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

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Abstract: The reaction of the methyl (dialkoxyphosphinyl)-dithioformates (= methyl dialkoxyphosphinecarbodithioate 1-oxides) 10 with CH₂N₂ at - 65° in THF yielded cycloadducts which eliminated N₂ between - 40 and - 35° to give the corresponding phosponodithioformate S-methanides (=methylene-sulfonium (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 9H-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[DOUBLE BOND]C dipolarophiles such as ethenetetracarbonitrile, maleic anhydride, and N-phenylmaleimide as well as the N[DOUBLE BOND]N dipolarophile dimethyl diazenedicarboxylate were shown to be efficient interceptors of 11 (Scheme 5).

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**[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 dialkylphosphonodithioformates **10** with CH_2N_2 at -65°C in THF yielded cycloadducts, which eliminated N_2 between -40 and -35°C to give the corresponding phosphonodithioformate *S*-methanides **11** (*Scheme 3*). These reactive 1,3-dipoles have been intercepted by aromatic thioketones to yield 1,3-dithiolanes. Whereas the reaction with thiobenzophenone led to the sterically more congested isomers **15** regioselectively, a mixture of both regioisomers was obtained with 9*H*-fluorene-9-thione. Trapping of **11** with phosphono- and sulfonodithioformates, respectively, led to the sterically less hindered 1,3-dithiolanes **16** and **18** exclusively (*Scheme 4*). In addition, reactive C=C dipolarophiles such as tetracyanoethene, maleic anhydride, and *N*-phenyl maleimide as well as the N=N dipolarophile dimethyl azodicarboxylate were shown to be efficient interceptors of **11** (*Scheme 5*).

1. Introduction. – Thiocarbonyl *S*-methanides are versatile sulfur-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 CH₂N₂ with C=S dipolarophiles and subsequent elimination of N₂ 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 non-enolizable 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 thiocarbonyl *S*-methanides. In a classical work, the reaction of methyl 1-dithionaphthoate with CH₂N₂ at room temperature yielded, in a regioselective manner, the sterically more hindered 1,3-dithiolane [5]. Similarly, treatment of methyl dithiobenzoate (**1a**) with CH₂N₂ at -5° led to a mixture of *cis*- and *trans*-1,3-dithiolanes **3** [6] (*Scheme 1*), while methyl dithiopropanoate (**1b**) gave the corresponding thiiranes of type **4** [6]. In both reactions, thiocarbonyl *S*-methanides **2** are proposed as the reactive intermediates.

Scheme 1

The reaction of CH₂N₂ with α -oxodithioesters of type **5** has been performed at -80°, and the evolution of N₂ leading to the corresponding *S*-methanide **6** occurred already at -60°. The reactivity of the latter compound depends on the type of R¹. Whereas, in the case of **5a** (R¹ = Ph, R² = PhCH₂), the interception of **6** with methyl acrylate gave the [2+3]-cycloadduct **7** exclusively, the reaction of **6** derived from **5b** (R¹ = C₇H₁₅, R² = Me) with maleic anhydride led to a mixture of the [2+3]-cycloadduct **8** and the 1,3-dithiole **9** [7] (*Scheme 2*). The latter is the product of a 1,5-dipolar electrocycloaddition of **6**. The generation of **6** (R¹ = C₇H₁₅, R² = 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 results in the formation of 5-alkoxy-4,5-dihydro-1,2,3-thiadiazoles [6], which cannot be used for the generation of thiocarbonyl *S*-methanides. Instead, they eliminate easily alcohol to yield 1,2,3-thiadiazoles [9,10].

In a previous paper we have described the behaviour of phosphonylated thiocarbonyl *S*-methanides, 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 present paper, reactions of phosphonylated thiocarbonyl *S*-methanides with $\text{C}=\text{S}$, $\text{C}=\text{C}$, and $\text{N}=\text{N}$ 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 thiocarbonyl *S*-methanides of type **11**, was observed between -40 and -35° . The crude mixtures were analyzed by $^1\text{H-NMR}$ spectroscopy.

The first experiment was carried out using the most efficient thiocarbonyl compound for [2+3]-cycloadditions with thiocarbonyl *S*-methanides, *i.e.*, 9*H*-fluorene-9-thione (**12a**) [13]. The reactions of the latter with thiobenzophenone *S*-methanide yields 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 **11a** with **12a** showed that two regioisomeric 1,3-

dithiolanes have been formed in comparable amounts along with some minor by-products²). 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 9*H*-fluorene-9-thione *S*-methanide [15]. In agreement with the expected value, the 2-CH₂ absorption in the ¹³C-NMR spectrum appeared at 32.2 ppm. The second isomer, **14a**, showed the signal of the 5-CH₂ group at 51.1 ppm, which is a typical value for ('5-CH₂-1,3-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.

Scheme 3

In a second series of experiments, thiobenzophenone (**12b**), which is another reactive dipolarophile, was used to intercept thiocarbonyl *S*-methanides **11**. Only the sterically more hindered cycloadducts **15a** and **15b** [15] were obtained in modest yields (*Scheme 3*). The ¹H-NMR spectrum of the crude mixture indicated the presence of substantial amounts of by-products, which result 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 decompose 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 ¹H-NMR spectrum.

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

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]).

In a previous paper, reactions of **10a** with aromatic and cycloaliphatic *S*-methanides, which lead to phosphorylated 1,3-dithiolanes, were described [15]. The results show that the electron-withdrawing phosphoryl group increases the dipolarophilicity of the C=S group in reactions with thiocarbonyl *S*-methanides. Therefore, the thiocarbonyl *S*-methanide **11a**, generated from **10a** and CH₂N₂, was treated with **10a** at *ca.* -40°, and after warming to room temperature, a single 1,3-dithiolane **16** was obtained. The absorption of CH₂ in the ¹³C-NMR spectrum appeared at 46.3 ppm, indicating that the sterically less crowded '5-CH₂' isomer was formed (*Scheme 4*). A similar result was obtained when the thiocarbonyl *S*-methanide **11b** was trapped with *C*-sulfonylated dithioformate **17**. Again, a single '5-CH₂' isomer **18** was formed ($\delta(\text{CH}_2) = 43.9$ ppm). No attempts were made to determine the relative configuration of the products.

Scheme 4

In contrast to the activated 'dithioesters' **10** and **17**, methyl dithiobenzoate was not able to intercept transient *S*-methanides **11**.

In general, thiocarbonyl *S*-methanides, being electron-rich 1,3-dipoles, react smoothly with electron-poor C=C-dipolarophiles. According to *Huisgen et al.*, tetracyanoethylene (TCNE) is the most reactive C=C interceptor of thiobenzophenone *S*-methanide [13]. As expected, TCNE undergoes an efficient [2+3]-cycloaddition with **11a** to give the tetrahydrothiophene derivative **19** in 75% yield (*Scheme 5*).

Scheme 5

The reactions with fumaronitrile and dimethyl acetylenedicarboxylate, 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. Similarly, the reactions of **11a** and **11b** with *N*-phenylmaleimide 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 (*Figure*). In both cases, the two five-membered rings are *cis*-fused and the phosphono group is *exo* oriented, while the methylsulfonyl group occupies the *endo* position. Both of the Et groups of **21b** are disordered over two conformations. In both compounds, **20a** and **21b**, both five-membered rings have half-chair conformations. The S-containing ring of **20a** is twisted on C(5)–S(1), 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).

Figure. ORTEP Plots [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)

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

In conclusion, the presented results show that phosphonylated dithioformates **10** can be used as precursors of phosphonylated thiocarbonyl *S*-methanides, which are versatile building blocks for the preparation of phosphonylated *S*-heterocycles. Moreover, compounds **10** were shown to act as dipolarophiles in reactions with thiocarbonyl *S*-methanides, to give phosphonylated 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 thiocarbonyl *S*-methanides, 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]. The $^{31}\text{P}\{1\text{H}\}$ NMR spectra were recorded on a *Bruker DRX 400* spectrometer, in CDCl_3 ; chemical shifts (δ) in ppm relative to H_3PO_4 (85%) as an external standard.

2. *Starting materials*. Methyl (Diisopropoxy)phosphonodithioformate (**10a**) and (diethoxy)phosphonodithioformate (**10b**) were prepared from the corresponding phosphites and CS_2 following a known protocol [19]. *9H*-Fluorene-9-thione (thiofluorenone) (**12a**) was prepared by treatment of *9H*-fluorene-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*-benzenesulfonyldithioformate (**17**) was prepared in a two step procedure from *S*-phenyl *C*-chlorodithioformate following a protocol of *Senning* and

coworkers [23]. Tetracyanoethene, dimethyl azodicarboxylate, maleic anhydride and *N*-phenyl maleimide were purchased from *Sigma-Aldrich* and used without further purification.

3. *Reactions of dithioformates 10a and 10b with CH₂N₂*. A soln. of **10a** or **10b** (1 mmol) in abs. THF (1 ml) was placed under an atmosphere of N₂ in a round-bottom flask equipped with a magnetic stirring bar. The orange-red soln. was cooled to –65° in an acetone/dry ice bath, and while stirring, a freshly prepared soln. of CH₂N₂ in Et₂O was added dropwise until the color of the starting material vanished.

4. *Reactions of in situ generated Phosphonylated Thiocarbonyl Ylides 11a and 11b with Dipolarophiles. General Procedure*. To a colorless soln. obtained according to the protocol described in *Section 3* and stirred at –65°, 1.1 mmol of the corresponding dipolarophile was added in portions. Then, the soln. was slowly warmed to r.t., and between –40° and –35° a rapid evolution of N₂ was observed. The mixture was stirred at r.t. for 1 h and evaporated i.v. The crude mixture was analysed by ¹H-NMR spectroscopy 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 reaction yielded **13a** and **14a**, which were separated on prep. TLC plates (SiO₂, CH₂Cl₂).

Diisopropyl {5-(Methylsulfonyl)spiro[1,3-dithiolane-4,9'-[9'H]fluoren]-5-yl}phosphonate (13a). More polar fraction. Yield: 150 mg (32%). Colorless crystals. M.p. 117–119° (hexane/CH₂Cl₂). IR (KBr): 2978_s, 2919_m, 1447_s, 1384_m, 1373_m, 1241_{vs} (P=O), 1104_s, 1009_{vs} (P–O–C), 992_{vs}, 741_s, 562_s. ¹H-NMR: 0.64, 0.78, 0.99, 1.04 (4_d, J_{H-H} = 6.2, 2 Me₂CH); 2.46 (d, ⁴J_{H-P} = 0.5, MeS); 4.22, 4.42 (AB, J_{H-H} = 8.7, CH₂); 4.30–4.53 (m, 2 Me₂CH); 7.18–7.61 (m, 6 arom. H); 8.16–8.19 (m, 2 arom. H). ¹³C-NMR: 17.0 (MeS); 22.2, 23.1, 23.5, 24.0 (4_d, ³J_{C-P} = 3.5, 2 (Me)₂CH); 32.2 (d, ³J_{C-P} = 10.6, CH₂); 71.1, 73.2 (2_d, ²J_{C-P} =

8.3, 2 Me₂CH); 72.0 (C_q); 74.5 (*d*, ¹J_{C-P} = 85.0, C_q); 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-C₄H₁₀): 467 (3, [M+1]⁺), 419 (100, [M-MeS]⁺), 389 (5), 377 (6). Anal. calc. for C₂₂H₂₇O₃PS₃ (466.61): C 56.63, H 5.83, S 20.62; found: C 56.75, H 5.92, S 20.36.

Diisopropyl {2-(Methylsulfanyl)spiro[1,3-dithiolane-4,9'-[9'H]fluoren]-2-yl}phosphonate (**14a**). Less polar fraction. Yield 150 mg (32%). Thick, pale yellow oil. IR (neat): 2981_{vs}, 2922_s, 1738_m, 1448_{vs}, 1385_s, 1244_{vs} (P=O), 1103_{vs}, 1010_{vs} (P-O-C), 989_{vs}, 897_s, 750_{vs}, 560_s. ¹H-NMR: 1.41 (*d*, J_{H-H} = 7.0, Me₂CH); 2.52 (*s*, MeS); 3.60, 4.03 (*AB*, J_{H-H} ≈ 14, ⁴J_{H-P} ≈ 1.3, CH₂); 4.71–5.20 (*m*, 2 Me₂CH); 7.20–8.29 (*m*, 8 arom. H). ¹³C-NMR: 16.9 (*d*, ³J_{C-P} = 0.7, MeS); 23.7, 24.0, 24.6 (2 Me₂CH); 51.1 (*d*, ³J_{C-P} ≈ 2.4, CH₂); 69.5 (*d*, ¹J_{C-P} ≈ 140, C_q); 73.7, 74.2 (2*d*, ²J_{C-P} ≈ 4.5, 2 Me₂CH); 73.8 (C_q); 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). ³¹P-NMR: 15.50. Anal. calc. for C₂₂H₂₇O₃PS₃ (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 reaction yielded products **13b** and **14b**, which were separated on prep. TLC plates (SiO₂, hexane/AcOEt (7:3)).

Diethyl {5-(Methylsulfanyl)spiro[1,3-dithiolane-4,9'-[9'H]fluoren]-4-yl}phosphonate (**13b**). More polar fraction. Yield: 220 mg (49%). Colorless crystals. M.p. 83–85° (hexane/Et₂O). IR (KBr): 2977_m, 1447_s, 1243_{vs} (P=O), 1055_{vs}, 1023_{vs} (P-O-C), 981_s, 746_s, 556_s. ¹H-NMR: 0.86 (*td*, J_{H-H} = 7.0, ⁴J_{H-P} = 0.5, MeCH₂); 0.92 (*t*, J_{H-H} = 7.0, MeCH₂); 2.47 (*s*, MeS); 3.41–3.87 (*m*, 2 MeCH₂); 4.23, 4.44 (*AB*, J_{H-H} = 8.7, CH₂); 7.19–7.39 (*m*, 4 arom. H); 7.59–7.64 (*m*, 2 arom. H); 8.14–8.19 (*m*, 2 arom. H). ¹³C-NMR: 15.8, 15.9 (2*d*, ³J_{C-P} ≈ 5.5, 2 MeCH₂); 16.9 (MeS); 32.4 (*d*, ³J_{C-P} = 10.8, CH₂); 63.0, 64.9 (2*d*, ²J_{C-P} ≈ 7.6, 2 MeCH₂); 72.3 (C_q); 74.9 (*d*, ¹J_{C-P} ≈ 85.0, C_q); 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 (NH₃): 456 (9, [M+NH₄]⁺), 439

(21, $[M+1]^+$), 391 (100, $[M-\text{MeS}]^+$), 361 (30). Anal. calc. for $\text{C}_{20}\text{H}_{23}\text{O}_3\text{PS}_3$ (438.55): C 54.77, H 5.27, S 21.93; found: C 54.54, H 5.39, S 21.70.

Diethyl {2-(Methylsulfanyl)spiro[1,3-dithiolane-4,9'-[9'H]fluoren]-2-yl}phosphonate (14b). Less polar fraction. Yield: 120 mg (27%). Colorless crystals. M.p. 56–58° (Et₂O, –76°). IR (KBr): 2981_s, 2917_m, 1447_s, 1247_{vs} (P=O), 1162_m, 1050_{vs}, 1019_{vs} (P–O–C), 747_{vs}, 738_{vs}, 560_{vs}. ¹H-NMR: 1.31 (*t*, $J_{\text{H-H}} = 7.0$, 2 MeCH₂); 2.56 (*s*, MeS); 3.70, 3.98 (*AB*, $J_{\text{H-H}} \approx 14$, $^4J_{\text{H-P}} \approx 1.3$ (only for the low-field H), CH₂); 4.20–4.60 (*m*, 2 MeCH₂); 7.20– 8.20 (*m*, 8 arom. H). ¹³C-NMR: 16.5, 16.7 (*d*, $^3J_{\text{C-P}} \approx 5.5$, 2 MeCH₂); 17.3 (MeS); 51.0 (*d*, $^3J_{\text{C-P}} \approx 3$, CH₂); 65.2, 65.5 (*2d*, $^2J_{\text{C-P}} \approx 7.5$ and 6.7, resp., 2 MeCH₂); 73.8 (*d*, $^3J_{\text{C-P}} = 5.0$, C_q(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_q(2) not found. CI-MS (NH₃): 456 (12, $[M+\text{NH}_4]^+$), 439 (11, $[M+1]^+$), 391 (100, $[M-\text{MeS}]^+$). Anal. calc. for $\text{C}_{20}\text{H}_{23}\text{O}_3\text{PS}_3$ (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 reaction yielded **15a**, which was isolated by trituration of the solid residue, obtained after evaporation of the solvent, with hexane. After filtration, the crude material was purified by crystallisation from hexane/Et₂O.

Diisopropyl {4-(Methylsulfanyl)-5,5-diphenyl-1,3-dithiolan-4-yl}phosphonate (15a). Yield: 150 mg (32%). Colorless crystals. M.p. 170–172° (hexane/Et₂O). IR (KBr): 2980_m, 2920_w, 1244_s (P=O), 1105_m, 1005_{vs} (P–O–C), 699_m, 559_m. ¹H-NMR: 1.05, 1.13, 1.19, 1.21 (*4d*, $J_{\text{H-H}} = 6.2$, 2 Me₂CH); 2.45 (*d*, $^4J_{\text{H-P}} = 0.50$, MeS); 3.86, 3.94 (*AB*, $J_{\text{H-H}} = 16.0$, CH₂); 4.46–4.56, 4.59–4.69 (*2m*, 2 Me₂CH); 7.01–7.76 (*m*, 10 arom. H). ¹³C-NMR: 18.9 (MeS); 23.3, 23.5 (*2d*, $^3J_{\text{C-P}} = 6.8$ and 6.0, resp., Me₂CH); 24.2 (Me₂CH); 31.8 (*d*, $^3J_{\text{P-C}} = 5.6$, CH₂); 72.7 (*d*, $^2J_{\text{C-P}} = 8.5$, 2 Me₂CH); 126.7, 126.8 (*2d*, $^4J_{\text{C-P}} = 3.8$, 4 arom. CH); 127.4 (2 arom. CH); 130.7, 131.1 (4 arom. CH); 143.0 (*d*, $^3J_{\text{C-P}} = 6.0$, arom. C); 145.0 (*d*, $^3J_{\text{C-P}} = 1.6$, arom.

C); C_q(4), C_q(5) not found. ³¹P-NMR: 15.7. CI-MS (NH₃): 469 (43, [M+1]⁺), 421 (100, [M-MeS]⁺), 391 (57), 377 (98), 199 (33).

4.4. *Reaction of 11b with 12b.* The reaction yielded **15b**, which was isolated by trituration of the semi-solid residue, obtained after evaporation of the solvent, with hexane. After filtration, the crude material was purified by crystallisation from hexane/CH₂Cl₂.

Diethyl {4-(Methylsulfanyl)-5,5-diphenyl-1,3-dithiolan-4-yl}phosphonate (15b). Yield: 140 mg (32%). Colorless crystals. M.p. 189–191° (hexane/CH₂Cl₂). IR (KBr): 2985_w, 1443_w, 1249_s (P=O), 1055_{vs}, 1023_{vs} (P–O–C), 971_s, 700_s, 560_s. ¹H-NMR: 0.97, 1.23 (2_t, J_{H-H} = 6.9, 2 MeCH₂); 2.49 (d, ⁴J_{H-P} = 0.55, MeS); 3.62–4.22 (m, 2 MeCH₂); 3.88, 3.97 (AB, J_{H-H} = 9.3, CH₂); 7.17–7.27, 7.60–7.66, 7.76–7.79 (3_m, 10 arom. H). ¹³C-NMR: 15.9, 16.3 (2_d, ³J_{C-P} = 5.6, 2 MeCH₂); 18.5 (MeS); 31.7 (d, ³J_{C-P} = 5.7, CH₂); 63.7, 64.1 (2_d, ²J_{C-P} = 8.2, 2 MeCH₂); 126.8, 127.6, 130.4, 131.0 (10 arom. CH); 141.6, 142.9 (2 arom. C); C_q(4), C_q(5) not found. CI-MS (NH₃): 441 (30, [M+1]⁺), 393 (100, [M-MeS]⁺). Anal. calc. for C₂₀H₂₅O₃PS₃ (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 reaction yielded **16**, which was purified by prep. TLC (SiO₂, Et₂O). An analytically pure sample was obtained by crystallisation from pentane at –76°.

Tetraisopropyl [2,4-Bis(methylsulfanyl)-1,3-dithiolane]-1,4-diphosphonate (16). Yield: 260 mg (51%). Colorless crystals. M.p. 47–49° (pentane). IR (KBr): 2978_s, 2923_m, 1467_m, 1383_s, 1244_{vs} (P=O), 1142_m, 1104_s, 1012_{vs} (P–O–C), 982_{vs} (P–O–C), 894_m, 553_s. ¹H-NMR: 1.35 (d, J_{H-H} = 7.0, 4 Me₂CH); 2.41 (br.s, 2 MeS); 3.30, 4.10 (AB-like m, J_{H-H} ≈ 13.0, CH₂); 4.61–5.10 (m, 4 Me₂CH). ¹³C-NMR (C₆D₆): 16.1, 19.1 (2 MeS); 23.7, 23.8, 24.0, 24.1, 24.6, 24.7, 24.8 (4 Me₂CH); 46.3 (d, ³J_{C-P} ≈ 6.7, CH₂); 72.8 (dd, ¹J_{C-P} = 147.0, ³J_{C-P} = 5.2,

$C_q(4)$); 73.7, 73.9, 74.1, 74.3 (4 Me_2CH); $C_q(2)$ 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 reaction yielded **18**, which was purified by prep. TLC (SiO_2 , hexane/AcOEt (3:2)).

Diethyl (4-Benzenesulfonyl-2-methylsulfanyl-4-phenylsulfanyl-1,3-dithiolan-2-yl)phosphonate (18). Yield: 350 mg (65%). Thick, pale yellow oil. IR (neat): 2985 m , 1446 m , 1325 s , 1252 s (P=O), 1147 s , 1049 vs , 1020 vs (P–O–C), 974 s , 754 s . 1H -NMR: 1.37, 1.38 (2 td , $J_{H-H} = 7$, $^4J_{H-P} = 0.62$ and 0.66 , resp., $MeCH_2$); 2.18 (d , $^4J_{H-P} = 0.75$, MeS); 3.47, 4.10 (AB -like, $J_{H-H} = 13$, $^3J_{H-P} = 1.6$ 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 , $^3J_{C-P} = 5.5$, CH_2); 65.3, 65.5 (2 d , $^2J_{C-P} = 7.3$, 2 $MeCH_2$); 71.5 (d , $^1J_{C-P} = 160$, C_q); 97.3 (d , $^3J_{C-P} = 7$, C_q); 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 tetracyanoethylene (TCNE)*. The mixture was separated chromatographically on a SiO_2 column using hexane with increasing amounts of CH_2Cl_2 as the eluent. An analytically pure sample was obtained by crystallisation from MeOH at -76° .

Diisopropyl [3,3,4,4-Tetracyano-2-(methylsulfanyl)tetrahydrothiophen-2-yl]phosphonate (19). Yield: 300 mg (75%). Colorless crystals. M.p. 26–27° (MeOH). IR (KBr): 2985 s , 2937 m , 2254 w ($C\equiv N$), 1452 m , 1389 s , 1259 s (P=O), 1099 s , 1001 vs (P–O–C), 758 vs . 1H -NMR: 1.44–1.51 (m , 2 Me_2CH); 2.58 (d , $^4J_{H-P} = 0.5$, 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 C_q 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-phenyl maleimide.* Products **20a** and **21a** were isolated by trituration of the semi-solid residues obtained, after evaporation of the solvent, with hexane/CH₂Cl₂. Analytically pure samples were obtained by crystallization from hexane/CH₂Cl₂.

Diisopropyl exo-(6-endo-Methylsulfanyl-2,4-dioxo-3-oxa-7-thiabicyclo[3.3.0]octan-6-yl)phosphonate (20a). Yield: 300 mg (81%). Colorless crystals. M.p. 121–123° (hexane/CH₂Cl₂). IR (KBr): 2983*m*, 2976*m*, 2929*m*, 1856*m*, 1782*vs*, 1388*m*, 1376*m*, 1243*vs* (P=O), 1218*s*, 1012*vs* (P–O–C), 997*s*, 986*s*, 934*m*, 558*s*. ¹H-NMR: 1.41, 1.42 (*2dd*, ⁴J_{H-P} ≈ 4.0 and ≈ 5.0, resp., 2 Me₂CH); 2.38 (*s*, MeS); 3.44–3.56 (*m*, CH₂); 4.03–4.19 (*m*, 2 CH); 4.77–4.99 (*m*, 2 Me₂CH). ¹³C-NMR: 16.0 (MeS); 23.4, 23.7, 23.9 (*3d*, ³J_{C-P} ≈ 6.7, 5.4, and 3.6, resp., 3 Me of 2 Me₂CH); 24.5 (*s*, 1 Me of 2 Me₂CH); 33.5 (*d*, ³J_{C-P} ≈ 2.5, CH₂); 53.1 (*d*, ²J_{C-P} ≈ 4.7, CH); 56.6 (*d*, ³J_{C-P} ≈ 3.5, CH); 73.3, 75.1 (2 Me₂CH); 171.1 (CO). CI-MS (NH₃): 386 (100, [M+NH₄]⁺), 369 (27, [M+1]⁺), 344 (10), 277 (6). Anal. calc. for C₁₃H₂₁O₆PS₂ (368.41): C 42.38, H 5.75, S 17.41; found: C 42.40, H 5.69, S 17.18.

Diisopropyl exo-(2-endo-Methylsulfanyl-7-phenyl-6,8-dioxo-3-thia-7-azabicyclo[3.3.0]octan-2-yl)phosphonate (21a). Yield: 240 mg (54%). Colorless crystals. M.p. 99–100° (hexane/CH₂Cl₂). IR (KBr): 2981*m*, 2925*w*, 1776*w*, 1713*vs*, 1498*s*, 1387*s*, 1241*s* (P=O), 1193*m*, 1011*vs* (P–O–C), 984*vs*, 565*m*. ¹H-NMR: 1.40, 1.42 (*2d*, J = 7.8 and 5.9, resp., 2 Me₂CH); 2.41 (*s*, MeS); 3.51 (*d*, ⁴J_{H-P} ≈ 5.5, CH₂); 3.88–3.94 (*m*, CH); 4.07 (*dd*, J_{H-H} = 14.6, ⁴J_{H-P} ≈ 8.5, CH); 4.83–4.98 (*2m*, 2 Me₂CH); 7.26–7.49 (*m*, 5 arom. CH). ¹³C-NMR: 16.2 (MeS); 23.5, 23.6, 24.2, 24.3 (*4d*, ³J_{C-P} ≈ 4.0, 2 Me₂CH); 33.2 (*d*, ³J_{C-P} ≈ 2.5, CH₂); 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., Me₂CH); 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 (NH₃): 461 (64 [M+NH₄]⁺), 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*-phenyl maleimide. Products **20b** and **21b** were isolated by trituration of the solid residues, obtained after evaporation of the solvent, with hexane/Et₂O and hexane/CH₂Cl₂, respectively. Analytically pure products were obtained by crystallization from the same solvents.

Diethyl *exo*-(6-endo-Methylsulfanyl-2,4-dioxo-3-oxa-7-thiabicyclo[3.3.0]octan-6-yl)phosphonate (**20b**). Yield: 143 mg (42%). Colorless crystals. M.p. 104–106° hexane/Et₂O). IR (KBr): 2981*m*, 2964*m*, 2928*w*, 1861*m*, 1786*vs* (C=O), 1254*m*, 1233*s* (P=O), 1086*s*, 1060*s*, 1020*s* (P–O–C), 973*m*, 957*m*, 555*s*. ¹H-NMR: 1.40, 1.41 (2*t*, $J_{H-H} = 2$ MeCH₂); 2.38 (*s*, MeS); 3.49 (*d*, $^4J_{H-P} \approx 4.4$, CH₂); 4.07–4.42 (*m*, 2 MeCH₂, 2 CH). ¹³C-NMR: 15.9 (MeS); 16.3, 16.4 (2*d*, $^3J_{C-P} \approx 6.0$, 2 MeCH₂); 33.3 (*d*, $^3J_{C-P} \approx 3.0$, CH₂); 52.9 (*d*, $^2J_{C-P} \approx 5.5$, CH); 56.8 (*d*, $^3J_{C-P} \approx 3.7$, CH); 61.5 (*d*, $^1J_{C-P} \approx 150.0$, C_q); 64.2(*d*, $^2J_{C-P} \approx 7.7$, MeCH₂); 65.9 (*d*, $^2J_{C-P} \approx 7.4$, MeCH₂); 165.8, 170.9 (2 C=O). CI-MS (NH₃): 358 (100, [M+NH₄]⁺), 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 *exo*-(2-endo-methylsulfanyl-7-phenyl-6,8-dioxo-3-thia-7-azabicyclo[3.3.0]octan-2-yl)phosphonate (**21b**). Yield: 255 mg (61%). Colorless crystals. M.p. 141–143° (hexane/CH₂Cl₂). IR KBr): 2981*w*, 2923*w*, 1775*w*, 1713*vs* (C=O), 1497*m*, 1389*s*, 1241*s* (P=O), 1196*s*, 1048*s*, 1017*s* (P–O–C), 564*m*. ¹H-NMR: 1.40, 1.41 (2*td*, $J_{H-H} = 7.8$, $^4J_{H-P} \approx 1.1$ and 0.7, resp., 2 MeCH₂); 2.40 (*d*, $^4J_{H-P} \approx 0.5$, MeS); 3.43–3.55 (*m*, CH₂); 3.91–3.98 (*m*, CH); 4.15 (*dd*, $J_{H-H} = 14.0$, $^3J_{H-P} \approx 8.8$, CH); 4.26–4.43 (*m*, 2 MeCH₂); 7.27–7.49 (*m*, 5 arom. CH). ¹³C-NMR: 16.0 (MeS); 16.3, 16.4 (2*d*, $^3J_{C-P} \approx 5.4$, 2 MeCH₂); 32.9 (*d*, $^3J_{C-P} \approx 3.2$, CH₂); 52.5 (*d*, $^2J_{C-P} \approx 6.3$, CH); 55.9 (*d*, $^3J_{C-P} \approx 2.6$, CH); 62.5 (*d*, $^1J_{C-P} \approx 160.0$, C_q); 63.9, 65.4 (2*d*, $^2J_{C-P} \approx 7.5$ and 7.4, resp., 2 MeCH₂); 126.4, 128.7, 129.1 (5 arom. CH); 131.7 (1 arom. C); 171.2 (*d*, $^3J_{C-P} \approx 5.4$, C=O); 175.6 (C=O). CI-MS (NH₃): 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 azodicarboxylate.* Product **22** was purified by prep. TLC (SiO_2 , CH_2Cl_2/Et_2O 1:4). The isolated material was purified by crystallisation from hexane/ CH_2Cl_2 .

Dimethyl 2-(Diisopropoxy)phosphonyl-2-methylsulfanyl-1,3,4-thiadiazolidine-3,4-dicarboxylate (22). Yield: 300 mg (72%). Colorless crystals. M.p. 97–99° (hexane/ CH_2Cl_2). IR (KBr): 2981 m , 1736 vs (C=O), 1735 vs (C=O), 1448 s , 1352 vs , 1254 vs (P=O), 1238 s , 1200 s , 1024 s , 995 vs (P–O–C), 565 s . 1H -NMR: 1.25–1.40 (m , 2 Me_2CH); 2.40 (s , MeS); 3.80, 3.81 ($2s$, 2 MeO); 4.36, 5.25 (AB , $J_{H-H} \approx 9.6$, CH_2); 4.70–5.17 (m , 2 Me_2CH). ^{13}C -NMR: 17.1 (MeS); 23.3, 23.7, 24.0, 24.3 (2 Me_2CH); 49.4 (d , $^3J_{C-P} \approx 2.4$, CH_2); 53.8, 54.2 (2 MeO); 73.7, 74.7 ($2d$, $^2J_{C-P} \approx 8$, 2 Me_2CH); 83.6 (C_q); 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] using 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

⁴⁾ CCDC-265652–265653 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the *Cambridge Crystallographic Data Centre*, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax: + 44-(0)1223-336033; e-mail: deposit@ccdc.cam.ac.uk).

absorption correction based on the multi-scan method [26] was applied. The structures were solved by direct methods 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. Similar 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 restraint 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 using 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 using full-matrix least-squares procedures, which minimized the function $\sum w(F_o^2 - F_c^2)^2$. 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 using the *SHELXL97* [31] program.

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

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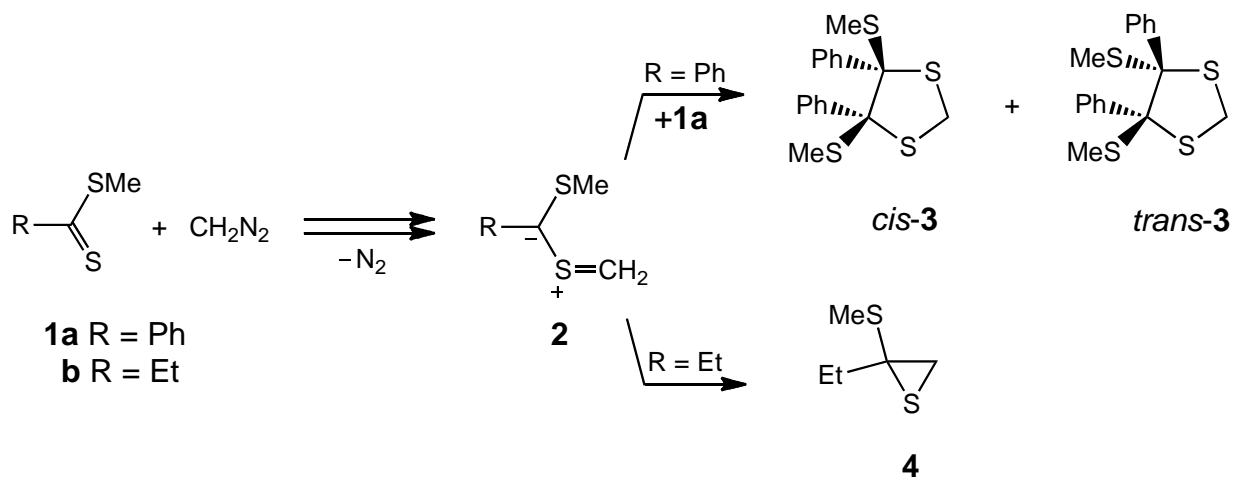
Legends

Figure. *ORTEP Plots* [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)

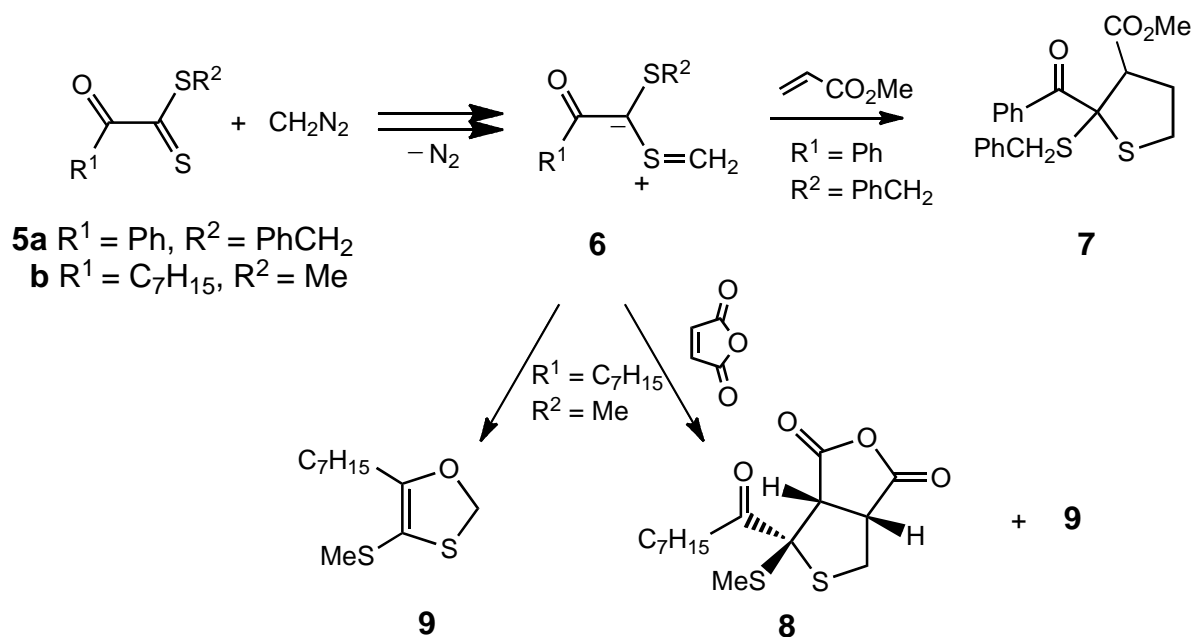
Table. Crystallographic Data for Compounds **20a** and **21b**

	20a	21b
Crystallized from	hexane/CH ₂ Cl ₂	hexane/CH ₂ Cl ₂
Empirical formula	C ₁₃ H ₂₁ O ₆ PS ₂	C ₁₇ H ₂₂ NO ₅ PS 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	<i>Pbca</i>	<i>P</i> $\bar{1}$
<i>Z</i>	8	2
Reflections for cell determination	74215	18089
2 θ range for cell determination [°]	4–55	4–60
Unit cell parameters <i>a</i> [Å]	13.0300(2)	8.0919(1)
<i>b</i> [Å]	15.6875(2)	11.2992(3)
<i>c</i> [Å]	17.4460(3)	12.1758(3)
α [°]	90	105.546(1)
β [°]	90	109.344(1)
γ [°]	90	102.319(1)
<i>V</i> [Å ³]	3566.10(9)	954.46(4)
<i>D_x</i> [g cm ⁻³]	1.372	1.445
μ (Mo <i>K</i> α) [mm ⁻¹]	0.410	0.391
Scan type	ϕ and ω	ϕ and ω
2 θ (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>I</i> > 2 σ (<i>I</i>)	3068	4328
Reflections used in refinement	4088	5573
Parameters refined; restraints	204; 0	278; 70
Final <i>R</i> (<i>F</i>) [<i>I</i> > 2 σ (<i>I</i>) reflections]	0.0374	0.0400
<i>wR</i> (<i>F</i> ²) (all data)	0.0945	0.1035
Weighting parameters [<i>a</i> ; <i>b</i>] ^a)	0.0408; 2.1826	0.0473; 0.4212
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

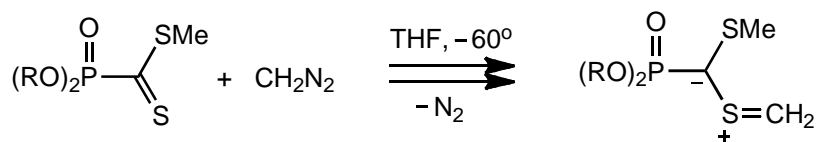
^a) $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$ where $P = (F_o^2 + 2F_c^2)/3$



Scheme 1

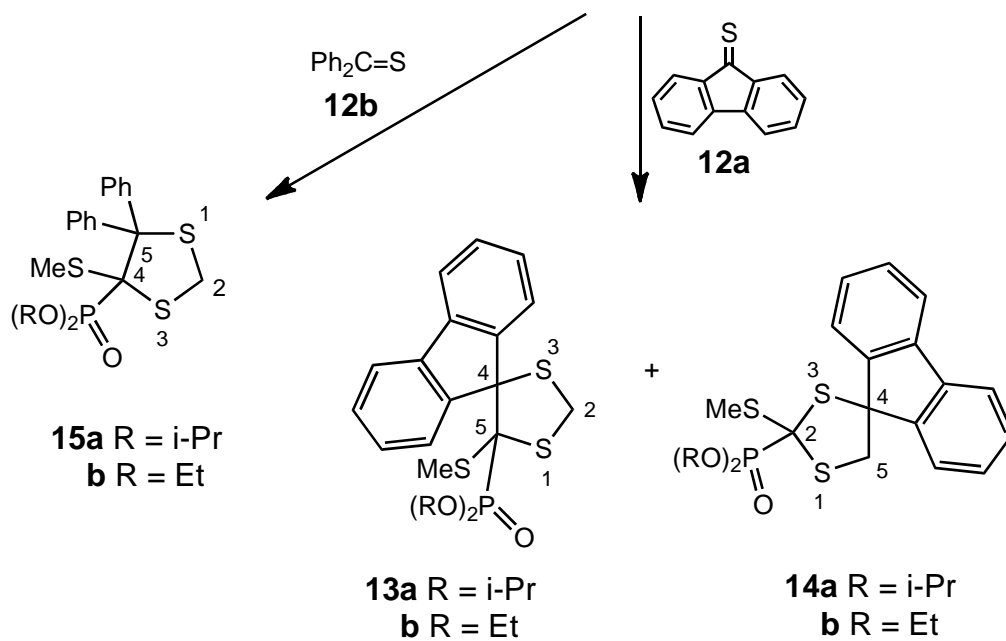


Scheme 2

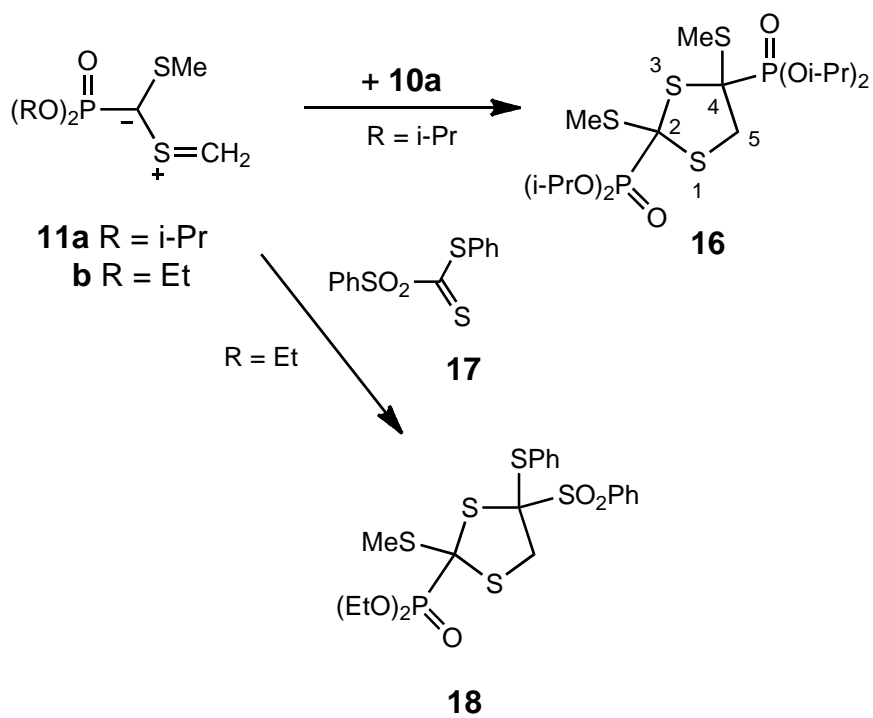


10a R = i-Pr
b R = Et

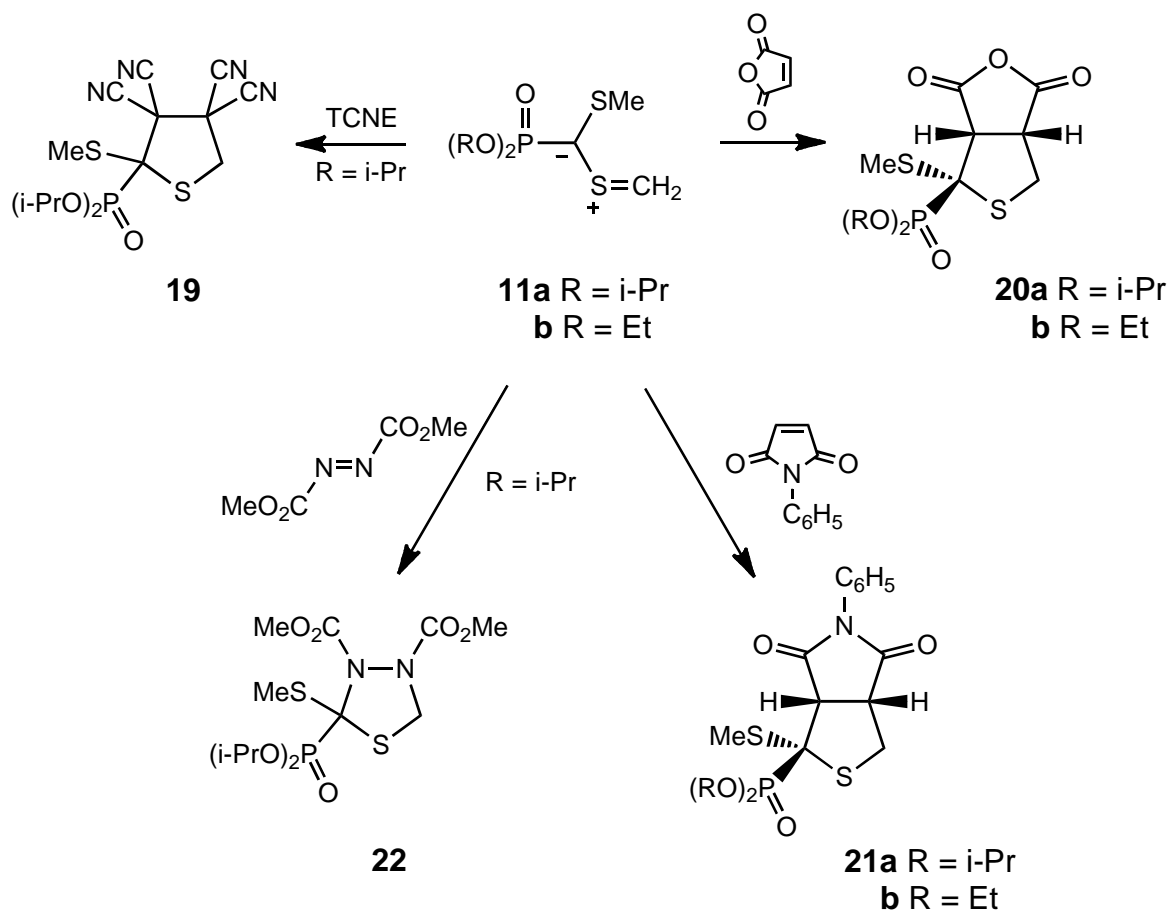
11a R = i-Pr
b R = Et



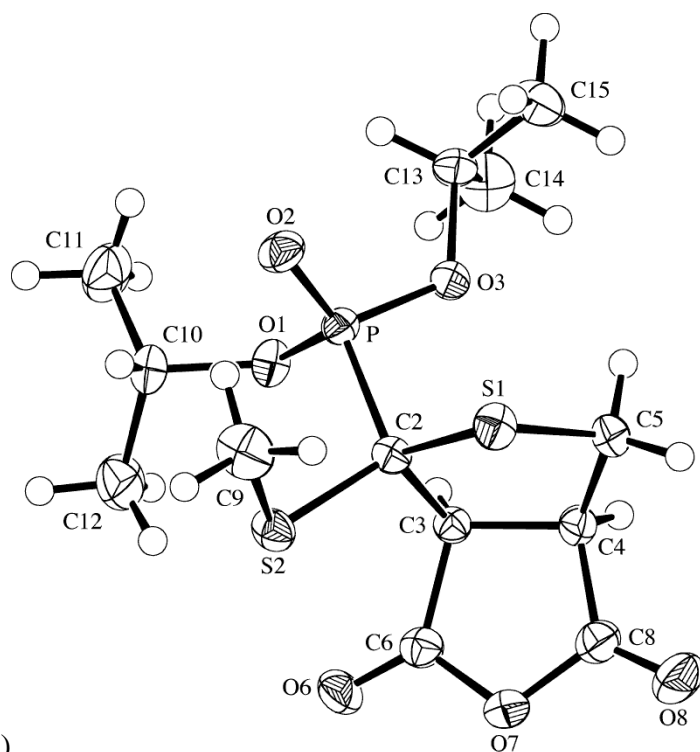
Scheme 3



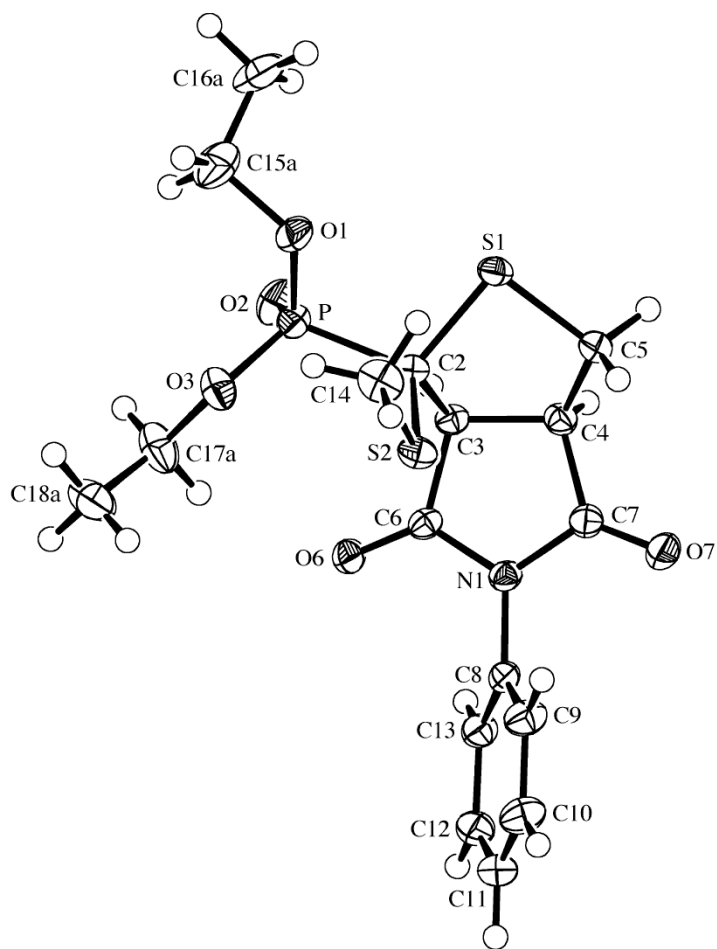
Scheme 4



Scheme 5



a)



b)

Figure