[2+3]-Cycloadditions of Phosphonodithioformate *S*-Methanides with C=S, N=N, and C=C Dipolarophiles

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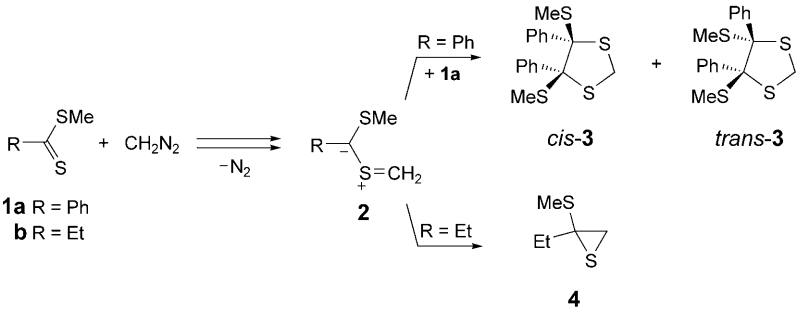
The reaction of the methyl (dialkoxyphosphinyl)-dithioformates (=methyl dialkoxyphosphinecarbodithioate 1-oxides) **10** with CH_2N_2 at $-65°$ in THF yielded cycloadducts which eliminated N_2 between -40 and $-35°$ to give the corresponding phosphonodithioformate *S*-methanides (=methylenesulfonium (dialkoxyoxidophosphino)(methylthio)methylides) **11** (*Scheme 3*). These reactive 1,3-dipoles were intercepted by aromatic thioketones to yield 1,3-dithiolanes. Whereas the reaction with thiobenzophenone (**12b**) led to the sterically more congested isomers **15** regioselectively, a mixture of both regioisomers was obtained with 9*H*-fluorene-9-thione (**12a**). Trapping of **11** with phosphono- and sulfonodithioformates led exclusively to the sterically less hindered 1,3-dithiolanes **16** and **18**, respectively (*Scheme 4*). In addition, reactive C=C dipolarophiles such as ethenetetracarbonitrile, maleic anhydride, and *N*-phenylmaleimide as well as the N=N dipolarophile dimethyl diazenedicarboxylate were shown to be efficient interceptors of **11** (*Scheme 5*).

1. Introduction. – Sulfoniomethanides (='thiocarbonyl methylides'='thiocarbonyl *S*-methanides') are versatile S-containing 1,3-dipoles, which have been extensively studied in terms of the reaction mechanism of their [2+3] cycloadditions (concerted *vs.* stepwise reaction) and their use in the synthesis of diverse S-heterocycles [1–3]. Among the few methods of their generation, the reaction of CH_2N_2 with C=S dipolarophiles and subsequent elimination of N_2 is applied most frequently. The reactive 1,3-dipoles formed *in situ* can be trapped by different electron-deficient dipolarophiles, but aromatic thioketones proved to be the most reactive ones (superdipolarophiles [4]). Less reactive C=S dipolarophiles are nonenolizable aliphatic thioketones, 1,3-thiazole-5(4*H*)-thiones, dithioesters, and *O*-alkyl thioesters.

In contrast to thioketones, dithioesters have been less often used as precursors of sulfoniomethanides. In a classical work, the reaction of methyl 1-dithionaphthoate (=methyl naphthalene-1-carbodithioate) with CH_2N_2 at room temperature yielded, in a regioselective manner, the sterically more hindered 1,3-dithiolane [5]. Similarly, treatment of methyl dithiobenzoate (=methyl benzenecarbodithioate; **1a**) with CH_2N_2 at $-5°$ led to a mixture of *cis*- and *trans*-1,3-dithiolanes **3** [6] (*Scheme 1*), while methyl propanedithioate (**1b**) gave the corresponding thiiranes of type **4** [6]. In both reactions, thiocarbonyl *S*-methanides **2** are proposed as the reactive intermediates.

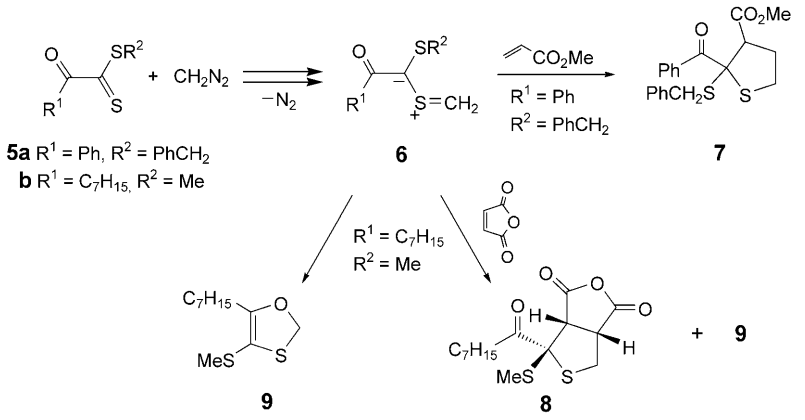
[1]) Part of the Ph.D. thesis of *K. U.*, University Łódź, 2004.

Scheme 1



The reaction of CH_2N_2 with α-oxo dithioesters of type **5** has been performed at $-80°$, and the evolution of N_2 leading to the corresponding sulfoniomethanide **6** occurred already at $-60°$. The reactivity of the latter compound depends on the type of R^1. Whereas, in the case of **5a** (R^1 = Ph, R^2 = $PhCH_2$), the interception of **6** with methyl prop-2-enoate gave the [2+3] cycloadduct **7** exclusively, the reaction of **6** derived from **5b** (R^1 = C_7H_{15}, R^2 = Me) with maleic anhydride (= furan-2,5-dione) led to a mixture of the [2+3] cycloadduct **8** and the 1,3-oxathiole **9** [7] (*Scheme 2*). The latter is the product of a 1,5-dipolar electrocyclization of **6**. The generation of **6** (R^1 = C_7H_{15}, R^2 = Me) in the absence of trapping agents yielded **9** as the sole product. This reaction corresponds with the formation of analogous products from thioketones and α-diazo carbonyl derivatives [8].

Scheme 2



In the case of *O*-alkyl thioesters, the analogous reaction with CH_2N_2 in Et_2O resulted in the formation of 5-alkoxy-4,5-dihydro-1,2,3-thiadiazoles [6], which cannot be used for the generation of sulfoniomethanides. Instead, they eliminate easily alcohol to yield 1,2,3-thiadiazoles [9][10].

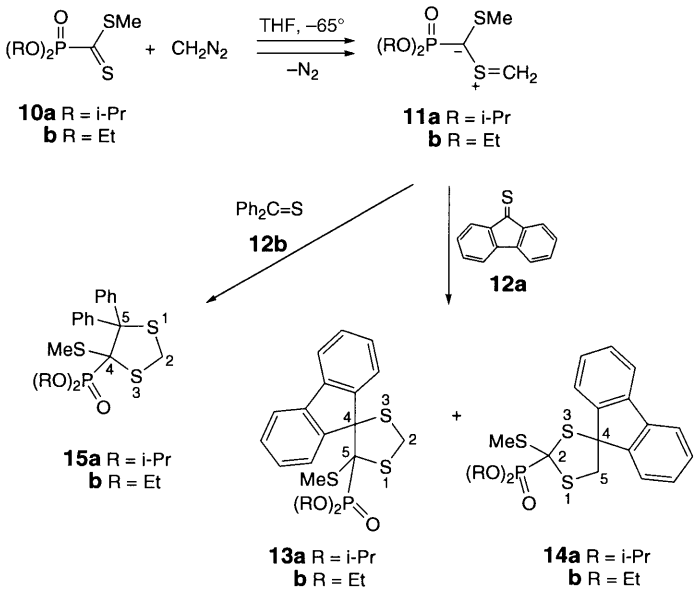
In a previous paper, we have described the behavior of phosphinylated sulfoniomethanides, which easily undergo a dimerization process to give zwitterionic dimers. The latter could either cyclize or be trapped by nucleophiles [11] (see also [12]). In the pres-

ent paper, reactions of phosphinylated sulfoniomethanides with C=S, C=C, and N=N dipolarophiles are described.

2. Results and Discussion. – In all experiments described below, the reaction of CH_2N_2 with dithioesters **10a** and **10b** was carried out in THF at $-65°$, and an equimolar amount of the respective dipolarophile was added at *ca.* $-60°$. The evolution of N_2, indicating the formation of the sulfonium methylide of type **11**, was observed between -40 and $-35°$. The crude mixtures were analyzed by ^{1}H-NMR spectroscopy.

The first experiment was carried out with the most efficient thiocarbonyl compound for [2+3] cycloadditions with sulfoniomethanides, *i.e.*, 9*H*-fluorene-9-thione (**12a**) [13] (*Scheme 3*). The reactions of the latter with the sulfoniomethanide derived from thiobenzophenone (=diphenylmethanethione; **12b**) yielded regioselectively the 4,4,5,5-tetrasubstituted 1,3-dithiolane ('2-CH_2-1,3-dithiolane') [14], whereas the analysis of the crude mixture of the reaction of sulfoniomethanide **11a** with **12a** showed that two regioisomeric 1,3-dithiolanes were formed in comparable amounts, along with some minor by-products[2]). Chromatographic separation led to the pure isomers **13a** and **14a** in *ca.* 32% yield each (*Scheme 3*). The product **13a** of the more polar fraction was identical with the cycloadduct obtained earlier from the reverse reaction, *i.e.*, from **10a** and the sulfoniomethanide derived from 9*H*-fluorene-9-thione [15]. In agreement with the expected value, the CH_2(2) signal in the ^{13}C-NMR spectrum of **13a** appeared at δ(C) 32.2. The second isomer, **14a**, showed the signal of the CH_2(5) at δ(C) 51.1, which

Scheme 3



[2]) According to the ^{1}H-NMR spectrum, these compounds are the products of the dimerization of **11** also formed in the absence of a trapping reagent [11].

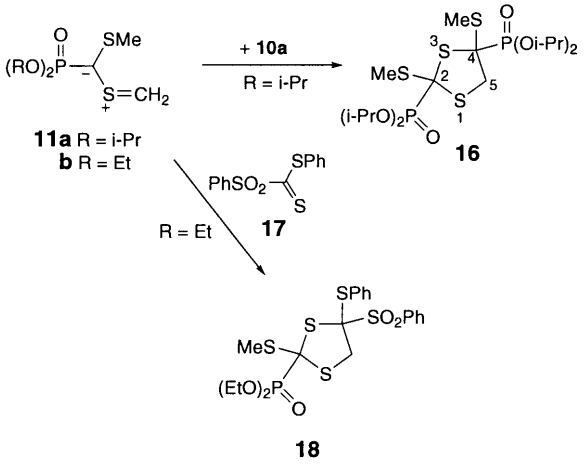
is a typical value for '5-CH_2-1,3-dithiolanes' [16]. Comparable results were obtained with **11b** and **12a**, but in this case, the products **13b** and **14b** were formed in a ratio of *ca.* 3:2.

In a second series of experiments, thiobenzophenone (**12b**), which is another reactive dipolarophile, was used to intercept sulfoniomethanides **11**. Only the sterically more hindered cycloadducts **15a** and **15b** [15] were obtained in modest yields (*Scheme 3*). The ^{1}H-NMR spectrum of the crude mixture indicated the presence of substantial amounts of by-products, which resulted from the competitive dimerization of **11**[3]). Apparently, in this system, **12b** is not reactive enough to suppress the formation of dimers of **11** (see [11]), which decomposed during chromatographic workup. All attempts to intercept **11** with cycloaliphatic thioketones, such as adamantanethione or 2,2,4,4-tetramethyl-3-thioxocyclobutanone, which are known to be significantly less reactive than aromatic thioketones, were unsuccessful. Only products resulting from the dimerization of **11** were detected in the ^{1}H-NMR spectrum.

In a previous paper, reactions of **10a** with aromatic and cycloaliphatic sulfoniomethanides, which led to phosphinylated 1,3-dithiolanes, were described [15]. The results showed that the electron-withdrawing phosphinyl group increases the dipolarophilicity of the C=S group in reactions with sulfoniomethanides. Therefore, the sulfoniomethanide **11a**, generated from **10a** and CH_2N_2, was treated with **10a** at *ca.* −40°, and after warming to room temperature, a single 1,3-dithiolane **16** was obtained (*Scheme 4*), *i.e.*, the sterically less crowded '5-CH_2' isomer (^{13}C-NMR: CH_2(5) at δ(C) 46.3). A similar result was obtained when the sulfoniomethanide **11b** was trapped with *C*-sulfonylated dithioformate **17**. Again, a single '5-CH_2' isomer **18** was formed (CH_2(5) δ 43.9). No attempts were made to determine the relative configuration of the products.

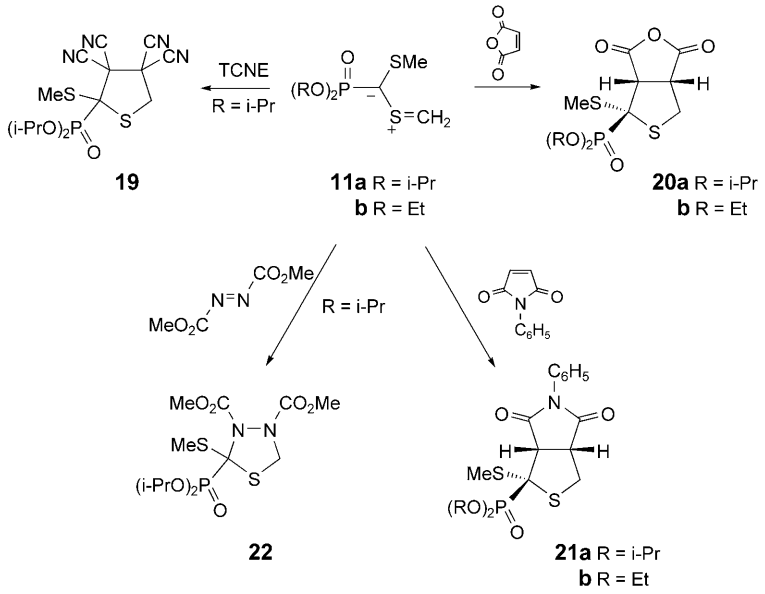
In contrast to the activated 'dithioesters' **10** and **17**, methyl dithiobenzoate (**1a**) was not able to intercept transient sulfoniomethanides **11**.

Scheme 4



[3]) An additional experiment with **12b** was carried out in MeOH. In this case, the crude mixture consisted of **15a** and the MeOH adduct of the dimer of **11a** (see [11]).

Scheme 5



In general, sulfoniomethanides, being electron-rich 1,3-dipoles, react smoothly with electron-poor C=C dipolarophiles. According to *Huisgen* and co-workers, ethenetetracarbonitrile (=tetracyanoethylene; TCNE) is the most reactive C=C interceptor of the methylide derived from thiobenzophenone [13]. As expected, TCNE underwent an efficient [2+3] cycloaddition with **11a** to give the tetrahydrothiophene derivative **19** in 75% yield (*Scheme 5*).

The reactions with fumaronitrile (=(2*E*)-but-2-enedinitrile) and dimethyl ethynedicarboxylate, respectively, were not successful, and again only products of the dimerization of **11** were detected. However, in the case of maleic anhydride, the cycloaddition competes with the dimerization, and the expected [2+3] cycloadducts **20** were isolated in *ca*. 60% yield (*Scheme 5*). Similarly, the reactions of **11a** and **11b** with *N*-phenylmaleimide (=1-phenyl-1*H*-pyrrole-2,5-dione) led smoothly to the bicyclic products **21a** and **21b**, respectively. In these cases, no dimerization of **11** was observed. The molecular structures of **20a** and **21b** were established by X-ray crystallography (*Fig.*). In both cases, the two five-membered rings are *cis*-fused, and the phosphinyl group is '*exo*' oriented, while the methylthio group occupies the '*endo*' position. Both Et groups of **21b** are disordered over two conformations. In both compounds **20a** and **21b**, the two five-membered rings have half-chair conformations. The S-containing ring of **20a** is twisted on C(5)–S(1) (for numbering, see *Fig.*), while the O-containing ring is twisted on C(3)–C(4). In **21b**, the S-containing ring is twisted on C(2)–S(1), while the O-containing ring is quite flat but twisted slightly on C(3)–C(4).

Similarly to electron-deficient C=C dipolarophiles, diazenedicarboxylates are superior reaction partners for sulfoniomethanides [18]. Also in the reaction with **11a**, dimethyl diazenedicarboxylate showed a reactivity comparable with that of TCNE, and the 1,3,4-thiadiazolidine **22** was obtained in 72% yield (*Scheme 5*).

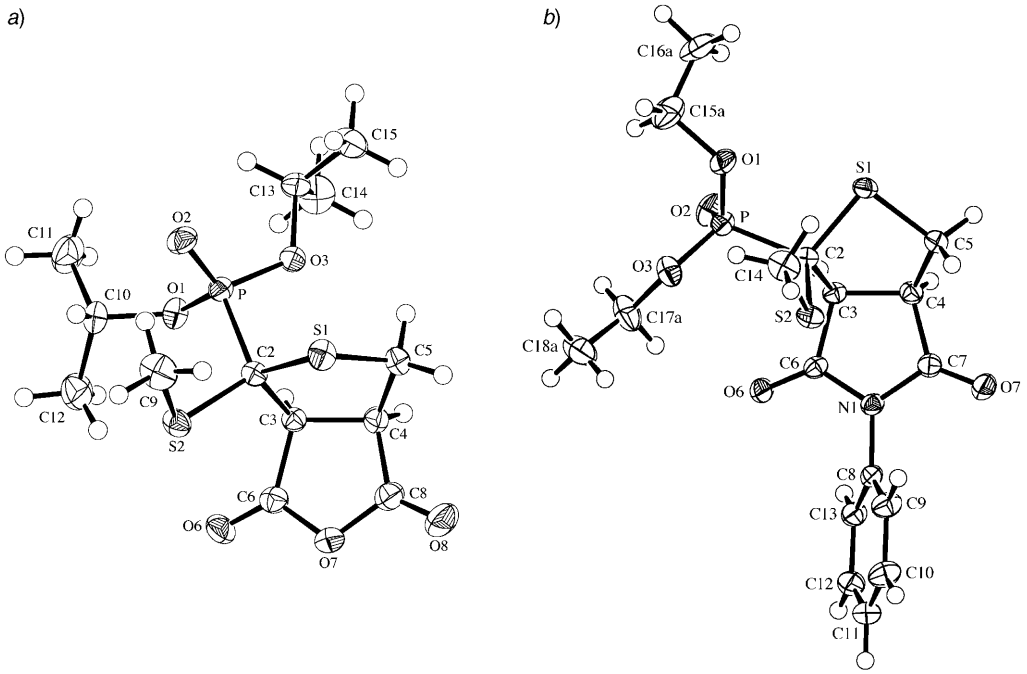


Figure. *ORTEP Representations* [17] *of the molecular structures of* a) **20a** *and* b) *of one of the two conformations of* **21b** (50% probability ellipsoids; arbitrary numbering of atoms)

In conclusion, the presented results show that phosphinylated dithioformates **10** can be used as precursors of phosphinylated sulfoniomethanides, which are versatile building blocks for the preparation of phosphinylated S-heterocycles. Moreover, compounds **10** act as dipolarophiles in reactions with sulfoniomethanides, to give phosphinylated 1,3-dithiolanes (see also [15]). It is noteworthy that 'thiocarbonyl *S*-methanides' **11** lead to [2+3] cycloadducts only with very reactive dipolarophiles. In these systems, dimerization of the dipolar species always competes with the cycloaddition and, therefore, in the case of less reactive dipolarophiles, no cycloaddition is observed. Unlike aromatic and aliphatic sulfonium methylides, no 1,3-dipolar electrocyclization to give thiiranes occurs in the case of **11**.

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Experimental Part

1. *General*. For general information on instruments and methods, see [15]. $^{31}P\{1H\}$-NMR Spectra: *Bruker-DRX-400* spectrometer, in $CDCl_3$; chemical shifts δ in ppm relative to H_3PO_4 (85%) as external standard.

2. *Starting Materials*. Methyl [(diisopropoxy)phosphinyl]dithioformate (=methyl bis(1-methylethoxy)-phoshinecarbodithioate 1-oxide; **10a**) and methyl (diethoxyphosphinyl)dithioformate (=methyl diethoxyphosphinecarbodithioate 1-oxide; **10b**) were prepared from the corresponding phosphites and CS_2 following a known

protocol [19]. The 9*H*-fluorene-9-thione (**12a**) was prepared by treatment of 9*H*-fluoren-9-one in EtOH soln. either with a mixed stream of H_2S and HCl [20] or by heating with *Lawesson*'s reagent in boiling toluene [21]. Thiobenzophenone (**12b**) was obtained from benzophenone and *Lawesson*'s reagent in boiling toluene according to [22]. *S*-Phenyl *C*-(phenylsulfonyl)dithioformate (= phenyl (phenylsulfonyl)methanedithioic acid; **17**) was prepared in a two step procedure from phenyl carbonochloridothioate following a protocol of *Senning* and co-workers [23]. Ethenetetracarbonitrile, dimethyl diazenedicarboxylate, maleic anhydride, and *N*-phenylmaleimide were purchased from *Sigma–Aldrich* and used without further purification.

3. *Reactions of Dithioformates* **10a** *and* **10b** *with* CH_2N_2. An orange-red soln. of **10a** or **10b** (1 mmol) in abs. THF (1 ml) under N_2 was cooled to $-65°$ in an acetone/dry ice bath, and while stirring, a freshly prepared soln. of CH_2N_2 in Et_2O was added dropwise until the color of the starting material vanished.

4. *Reactions of* in situ *Generated Phosphinylated Sulfonium Ylides* **11a** *and* **11b** *with Dipolarophiles: General Procedure.* To a colorless soln. obtained according to *Exper. 3* and stirred at $-65°$, the corresponding dipolarophile (1.1 mmol) was added in portions. Then, the soln. was slowly warmed to r.t., and between $-40°$ and $-35°$, a rapid evolution of N_2 was observed. The mixture was stirred at r.t. for 1 h and evaporated. The crude mixture was analyzed by ^{1}H-NMR and, after removal of the solvent, the oily or solid residue was separated chromatographically or by crystallization.

4.1. *Reaction of* **11a** *with* **12a**. The products **13a** and **14a** were separated by prep. TLC (SiO_2, CH_2Cl_2).

*Diisopropyl {5-(Methylthio)spiro[1,3-dithiolane-4,9′-[9*H*]fluoren]-5-yl}phosphonate* (**13a**): More polar fraction (150 mg, 32%). Colorless crystals. M.p. 117–119° (hexane/CH_2Cl_2). IR (KBr): 2978*s*, 2919*m*, 1447*s*, 1384*m*, 1373*m*, 1241v*s* (P=O), 1104*s*, 1009v*s* (P–O–C), 992v*s*, 741*s*, 562*s*. ^{1}H-NMR: 0.64, 0.78, 0.99, 1.04 (4*d*, J(H,H) = 6.2, 2 *Me*$_2$CH); 2.46 (*d*, ^4J(H,P) = 0.5, MeS); 4.22, 4.42 (*AB*, J(H,H) = 8.7, CH_2); 4.30–4.53 (*m*, 2 Me$_2$C*H*); 7.18–7.61 (*m*, 6 arom. H); 8.16–8.19 (*m*, 2 arom. H). ^{13}C-NMR: 17.0 (MeS); 22.2, 23.1, 23.5, 24.0 (4*d*, ^3J(C,P) = 3.5, 2 *Me*$_2$CH); 32.2 (*d*, ^3J(C,P) = 10.6, CH_2); 71.1, 73.2 (2*d*, ^2J(C,P) = 8.3, 2 Me$_2$*C*H); 72.0 (quat. C); 74.5 (*d*, ^1J(C,P) = 85.0, quat. C); 118.8, 119.4, 126.1, 126.8, 128.5, 128.9, 129.0, 129.6 (8 arom. CH); 139.3, 141.4, 142.4, 149.0 (4 arom. C). CI-MS (i-C_4H_{10}): 467 (3, $[M+1]^+$), 419 (100, $[M-\text{MeS}]^+$), 389 (5), 377 (6). Anal. calc. for $C_{22}H_{27}O_3PS_3$ (466.61): C 56.63, H 5.83, S 20.62; found: C 56.75, H 5.92, S 20.36.

*Diisopropyl {2-(Methylthio)spiro[1,3-dithiolane-4,9′-[9*H*]fluoren]-2-yl}phosphonate* (**14a**): Less polar fraction (150 mg, 32%). Thick, pale yellow oil. IR (neat): 2981v*s*, 2922*s*, 1738*m*, 1448v*s*, 1385*s*, 1244v*s* (P=O), 1103v*s*, 1010v*s* (P–O–C), 989vs, 897*s*, 750v*s*, 560*s*. ^{1}H-NMR: 1.41 (*d*, J(H,H) = 7.0, *Me*$_2$CH); 2.52 (*s*, MeS); 3.60, 4.03 (*AB*, J(H,H) ≈ 14, ^4J(H,P) ≈ 1.3, CH_2); 4.71–5.20 (*m*, 2 Me$_2$C*H*); 7.20–8.29 (*m*, 8 arom. H). ^{13}C-NMR: 16.9 (*d*, ^3J(C,P) = 0.7, MeS); 23.7, 24.0, 24.6 (2 *Me*$_2$CH); 51.1 (*d*, ^3J(C,P) ≈ 2.4, CH_2); 69.5 (*d*, ^1J(C,P) ≈ 140, quat. C); 73.7, 74.2 (2*d*, ^2J(C,P) ≈ 4.5, 2 Me$_2$*C*H); 73.8 (quat. C); 119.9, 120.2, 125.5, 126.5, 128.4, 128.6, 129.1 (8 arom. CH); 139.2, 139.6, 147.9, 148.6 (4 arom. C). ^{31}P-NMR: 15.50. Anal. calc. for $C_{22}H_{27}O_3PS_3$ (466.61): C 56.63, H 5.83, S 20.62; found: C 56.56, H 5.81, S 20.58.

4.2. *Reaction of* **11b** *with* **12a**. The products **13b** and **14b** were separated by prep. TLC (SiO_2, hexane/AcOEt 7:3).

*Diethyl {5-(Methylthio)spiro[1,3-dithiolane-4,9′-[9*H*]fluoren]-4-yl}phosphonate* (**13b**): More polar fraction (220 mg, 49%). Colorless crystals. M.p. 83–85° (hexane/Et_2O). IR (KBr): 2977*m*, 1447*s*, 1243v*s* (P=O), 1055v*s*, 1023v*s* (P–O–C), 981*s*, 746*s*, 556*s*. ^{1}H-NMR: 0.86 (*td*, J(H,H) = 7.0, ^4J(H,P) = 0.5, *Me*CH$_2$); 0.92 (*t*, J(H,H) = 7.0, *Me*CH$_2$); 2.47 (*s*, MeS); 3.41–3.87 (*m*, 2 MeC*H*$_2$); 4.23, 4.44 (*AB*, J(H,H) = 8.7, CH_2); 7.19–7.39 (*m*, 4 arom. H); 7.59–7.64 (*m*, 2 arom. H); 8.14–8.19 (*m*, 2 arom. H). ^{13}C-NMR: 15.8, 15.9 (2*d*, ^3J(C,P) ≈ 5.5, 2 *Me*CH$_2$); 16.9 (MeS); 32.4 (*d*, ^3J(C,P) = 10.8, CH_2); 63.0, 64.9 (2*d*, ^2J(C,P) ≈ 7.6, 2 MeCH$_2$); 72.3 (quat. C); 74.9 (*d*, ^1J(C,P) ≈ 85.0, quat. C); 118.9, 119.4, 126.1, 126.8, 128.6, 128.9, 129.2 (8 arom. CH); 139.2, 140.9, 142.2, 149.1 (4 arom. C). CI-MS (NH_3): 456 (9, $[M+NH_4]^+$), 439 (21, $[M+1]^+$), 391 (100, $[M-\text{MeS}]^+$), 361 (30). Anal. calc. for $C_{20}H_{23}O_3PS_3$ (438.55): C 54.77, H 5.27, S 21.93; found: C 54.54, H 5.39, S 21.70.

*Diethyl {2-(Methylthio)spiro[1,3-dithiolane-4,9′-[9*H*]fluoren]-2-yl}phosphonate* (**14b**): Less polar fraction (120 mg, 27%). Colorless crystals. M.p. 56–58° (Et_2O, −76°). IR (KBr): 2981*s*, 2917*m*, 1447*s*, 1247v*s* (P=O), 1162*m*, 1050v*s*, 1019v*s* (P–O–C), 747v*s*, 738v*s*, 560v*s*. ^{1}H-NMR: 1.31 (*t*, J(H,H) = 7.0, 2 *Me*CH$_2$); 2.56 (*s*, MeS); 3.70, 3.98 (*AB*, J(H,H) ≈ 14, ^4J(H,P) ≈ 1.3 (only for the low-field H), CH_2); 4.20–4.60 (*m*, 2 MeC*H*$_2$); 7.20–8.20 (*m*, 8 arom. H). ^{13}C-NMR: 16.5, 16.7 (*d*, ^3J(C,P) ≈ 5.5, 2 *Me*CH$_2$); 17.3 (MeS); 51.0 (*d*, ^3J(C,P) ≈ 3, CH_2); 65.2, 65.5 (2*d*, ^2J(C,P) ≈ 7.5 and 6.7, resp., 2 MeCH$_2$); 73.8 (*d*, ^3J(C,P) = 5.0, C(4)); 120.0, 120.2, 125.5, 126.2, 128.5, 128.6, 129.2 (8 arom. CH); 139.2, 139.6, 147.9, 148.1 (4 arom. C); C(2) not found. CI-MS (NH_3): 456 (12, $[M+NH_4]^+$), 439 (11, $[M+1]^+$), 391 (100, $[M-\text{MeS}]^+$). Anal. calc. for $C_{20}H_{23}O_3PS_3$ (438.55): C 54.77, H 5.27, S 21.93; found: C 54.69, H 5.50, S 21.79.

4.3. *Reaction of* **11a** *with* **12b**. The product **15a** was isolated by trituration of the solid residue, obtained after evaporation, with hexane. After filtration, the crude material was purified by crystallization from hexane/Et_2O:

diisopropyl [4-(methylthio)-5,5-diphenyl-1,3-dithiolan-4-yl]phosphonate (**15a**; 150 mg, 32%). Colorless crystals. M.p. 170–172° (hexane/Et_2O). IR (KBr): 2980*m*, 2920*w*, 1244*s* (P=O), 1105*m*, 1005v*s* (P–O–C), 699*m*, 559*m*. ^{1}H-NMR: 1.05, 1.13, 1.19, 1.21 (4*d*, *J*(H,H) = 6.2, 2 Me_2CH); 2.45 (*d*, ^{4}*J*(H,P) = 0.50, MeS); 3.86, 3.94 (*AB*, *J*(H,H) = 16.0, CH_2); 4.46–4.56, 4.59–4.69 (2*m*, 2 Me_2CH); 7.01–7.76 (*m*, 10 arom. H). ^{13}C-NMR: 18.9 (MeS); 23.3, 23.5 (2*d*, ^{3}*J*(C,P) = 6.8 and 6.0, resp., $MeCH$); 24.2 ($MeCH$); 31.8 (*d*, ^{3}*J*(P,C) = 5.6, CH_2); 72.7 (*d*, ^{2}*J*(C,P) = 8.5, 2 Me_2CH); 126.7, 126.8 (2*d*, ^{4}*J*(C,P) = 3.8, 4 arom. CH); 127.4 (2 arom. CH); 130.7, 131.1 (4 arom. CH); 143.0 (*d*, ^{3}*J*(C,P) = 6.0, arom. C); 145.0 (*d*, ^{3}*J*(C,P) = 1.6, arom. C); C(4) and C(5) not found. ^{31}P-NMR: 15.7. CI-MS (NH_3): 469 (43, $[M+1]^+$), 421 (100, $[M-MeS]^+$), 391 (57), 377 (98), 199 (33).

4.4. *Reaction of* **11b** *with* **12b**. The product **15b** was isolated by trituration of the semi-solid residue, obtained after evaporation, with hexane. After filtration, the crude material was purified by crystallization from hexane/CH_2Cl_2: *diethyl [4-(methylthio)-5,5-diphenyl-1,3-dithiolan-4-yl]phosphonate* (**15b**; 140 mg, 32%). Colorless crystals. M.p. 189–191° (hexane/CH_2Cl_2). IR (KBr): 2985*w*, 1443*w*, 1249*s* (P=O), 1055v*s*, 1023v*s* (P–O–C), 971*s*, 700*s*, 560*s*. ^{1}H-NMR: 0.97, 1.23 (2*t*, *J*(H,H) = 6.9, 2 $MeCH_2$); 2.49 (*d*, ^{4}*J*(H,P) = 0.55, MeS); 3.62–4.22 (*m*, 2 $MeCH_2$); 3.88, 3.97 (*AB*, *J*(H,H) = 9.3, CH_2); 7.17–7.27, 7.60–7.66, 7.76–7.79 (3*m*, 10 arom. H). ^{13}C-NMR: 15.9, 16.3 (2*d*, ^{3}*J*(C,P) = 5.6, 2 $MeCH_2$); 18.5 (MeS); 31.7 (*d*, ^{3}*J*(C,P) = 5.7, CH_2); 63.7, 64.1 (2*d*, ^{2}*J*(C,P) = 8.2, 2 $MeCH_2$); 126.8, 127.6, 130.4, 131.0 (10 arom. CH); 141.6, 142.9 (2 arom. C); C(4) and C(5) not found. CI-MS (NH_3): 441 (30, $[M+1]^+$), 393 (100, $[M-MeS]^+$). Anal. calc. for $C_{20}H_{25}O_3PS_3$ (440.57): C 54.52, H 5.72, S 21.83; found: C 54.11, H 5.84, S 21.39.

4.5. *Reaction of* **11a** *with* **10a**. The product **16** was purified by prep. TLC (SiO_2, Et_2O). An anal. pure sample was obtained by crystallization from pentane at −76°: *tetraisopropyl [2,4-bis(methylthio)-1,3-dithiolane-2,4-diyl]bis[phosphonate]* (**16**; 260 mg, 51%). Colorless crystals. M.p. 47–49° (pentane). IR (KBr): 2978*s*, 2923*m*, 1467*m*, 1383*s*, 1244v*s* (P=O), 1142*m*, 1104*s*, 1012v*s* (P–O–C), 982v*s* (P–O–C), 894*m*, 553*s*. ^{1}H-NMR: 1.35 (*d*, *J*(H,H) = 7.0, 4 Me_2CH); 2.41 (br. *s*, 2 MeS); 3.30, 4.10 (*AB*-like *m*, *J*(H,H) ≈ 13.0, CH_2); 4.61–5.10 (*m*, 4 Me_2CH). ^{13}C-NMR (C_6D_6): 16.1, 19.1 (2 MeS); 23.7, 23.8, 24.0, 24.1, 24.6, 24.7, 24.8 (4 Me_2CH); 46.3 (*d*, ^{3}*J*(C,P) ≈ 6.7, CH_2); 72.8 (*dd*, ^{1}*J*(C,P) = 147.0, ^{3}*J*(C,P) = 5.2, C(4)); 73.7, 73.9, 74.1, 74.3 (4 Me_2CH); C(2) not found. Anal. calc. for $C_{17}H_{36}O_6P_2S_4$ (526.64): C 38.77, H 6.89, S 24.35; found: C 38.98, H 6.99, S 24.53.

4.6. *Reaction of* **11b** *with* **17**. The product **18** was purified by prep. TLC (SiO_2, hexane/AcOEt 3 : 2): *diethyl 2-(methylthio)-[4-(phenylsulfonyl)-4-(phenylthio)-1,3-dithiolan-2-yl]phosphonate* (**18**; 350 mg, 65%). Thick, pale yellow oil. IR (neat): 2985*m*, 1446*m*, 1325*s*, 1252*s* (P=O), 1147*s*, 1049v*s*, 1020v*s* (P–O–C), 974*s*, 754*s*. ^{1}H-NMR: 1.37, 1.38 (2*td*, *J*(H,H) = 7, ^{4}*J*(H,P) = 0.62, and 0.66, resp., $MeCH_2$); 2.18 (*d*, ^{4}*J*(H,P) = 0.75, MeS); 3.47, 4.10 (*AB*-like, *J*(H,H) = 13, ^{3}*J*(H,P) = 1.6, and 1.1, resp., CH_2); 4.21–4.35 (*m*, 2 $MeCH_2$); 7.33–7.48, 7.54–7.59, 7.66–7.72, 7.81–7.85, 8.04–8.08 (5*m*, 10 arom. H). ^{13}C-NMR: 16.3, 16.4 (2 $MeCH_2$); 18.0 (MeS); 43.9 (*d*, ^{3}*J*(C,P) = 5.5, CH_2); 65.3, 65.5 (2*d*, ^{2}*J*(C,P) = 7.3, 2 $MeCH_2$); 71.5 (*d*, ^{1}*J*(C,P) = 160, quat. C); 97.3 (*d*, ^{3}*J*(C,P) = 7, quat. C); 128.6, 128.7, 130.5, 131.7, 134.3, 138.0 (10 arom. CH); 129.8, 135.0 (2 arom. C). ESI-MS (NaI + KI): 559 ($[M+Na]^+$), 417 ($[M+1-PhS]^+$).

4.7. *Reaction of* **11a** *with Ethenetetracarbonitrile* (TCNE). The product mixture was separated by column chromatography (SiO_2, hexane with increasing amounts of CH_2Cl_2). An anal. pure sample was obtained by crystallization from MeOH at −76°: *diisopropyl [3,3,4,4-tetracyanotetrahydro-2-(methylthio)thiophen-2-yl]phosphonate* (**19**; 300 mg, 75%). Colorless crystals. M.p. 26–27° (MeOH). IR (KBr): 2985*s*, 2937*m*, 2254*w* (C≡N), 1452*m*, 1389*s*, 1259*s* (P=O), 1099*s*, 1001v*s* (P–O–C), 758v*s*. ^{1}H-NMR: 1.44–1.51 (*m*, 2 Me_2CH); 2.58 (*d*, ^{4}*J*(H,P) = 0.5, MeS); 3.92 (*s*, CH_2); 4.88–5.05 (*m*, 2 Me_2CH). ^{13}C-NMR: 17.8 (MeS); 23.4, 23.9 (2 Me_2CH); 40.4 (CH_2); 76.1, 76.5 (2 Me_2CH); 107.1, 109.6 (4 CN); 3 quat. C not found. CI-MS (NH_3): 416 (100, $[M+NH_4]^+$), 417(19), 418(11), 306(16). Anal. calc. for $C_{15}H_{19}N_4O_3PS_2$ (398.44): C 45.22, H 4.81, N 14.06, S 16.09; found: C 45.24, H 4.84, N 14.15, S 15.62.

4.8. *Reactions of* **11a** *with Maleic Anhydride and* N-*Phenylmaleimide.* Products **20a** and **21a** were isolated by trituration of the semi-solid residues, obtained after evaporation, with hexane/CH_2Cl_2. Anal. pure samples were obtained by crystallization from hexane/CH_2Cl_2.

Diisopropyl [6-'endo'*-(Methylthio)-2,4-dioxo-3-oxa-7-thiabicyclo[3.3.0]oct-6-*'exo'*-yl]phosphonate* (= *Diisopropyl [(3a*RS*,4*RS*,6a*SR*)-Tetrahydro-4-(methylthio)-1,3-dioxo-1*H*,3*H*-thieno[3,4-*c*]furan-4-yl]phosponate*; **20a**): 300 mg (81%). Colorless crystals. M.p. 121–123° (hexane/CH_2Cl_2). IR (KBr): 2983*m*, 2976*m*, 2929*m*, 1856*m*, 1782v*s*, 1388*m*, 1376*m*, 1243v*s* (P=O), 1218*s*, 1012v*s* (P–O–C), 997*s*, 986*s*, 934*m*, 558*s*. ^{1}H-NMR: 1.41, 1.42 (2*dd*, ^{4}*J*(H,P) ≈ 4.0 and 5.0, resp., 2 Me_2CH); 2.38 (*s*, MeS); 3.44–3.56 (*m*, CH_2); 4.03–4.19 (*m*, 2 CH); 4.77–4.99 (*m*, 2 Me_2CH). ^{13}C-NMR: 16.0 (MeS); 23.4, 23.7, 23.9 (3*d*, ^{3}*J*(C,P) ≈ 6.7, 5.4, and 3.6, resp., 3 Me of 2 Me_2CH); 24.5 (*s*, 1 Me of 2 Me_2CH); 33.5 (*d*, ^{3}*J*(C,P) ≈ 2.5, CH_2); 53.1 (*d*, ^{2}*J*(C,P) ≈ 4.7, CH); 56.6 (*d*, ^{3}*J*(C,P) ≈ 3.5, CH); 73.3, 75.1 (2 Me_2CH); 171.1 (CO). CI-MS (NH_3): 386 (100, $[M+NH_4]^+$), 369 (27,

$[M+1]^+$), 344 (10), 277 (6). Anal. calc. for $C_{13}H_{21}O_6PS_2$ (368.41): C 42.38, H 5.75, S 17.41; found: C 42.40, H 5.69, S 17.18.

Diisopropyl [2-'endo'-(*Methylthio-6,8-dioxo-7-phenyl-3-thia-7-azabicyclo[3.3.0]oct-2-*'exo'-yl*]phosphonate* (= *Diisopropyl [(1*RS,*3a*RS,*6a*SR*)-Hexahydro-1-(methylthio)-4,6-dioxo-5-phenyl-1*H-*thieno[3,4-*c*]pyrrol-1-yl]phosponate*; **21a**): 240 mg (54%). Colorless crystals. M.p. 99–100° (hexane/CH_2Cl_2). IR (KBr): 2981*m*, 2925*w*, 1776*w*, 1713v*s*, 1498*s*, 1387*s*, 1241*s* (P=O), 1193*m*, 1011v*s* (P–O–C), 984v*s*, 565*m*. ^{1}H-NMR: 1.40, 1.42 (2*d*, J = 7.8 and 5.9, resp., 2 *Me*$_2$CH); 2.41 (*s*, MeS); 3.51 (*d*, ^4J(H,P) ≈ 5.5, CH_2); 3.88–3.94 (*m*, CH); 4.07 (*dd*, J(H,H) = 14.6, ^4J(H,P) ≈ 8.5, CH); 4.83–4.98 (2*m*, 2 Me$_2$CH); 7.26–7.49 (*m*, 5 arom. CH). ^{13}C-NMR: 16.2 (MeS); 23.5, 23.6, 24.2, 24.3 (4*d*, ^3J(C,P) ≈ 4.0, 2 Me$_2$CH); 33.2 (*d*, ^3J(C,P) ≈ 2.5, CH_2); 52.9 (*d*, ^2J(C,P) ≈ 4.8, CH); 55.5 (*d*, ^3J(C,P) ≈ 3.4, CH); 62.1 (*d*, ^1J(C,P) = 163.0, C(2)); 72.6, 74.4 (2d, ^2J(C,P) ≈ 7.9 and 7.6, resp., Me$_2$CH); 126.4, 128.7, 129.1 (5 arom. CH); 131.8 (1 arom. C); 171.5 (*d*, ^3J(C,P) ≈ 6.8, CO); 175.8 (CO). CI-MS (NH_3): 461 (64, $[M+NH_4]^+$), 444 (100, $[M+1]^+$), 398 (22). Anal. calc. for $C_{19}H_{26}NO_5PS_2$ (443.52): C 51.45, H 5.91, N 3.16, S 14.46; found: C 51.44, H 5.86, N 3.12, S 14.41.

4.9. *Reactions of* **11b** *with Maleic Anhydride and* N-*Phenylmaleimide.* Products **20b** and **21b** were isolated by trituration of the solid residues, obtained after evaporation, with hexane/Et_2O and hexane/CH_2Cl_2, respectively. Anal. pure products were obtained by crystallization from the same solvents.

Diethyl [6-'endo'-*(Methylthio-2,4-dioxo-3-oxa-7-thiabicyclo[3.3.0]oct-6-*'exo'-*yl]phosphonate* (= *Diethyl [(3a*RS,*4*RS,*6a*SR*)-Tetrahydro-4-(methylthio)-1,3-dioxo-1*H,*3*H-*thieno[3,4-*c*]furan-4-yl]phoshonate*; **20b**): 143 mg (42%). Colorless crystals. M.p. 104–106° hexane/Et_2O). IR (KBr): 2981*m*, 2964*m*, 2928*w*, 1861*m*, 1786v*s* (C=O), 1254*m*, 1233*s* (P=O), 1086*s*, 1060*s*, 1020*s* (P–O–C), 973*m*, 957*m*, 555*s*. ^{1}H-NMR: 1.40, 1.41 (2*t*, J(H,H) = 2 MeCH$_2$); 2.38 (*s*, MeS); 3.49 (*d*, ^{4}J(H,P) ≈ 4.4, CH_2); 4.07–4.42 (*m*, 2 MeCH$_2$, 2 CH). ^{13}C-NMR: 15.9 (MeS); 16.3, 16.4 (2*d*, ^3J(C,P) ≈ 6.0, 2 MeCH$_2$); 33.3 (*d*, ^3J(C,P) ≈ 3.0, CH_2); 52.9 (*d*, ^2J(C,P) ≈ 5.5, CH); 56.8 (*d*, ^3J(C,P) ≈ 3.7, CH); 61.5 (*d*, ^1J(C,P) ≈ 150.0, quat. C); 64.2 (*d*, ^2J(C,P) ≈ 7.7, MeCH$_2$); 65.9 (*d*, ^2J(C,P) ≈ 7.4, MeCH$_2$); 165.8, 170.9 (2 C=O). CI-MS (NH_3): 358 (100, $[M+NH_4]^+$), 341 (18, $[M+1]^+$), 312 (7). Anal. calc. for $C_{11}H_{17}O_6PS_2$ (340.36): C 38.82, H 5.03, S 18.84; found: C 38.55, H 5.07, S 18.97.

Diethyl [2-'endo'-(*Methylthio-6,8-dioxo-7-phenyl-3-thia-7-azabicyclo[3.3.0]oct-2-*'exo'-*yl)phosphonate* (= *Diethyl [(1*RS,*3a*RS,*6a*SR*)-Hexahydro-1-(methylthio)-4,6-dioxo-5-phenyl-1*H-*thieno[3,4-*c*]pyrrol-1-yl]-phosponate*; **21b**): 255 mg (61%). Colorless crystals. M.p. 141–143° (hexane/CH_2Cl_2). IR KBr): 2981*w*, 2923*w*, 1775*w*, 1713v*s* (C=O), 1497*m*, 1389*s*, 1241*s* (P=O), 1196*s*, 1048*s*, 1017*s* (P–O–C), 564*m*. ^{1}H-NMR: 1.40, 1.41 (2*td*, J(H,H) = 7.8, ^4J(H,P) ≈ 1.1 and 0.7, resp., 2 *Me*CH$_2$); 2.40 (*d*, ^4J(H,P) ≈ 0.5, MeS); 3.43–3.55 (*m*, CH_2); 3.91–3.98 (*m*, CH); 4.15 (*dd*, J(H,H) = 14.0, ^3J(H,P) ≈ 8.8, CH); 4.26–4.43 (*m*, 2 MeCH$_2$); 7.27–7.49 (*m*, 5 arom. CH). ^{13}C-NMR: 16.0 (MeS); 16.3, 16.4 (2*d*, ^3J(C,P) ≈ 5.4, 2 *Me*CH$_2$); 32.9 (*d*, ^3J(C,P) ≈ 3.2, CH_2); 52.5 (*d*, ^2J(C,P) ≈ 6.3, CH); 55.9 (*d*, ^3J(C,P) ≈ 2.6, CH); 62.5 (*d*, ^1J(C,P) ≈ 160.0, quat. C); 63.9, 65.4 (2*d*, ^2J(C,P) ≈ 7.5 and 7.4, resp., 2 MeCH$_2$); 126.4, 128.7, 129.1 (5 arom. CH); 131.7 (1 arom. C); 171.2 (*d*, ^3J(C,P) ≈ 5.4, C=O); 175.6 (C=O). CI-MS (NH_3): 433 (69, $[M+NH_4]^+$), 416 (100, $[M+1]^+$), 370 (7), 278 (5). Anal. calc. for $C_{17}H_{22}NO_5PS_2$ (415.47): C 49.15, H 5.34, N 3.37, S 15.44; found: C 48.88, H 5.23, N 3.25, S 15.55.

4.10. *Reaction of* **11a** *with Dimethyl Diazenedicarboxylate.* Product **22** was purified by prep. TLC (SiO_2, CH_2Cl_2/Et_2O 1:4), followed by crystallization from hexane/CH_2Cl_2: *dimethyl 2-(diisopropoxyphosphinyl)-2-(methylthio)-1,3,4-thiadiazolidine-3,4-dicarboxylate* (**22**; 300 mg, 72%). Colorless crystals. M.p. 97–99° (hexane/CH_2Cl_2). IR (KBr): 2981*m*, 1736v*s* (C=O), 1735v*s* (C=O), 1448*s*, 1352v*s*, 1254v*s* (P=O), 1238*s*, 1200*s*, 1024*s*, 995v*s* (P–O–C), 565*s*. ^{1}H-NMR: 1.25–1.40 (*m*, 2 *Me*$_2$CH); 2.40 (*s*, MeS); 3.80, 3.81 (2*s*, 2 MeO); 4.36, 5.25 (*AB*, J(H,H) ≈ 9.6, CH_2); 4.70–5.17 (*m*, 2 Me$_2$C*H*). ^{13}C-NMR: 17.1 (MeS); 23.3, 23.7, 24.0, 24.3 (2 *Me*$_2$CH); 49.4 (*d*, ^3J(C,P) ≈ 2.4, CH_2); 53.8, 54.2 (2 MeO); 73.7, 74.7 (2*d*, ^2J(C,P) ≈ 8, 2 Me$_2$*C*H); 83.6 (quat. C); 153.4, 157.5 (2 C=O). ^{31}P-NMR: 9.08. Anal. calc. for $C_{13}H_{25}N_2O_7PS_2$ (416.46): C 37.49, H 6.05, N 6.73, S 15.40; found: C 37.58, H 6.10, N 6.95, S 15.28.

5. *X-Ray Crystal-Structure Determination of* **20a** *and* **21b** (*Table* and *Fig.*)[4]. All measurements were performed on a *Nonius-KappaCCD* diffractometer [24] with graphite-monochromated MoK_α radiation (λ 0.71073 Å) and an *Oxford-Cryosystems-Cryostream-700* cooler. The data collection and refinement parameters are given in the *Table*, and views of the molecules are shown in the *Figure*. Data reduction was performed with *HKL Denzo* and *Scalepack* [25]. The intensities were corrected for *Lorentz* and polarization effects, and an absorption correction based on the multi-scan method [26] was applied. The structures were solved by direct

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[4]) CCDC-265652–265653 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from the *Cambridge Crystallographic Data Centre via* www.ccdc.cam.ac.uk/data_request/cif.

Table. *Crystallographic Data for Compounds* **20a** *and* **21b**

		20a	**21b**
Crystallized from		hexane/CH_2Cl_2	hexane/CH_2Cl_2
Empirical formula		$C_{13}H_{21}O_6PS_2$	$C_{17}H_{22}NO_5PS_2$
Formula weight		368.40	415.46
Crystal color, habit		colorless, plate	colorless, tablet
Crystal dimensions [mm]		0.05×0.17×0.30	0.07×0.17×0.20
Temperature [K]		160(1)	160(1)
Crystal system		orthorhombic	triclinic
Space group		*Pbca*	$P\bar{1}$
Z		8	2
Reflections for cell determination		74215	18089
2θ Range for cell determination [°]		4–55	4–60
Unit cell parameters	a [Å]	13.0300(2)	8.0919(1)
	b [Å]	15.6875(2)	11.2992(3)
	c [Å]	17.4460(3)	12.1758(3)
	α [°]	90	105.546(1)
	β [°]	90	109.344(1)
	γ [°]	90	102.319(1)
	V [Å]^3	3566.10(9)	954.46(4)
D_x [g cm^{-3}]		1.372	1.445
μ(MoK_α) [mm^{-1}]		0.410	0.391
Scan type		ϕ and ω	ϕ and ω
$2\theta_{(max)}$ [°]		55	60
Transmission factors [min; max]		0.882; 0.982	0.865; 0.974
Total reflections measured		52401	28586
Symmetry-independent reflections		4088	5574
Reflections with $I>2\sigma(I)$		3068	4328
Parameters refined; restraints		204; 0	278; 70
Reflections used in refinement		4088	5573
Final $R(F)$ ($I>2\sigma(I)$ reflections)		0.0374	0.0400
$wR(F^2)$ (all data)		0.0945	0.1035
Weighting parameters (a; b)[a]		0.0408; 2.1826	0.0473; 04212
Goodness of fit		1.034	1.028
Final Δ_{max}/σ		0.002	0.001
$\Delta\rho$(max; min) [e Å^{-3}]		0.34; −0.41	0.39; −0.61

[a]) $w^{-1}=\sigma^2(F_o^2)+(aP)^2+bP$ where $P=(F_o^2+2F_c^2)/3$

methods by using SIR92 [27], which revealed the positions of all non-H-atoms. In the case of **21b**, both Et groups are disordered over two conformations. Two sets of overlapping positions were defined for the atoms of each Et group and the site occupation factors of the major conformations of these groups refined to 0.69(3) and 0.746(9) for the Et groups attached to O(1) and O(3), respectively. Similarity restraints were applied to the chemically equivalent C–O and C–C bond lengths within each disordered conformation. Neighboring atoms within and between each conformation were also restrained to have similar atomic displacement parameters. The non-H-atoms of **20a** and **21b** were refined anisotropically. All of the H-atoms were placed in geometrically calculated positions and refined with a riding model where each H-atom was assigned a fixed isotropic displacement parameter with a value equal to 1.2 U_{eq} of its parent C-atom (1.5 U_{eq} for the Me groups). The refinement of each structure was carried out on F^2 by using full-matrix least-squares procedures, which minimized the function $\Sigma w(F_o^2-F_c^2)^2$. A correction for secondary extinction was not applied. In **21b**, one reflection, whose intensity was considered to be an extreme outlier, was omitted from the final refinement. Neutral-atom scattering factors for non-H-atoms were taken from [28a], and the scattering factors for H-atoms were taken from [29]. Anomalous

dispersion effects were included in F_c [30]; the values for f' and f'' were those of [28b]. The values of the mass attenuation coefficients are those of [28c]. All calculations were performed with the SHELXL97 [31] program.

REFERENCES

[1] G. Mlostoń, H. Heimgartner, *Pol. J. Chem*. **2000**, *74*, 1503.
[2] G. Mlostoń, H. Heimgartner, in 'Synthetic Applications of 1,3-Dipolar Cycloaddition Chemistry toward Heterocycles and Natural Products', Eds. A. Padwa and W. H. Pearson, J. Wiley & Sons, New York, 2002, p. 315.
[3] R. Huisgen, in 'Chemistry and Biological Activity of Oxygen- and Sulfur-Containing Heterocycles', Ed. V. G. Kartsev, IBS Press, Moscow, 2003, p. 83.
[4] R. Sustmann, W. Sicking, R. Huisgen, *J. Am. Chem. Soc*. **2003**, *125*, 14425.
[5] A. Schönberg, S. Nickel, D. Cernik, *Ber. Dtsch. Chem. Ges*. **1932**, *65*, 289; A. Schönberg, S. Nickel, D. Cernik, *Ber. Dtsch. Chem. Ges*. **1932**, *65*, 293.
[6] J. M. Beiner, D. Lecadet, D. Paquer, A. Thuillier, J. Vialle, *Bull. Soc. Chim. Fr*. **1973**, 1979.
[7] J. R. Moran, I. Tapia, V. Alcazar, *Tetrahedron* **1990**, *46*, 1783.
[8] M. Kägi, A. Linden, G. Mlostoń, H. Heimgartner, *Helv. Chim. Acta* **1998**, *81*, 285; B. Kelmendi, G. Mlostoń, H. Heimgartner, *Heterocycles* **2000**, *52*, 475.
[9] E. Vedejs, D. A. Perry, *J. Am. Chem. Soc*. **1983**, *105*, 1683.
[10] Yu. E. Klimko, S. D. Isaev, A. G. Yurchenko, *Russ. J. Org. Chem*. **1994**, *30*, 1776.
[11] K. Urbaniak, G. Mlostoń, M. Gulea, S. Masson, H. Heimgartner, *Pol. J. Chem*. **2005**, *79*, 1483.
[12] V. Alcazar Montero, I. Tapia Hernandez, J. de Pascual Teresa, J. R. Moran, R. Olabarrieta, *J. Org. Chem*. **1989**, *54*, 3664.
[13] R. Huisgen, X. Li, H. Giera, E. Langhals, *Helv. Chim. Acta* **2001**, *84*, 981.
[14] R. Huisgen, X. Li, G. Mlostoń, C. Fulka, *Eur. J. Org. Chem*. **2000**, 1695.
[15] K. Urbaniak, G. Mlostoń, M. Gulea, S. Masson, A. Linden, H. Heimgartner, *Eur. J. Org. Chem*. **2005**, 1604.
[16] G. Mlostoń, R. Huisgen, K. Polborn, *Tetrahedron* **1999**, *55*, 11475; R. Huisgen, G. Mlostoń, K. Polborn, R. Sustmann, *Chem.–Eur. J*. **2003**, *9*, 2256.
[17] C. K. Johnson, 'ORTEP II', Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1976.
[18] R. Huisgen, X. Li, G. Mlostoń, R. Knorr, H. Huber, D. S. Stephenson, *Tetrahedron* **1999**, *55*, 12783.
[19] D. W. Grisley, *J. Org. Chem.* **1961**, *26*, 2544.
[20] E. Campaigne, W. B. Reid, *J. Am. Chem. Soc*. **1946**, *68*, 769.
[21] S. Scheibye, R. Shabana, S.-O. Lawesson, C. Romming, *Tetrahedron* **1982**, *38*, 993.
[22] B. S. Pedersen, S. Scheibye, N. H. Nilsson, S.-O. Lawesson, *Bull. Soc. Chim. Belg*. **1978**, *87*, 223.
[23] I. El-Sayed, F. M. Abdel Megeed, M. S. Yassin, A. Senning, *Phosphorus Sulfur Silicon Relat. Elem*. **1994**, *86*, 239.
[24] R. Hooft, 'KappaCCD', Collect Software, Nonius BV, Delft, The Netherlands, 1999.
[25] Z. Otwinowski, W. Minor, *Methods Enzymol*. **1997**, *276*, 307.
[26] R. H. Blessing, A*cta Crystallogr.*, *Sect. A* **1995**, *51*, 33.
[27] A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, SIR92, *J. Appl. Crystallogr.* **1994**, *27*, 435.
[28] a) E. N. Maslen, A. G. Fox, M. A. O'Keefe, in 'International Tables for Crystallography', Ed. A. J. C. Wilson, Kluwer Academic Publishers, Dordrecht, 1992 Vol. C, Table 6.1.1.1, p. 477; b) D. C. Creagh, W. J. McAuley, in 'International Tables for Crystallography', Ed. A. J. C. Wilson, Kluwer Academic Publishers, Dordrecht, 1992 Vol. C, Table 4.2.6.8, p. 219; c) D. C. Creagh, J. H. Hubbell, in 'International Tables for Crystallography', Ed. A. J. C. Wilson, Kluwer Academic Publishers, Dordrecht, 1992 Vol. C, Table 4.2.4.3, p. 200.
[29] R. F. Stewart, E. R. Davidson, W. T. Simpson, *J. Chem. Phys.* **1965**, *42*, 3175.
[30] J. A. Ibers, W. C. Hamilton, *Acta Crystallogr.* **1964**, *17*, 781.
[31] G. M. Sheldrick, 'SHELXL97, Program for the Refinement of Crystal Structures', University of Göttingen, Germany, 1997.

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