100, $[\text{M}+1]^+$), 447 (12), 446 (34). Anal. Calcd for $\text{C}_{20}\text{H}_{36}\text{NO}_5\text{PS}_2\text{Si}$: C, 48.66; H, 7.35; N, 2.84; S, 12.99. Found: C, 48.66; H, 7.27; N, 2.70; S, 12.76.

Diethyl (6-methylsulfanyl-2,4-dioxo-8-(trimethylsilyl)-3-oxa-7-thiabicyclo[3.3.0]octan-6-yl)phosphonate (13). Yield: 100 mg (25%). Colorless crystals after crystallization from Et₂O; mp 152–154°C. IR (KBr): 2988w, 2950w, 2919w, 1853w, 1785s (C=O), 1636w, 1251s (P=O), 1056s and 1032s (P–O–C), 1012s, 977m, 847m, 561m. ¹H-NMR: 0.28 (s, 9H, Me₃Si); 1.34, 1.40 (2t, ³J_{H,H} = 7.1 Hz, 6H, 2 MeCH₂O); 2.36 (s, 3H, MeS); 3.05 (d, ³J_{H,H} = 5.5 Hz, ⁴J_{H,P} = 1.5 Hz, H–C(8)); 3.42 (d, ³J_{H,H} = 7.5 Hz, ³J_{H,P} = 2.5 Hz, H–C(5)); 4.00 (dd, ³J_{H,H} = 7.5 and 5.5 Hz, H–C(1)); 4.21–4.32 (m, 4H, 2 MeCH₂O). ¹³C-NMR: –1.0 (Me₃Si); 16.5 (d, ³J_{C,P} = 6.0 Hz, 2 MeCH₂O); 16.7 (MeS); 36.2 (CH); 56.2 (d, ²J_{C,P} = 10.3 Hz, C(5)); 58.2 (CH); 64.8 (d, ²J_{C,P} = 7.4 Hz, MeCH₂O); 65.2 (d, ²J_{C,P} = 7.3 Hz, MeCH₂O); 68.7 (d, ¹J_{C,P} = 162.0 Hz, C_q); 167.1, 171.2 (2 C=O). ³¹P-NMR: 15.13. C-IMS (NH₃): 430 (19), 415 (16), 414 (21), 413 (100, [M+1⁺]), 366 (8), 365 (18). Anal. Calcd for C₁₄H₂₅O₆PS₂Si: C, 40.76; H, 6.11; S, 15.55. Found: C, 40.55; H, 5.95; S, 15.29.

Suitable crystals for the X-Ray crystal structure determination were obtained by slow evaporation of the solvent (Et₂O/cyclohexane).

Diethyl 4-methylsulfanyl-5,5-diphenyl-2-(trimethylsilyl)-1,3-dithiolan-4-yl)phosphonate (14b). Yield: 400 mg (78%). Yellowish oil after PLC (hexane/AcOEt 3.5:1.5), which was crystallized from hexane in the refrigerator to give colorless crystals; mp 122–124°C. IR (KBr): 2984m, 2975m, 2904m, 1489m, 1442m, 1249s, 1236vs (P=O), 1063vs and 1034vs (P–O–C), 974m, 859s, 844s, 699m, 544s. ¹H-NMR: 0.28 (s, 9, Me₃Si); 1.01, 1.18 (2t, ³J_{H,H} = 7.1 Hz, 6H, 2 MeCH₂O); 2.50 (s, 3H, MeS); 3.65 (s, CHSi); 3.70–4.05 (m, 4H, 2 MeCH₂O); 7.18–7.27 (m, 6 arom. H); 7.67–7.76 (m, 4 arom. H). ¹³C-NMR: –1.6 (Me₃Si); 16.3 (d, ³J_{C,P} = 5.8 Hz, MeCH₂O); 16.5 (d, ³J_{C,P} = 5.6 Hz, MeCH₂O); 19.1 (MeS); 34.5 (CHSi); 63.2 (d, ²J_{C,P} = 7.8 Hz, MeCH₂O); 64.3 (MeCH₂O); 126.6, 126.7, 127.0, 127.8, 130.6, 131.5 (10 arom. CH); 141.3 (br., arom. C_q); 143.7 (arom. C_q). C(4) and C(5) could not be detected. ³¹P-NMR: 16.65. ESI-MS: 535 (100, [M+Na]⁺). Anal. Calcd for C₂₃H₃₃O₃PS₃Si: C, 53.88; H, 6.49; S, 18.76. Found: C, 53.79; H, 6.52; S, 18.54.

Suitable crystals for the X-Ray crystal structure determination were obtained by slow evaporation of the solvent (hexane).

Diethyl [5-(diethoxyphosphonyl)-4,5-bis(methylsulfanyl)-2-trimethylsilyl-1,3-dithiolan-4-yl]phosphonate (18). Yield: 350 mg (65%). Yellowish oil after PLC (hexane/AcOEt 2:3). IR (neat): 2980m, 2927m, 2916m, 1442m, 1389m, 1251vs (P=O), 1163m, 1097m, 1030vs and 1028vs (P–O–C), 970s, 859m, 848m, 794w, 766w. ¹H-NMR (700 MHz): 0.29 (s, 9H, Me₃Si); 1.39, 1.40 (2t, ³J_{HH} = 7.7 Hz, 12H, 4 MeCH₂O); 2.40 (s, 6H, 2 MeS); 3.86 (s, CH); 4.20–4.47 (m, 8H, 4 MeCH₂O). ¹³C-NMR (176 MHz): –1.7 (Me₃Si); 16.4 (dd, ³J_{C,P} = 3.0 Hz and J_{C,P} = 2.8 Hz, 2 MeCH₂O); 16.5 (dd, ³J_{C,P} = 2.8 Hz and J_{C,P} = 2.8 Hz, 2

MeCH₂O); 18.4 (*br*, 2 MeS); 35.6 (C(2)); 63.9 (*dd*, ²J_{C,P} = 3.7 Hz and J_{C,P} = 3.7 Hz, 2 MeCH₂O); 65.2 (*dd*, ²J_{C,P} = 3.7 Hz and J_{C,P} = 3.7 Hz, 2 MeCH₂O); 75.7 (*dd*, ¹J_{C,P} = 159.3 Hz and ²J_{C,P} = 5.4 Hz, C(4), C(5)). ³¹P-NMR: 15.69. CI-MS (NH₃): 543 (9, [M+1]⁺), 449 (22), 393 (100), 377 (8), 347 (14), 336 (10), 316 (21). HRMS Calcd for C₁₅H₃₃O₆P₂S₄Si [M-CH₃]: 527.04046. Found: 527.04060.

*X-Ray Crystal-Structure Determination of 13 and 14b (Figure 1).*²² All measurements were made on a *Nonius KappaCCD diffractometer*²³ using graphite-monochromated MoK_α radiation (λ = 0.71073 Å) and an Oxford Cryosystems Cryostream 700 cooler. Data reduction was performed with *HKL Denzo and Scalepack*.²⁴ The intensities were corrected for *Lorentz* and polarization effects, and absorption corrections based on the multi-scan method²⁵ were applied. Data collection and refinement parameters are given below, and views of the molecules are shown in *Figure 1*. Each structure was solved by direct methods using SIR92,²⁶ which revealed the positions of all non-hydrogen atoms. In the case of **13**, one ethyl group is disordered over two conformations. Two sets of overlapping positions were defined for the atoms of the disordered ethyl group and the site occupation factor of the major conformation of this group refined to 0.66(2). Similarity restraints were applied to the chemically equivalent bond lengths and angles involving all disordered C-atoms, while neighboring atoms within and between each conformation of the disordered ethyl groups were restrained to have similar atomic displacement parameters. The non-hydrogen atoms were refined anisotropically. All of the H-atoms were placed in geometrically calculated positions and refined using a riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to 1.2U_{eq} of its parent C-atom (1.5U_{eq} for the Me groups). The refinement of the structure was carried out on F² using full-matrix least-squares procedures, which minimized the function Σw(F_o² - F_c²)². Corrections for secondary extinction were applied. In the case of **13**, one reflection, whose intensity was considered to be an extreme outlier, was omitted from the final refinement, while the refinement of the absolute structure parameter²⁷ yielded a value of 0.01(11), which confidently confirms that the refined model corresponds with the true enantiomorph. Neutral atom scattering factors for non-H-atoms were taken from ref.²⁸, and the scattering factors for H-atoms were taken from ref.²⁹. Anomalous dispersion effects were included in F_c³⁰; the values for *f* and *f*' were those of ref.³¹. The values of the mass attenuation coefficients are those of ref.³². All calculations were performed using the SHELXL97 program.³³ Crystal data for **13**: Crystallized from Et₂O/cyclohexane, C₁₄H₂₅O₆PS₂Si, M = 412.52, colorless, prism, crystal dimensions 0.12 × 0.17 × 0.22 mm, orthorhombic, space group P2₁2₁2₁, Z = 4, reflections for cell determination 60099, a = 7.1585(2) Å, b = 10.3374(2) Å, c = 28.690(1) Å, V = 2123.0(1) Å³, D_X = 1.291 g·cm⁻³, μ(MoK_α) = 0.406 mm⁻¹, T = 253(1) K, φ and ω scans, 2θ_{max} = 50°, transmission factors (min; max) 0.842; 0.952, total reflections measured 18656, symmetry independent reflections 3582, reflections with I > 2σ(I) 3036, reflections used in refinement 3581, parameters refined

244, restraints 38, R (on F ; $I > 2\sigma(I)$ reflections) = 0.0436, $wR(F^2)$ (all reflections) = 0.1059 ($w = (\sigma^2(F_o^2) + (0.0507P)^2 + 0.9204P)^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$), goodness of fit 1.115, secondary extinction coefficient 0.006(1), final Δ_{\max}/σ 0.002, $\Delta\rho$ (max; min) = 0.31; $-0.23 \text{ e } \text{\AA}^{-3}$. Crystal data for **14b**: Crystallized from hexane, $\text{C}_{23}\text{H}_{33}\text{O}_3\text{PS}_3\text{Si}$, $M = 512.74$, colorless, tablet, crystal dimensions $0.10 \times 0.22 \times 0.28 \text{ mm}$, monoclinic, space group $P2_1/c$, $Z = 4$, reflections for cell determination 55719, $a = 13.7231(2) \text{ \AA}$, $b = 10.3682(2) \text{ \AA}$, $c = 18.9766(4) \text{ \AA}$, $\beta = 105.212(1)$, $V = 2605.46(8) \text{ \AA}^3$, $D_x = 1.307 \text{ g}\cdot\text{cm}^{-3}$, $\mu(\text{MoK}\alpha) = 0.414 \text{ mm}^{-1}$, $T = 160(1) \text{ K}$, ϕ and ω scans, $2\theta_{\max} = 60^\circ$, transmission factors (min; max) 0.822; 0.962, total reflections measured 68443, symmetry independent reflections 7591, reflections with $I > 2\sigma(I)$ 5996, reflections used in refinement 7591, parameters refined 287, R (on F ; $I > 2\sigma(I)$ reflections) = 0.0386, $wR(F^2)$ (all reflections) = 0.0995 ($w = (\sigma^2(F_o^2) + (0.0497P)^2 + 1.237P)^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$), goodness of fit 1.037, secondary extinction coefficient 0.0114(8), final Δ_{\max}/σ 0.002, $\Delta\rho$ (max; min) = 0.55; $-0.34 \text{ e } \text{\AA}^{-3}$.

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