Thio- and Dithioesters as Dipolarophiles in Reactions with Thiocarbonyl Ylides

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The thiocarbonyl *S*-methylides **3a**–**c**, generated in situ by thermal decomposition of the corresponding 2,5-dihydro-1,3,4-thiadiazoles, undergo [3+2] cycloadditions with diphenyl trithiocarbonate (**5a**) to give 1,3-dithiolanes. The regioselectivity of the reaction of the cycloaliphatic dipoles **3b** and **3c** is reversed in comparison with that of the aromatic **3a**. A mixture of both regioisomeric cycloadducts is formed in the reaction between **3b** and methyl dithiobenzoate (**6a**), whereas only one regioisomer is obtained with thiophthalide (**7**). Dialkyl phosphonodithioformates **8** are shown to be efficient C=S dipolarophiles in reactions with thiocarbonyl *S*-methylides **3a**–**3d**, affording 1,3-dithiolane-4-phosphonates.

Introduction

As shown in numerous recent papers, thiocarbonyl ylides undergo efficient [3+2] cycloadditions with different dipolarophiles (cf. ref.[1,2]). As expected, electron-poor C=C dipolarophiles react easily with thiocarbonyl ylides to give thiophene derivatives. However, competitive experiments reported by Huisgen and co-workers showed that the C=S groups of thiocarbonyl compounds, especially of aromatic thioketones, are even more reactive than C=C bonds.[3] Whereas thioketones in general are known to be unstable compounds and therefore have limited use for preparative applications, thio- and dithioesters are relatively stable and conveniently available by diverse methods.[4] For this reason, they are promising starting materials in reactions with thiocarbonyl ylides for the preparation of multiple sulfur-containing heterocycles. The relative rate constants have shown that the reactivity of dithioesters and trithiocarbonates toward thiobenzophenone *S*-methylide (**3a**), generated by thermal decomposition of 2,5-dihydro-1,3,4-thiadiazole (**2a**; Scheme 1), is comparable with that of cycloaliphatic thioketones.[3] As examples of "cyclic dithioesters" (dithiolactones), 1,3-thiazole-5(4*H*)-thiones **4** (Figure 1) have frequently been used in 1,3-dipolar cycloadditions, including in reactions with thiocarbonyl ylides.[5,6] On the other hand, no cycloadditions of these dipoles with O-substituted monothioesters have been reported so far.

In this paper we report on reactions between 2,2,4,4-tetramethyl-3-thioxocyclobutanone *S*-methylide (**3b**) and different thio- and dithioesters (Figure 1). For comparison, some reactions with **3a**, adamantanethione *S*-methylide (**3c**), and 9*H*-fluorene-9-thione *S*-methylide (**3d**) are also included. For the first time, phosphonodithioformates **8**, which have recently been shown to be powerful heterodienophiles,[7] are used in reactions with thiocarbonyl ylides.

Results and Discussion

Treatment of thiocarbonyl ylide **3a** with diphenyl trithiocarbonate (**5a**) was previously reported to give 5,5-diphenyl-4,4-bis(phenylthio)-1,3-dithiolane (**10**) as a labile compound, which easily isomerized to an open-chain compound in the presence of acids in solution or during chromatography on silica gel.[8] The decomposition of 2,5-dihydro-1,3,4-thiadiazole **2b**, the precursor of **3b**, in THF at 45 °C in the presence of 2.5 equiv. of **5a** resulted in the formation of a single cycloadduct **9** with a characteristic ^{1}H NMR absorption for CH_2 at δ = 3.01 ppm. The product was isolated in moderate yields after chromatographic workup (Scheme 2). In the ^{13}C NMR spectrum, the CH_2 group absorbed at δ = 49.2 ppm, which is indicative of "5-CH_2 1,3-dithiolanes".[9] The structure assignment was confirmed by an X-ray crystal structure determination (Figure 2). The regioselectivity of the cycloaddition is the opposite of that observed with **3a**, but analogous to that seen with **3c**, which afforded **11**.[12]

In order to compare the dipolarophilicity of **5a** with that of its *O*,*O*-diphenyl analogue **5b**, its reaction with **2b**, the precursor of **3b**, was carried out under similar conditions.

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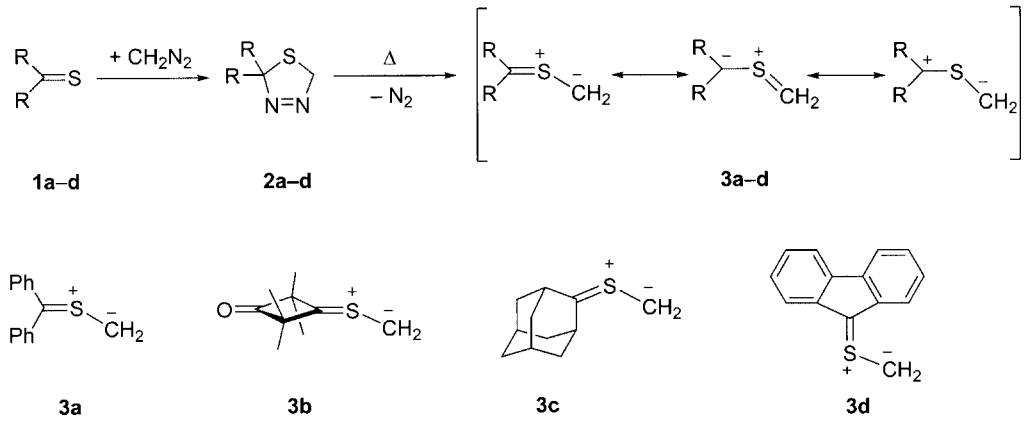


Scheme 1. Synthesis of thiocarbonyl ylides **3**.

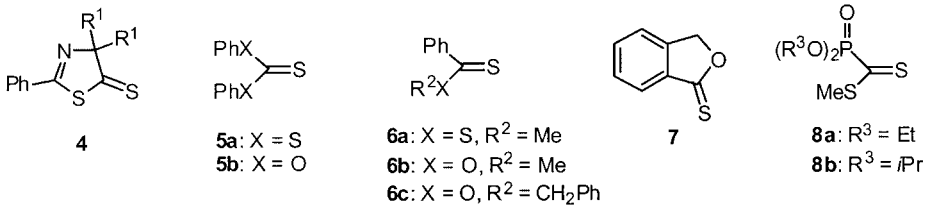
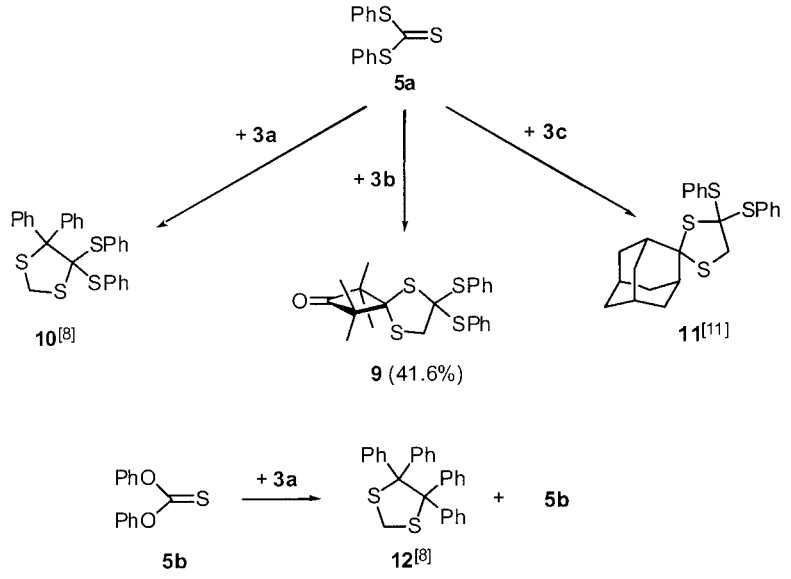


Figure 1. Thiocarbonyl compounds as dipolarophiles.



Scheme 2. Reactions of thiocarbonyl ylides **3** with trithiocarbonate **5a** and thiocarbonate **5b**.

In this case, however, ^{1}H NMR analysis of the crude mixture showed that no cycloadduct had been formed. Similarly, no cycloadditions could be achieved on treatment of *O*,*O*-diphenyl thiocarbonate (**5b**) with **3a** and **3c**. In the case of **3a**, only the formation of 4,4,5,5-tetraphenyl-1,3-dithiolane **12** was observed.[8]

Prompted by the different reactivities of **5a** and its *O*,*O*-diphenyl derivative **5b**, we carried out similar studies with methyl dithiobenzoate (**6a**), *O*-methyl thiobenzoate (**6b**), "thiophthalide" (**7**), and thiocarbonyl ylides **3**.[14] Thermolysis of **2b** in the presence of 1.1 equiv. of **6a** in THF at 45 °C resulted in a mixture of thiirane **15** and two cycloadducts **13** and **14** in a ratio of ca. 3:1 (^{1}H NMR; Scheme 3). The main cycloadduct was obtained in pure form after chromatographic workup and crystallization from hexane. The ^{1}H and ^{13}C NMR chemical shifts of the CH_2 group at 3.70/3.79 ppm (*AB* system) and 27.6 ppm, respectively, confirm the structure of the regioisomer **13**. The second isomer **14** was obtained as a 3:2 mixture with **13**. The characteristic NMR signals for the CH_2 group appear as an *AB* system at 3.86/3.95 ppm and 49.3 ppm. The analogous reaction of **3b** with the *O*-methyl thioester **6b** gave thiirane **15** as the

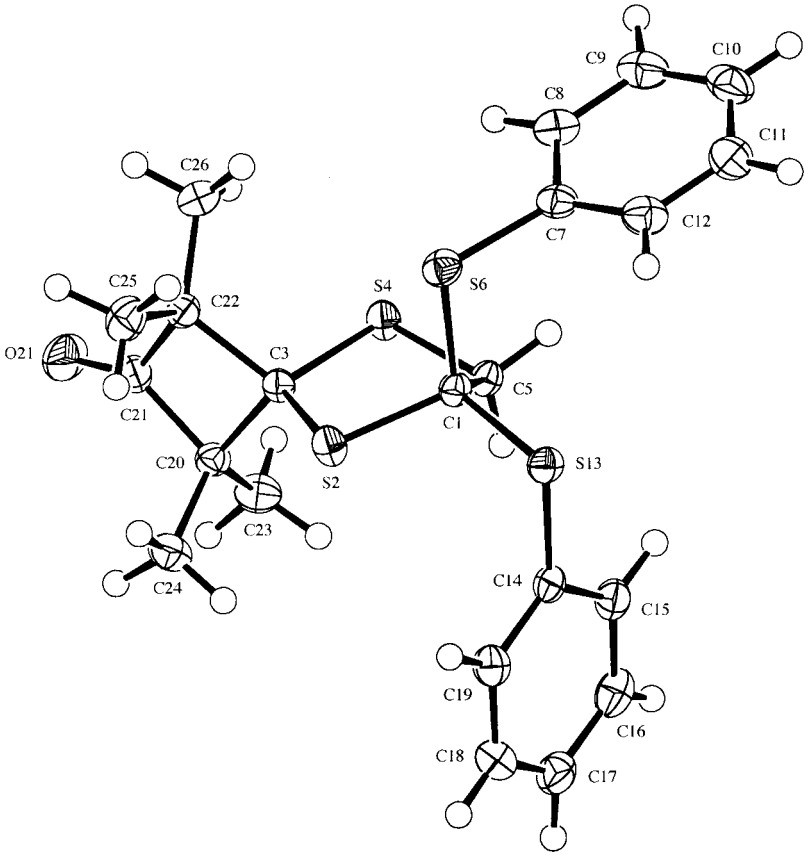
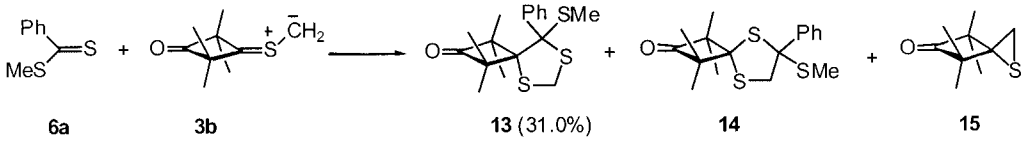


Figure 2. ORTEP plot[11] of the molecular structure of **9** (50% probability ellipsoids).



Scheme 3. Reaction between dithioester **6a** and thiocarbonyl ylide **3b**.

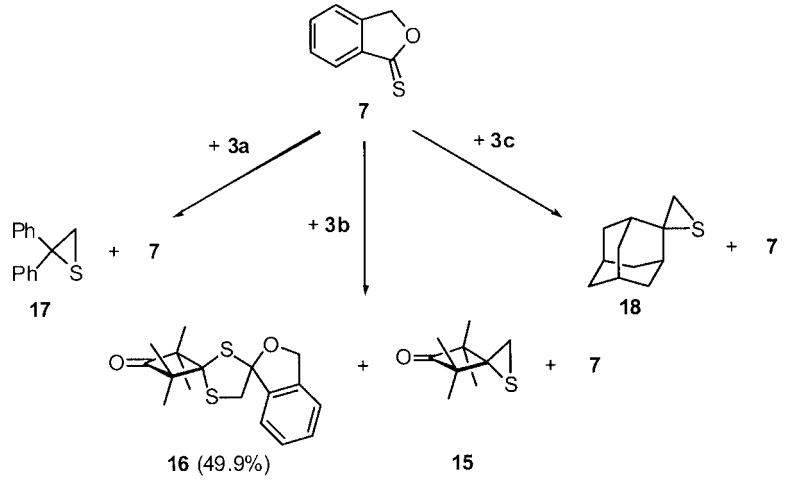
only product. Apparently, the ester **6b** is not reactive enough to intercept the intermediate **3b**.[14]

Thiophthalide (**7**) can be regarded as a cyclic *O*-alkyl thioester (i.e., a thionolactone).[15] The reaction between equimolar amounts of **7** and **3b** under typical conditions resulted in a crude mixture containing thiirane **15**, a 1:1 cycloadduct **16**, and starting material **7** (Scheme 4). The formation of **16** occurred regioselectively and no other cycloadduct could be detected (^{1}H NMR). The ratio of **15** to **16** was established as 1:2, similarly to the case of the experiment with **6a** described above. Characteristic signals for *AB* systems of two CH_2 groups of **16** were found in the ^{1}H NMR spectra: CH_2(11) appeared at δ = 3.67 and 3.46 ppm (J = 12 Hz) and CH_2(8) at δ = 5.16 and 5.09 ppm (J = 13 Hz). The corresponding signals in the ^{13}C NMR spectrum are at δ = 50.8 and 71.5 ppm. The chemical shift of CH_2(11) indicates the presence of the "5-CH_2 1,3-dithiolane" structure.

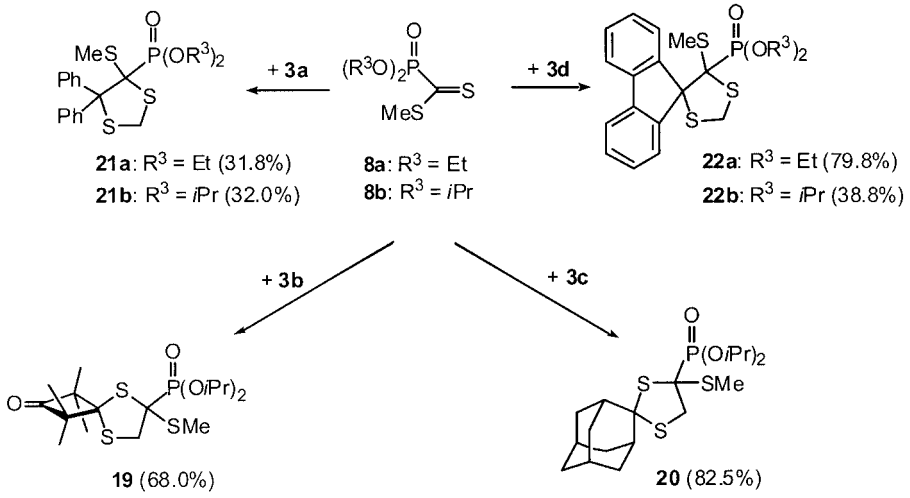
In contrast to the results obtained with **3b**, analogous treatment of thionolactone **7** with **3a** or **3c** did not yield the expected cycloadducts of type **16**. The only detectable products were the corresponding thiiranes **17** and **18**, formed by the 1,3-dipolar electrocyclization of **3a** and **3c**.

In particular, we were interested in the dipolarophilic reactivity of phosphonylated dithioformates **8**. Despite the fact that those compounds have been known since 1961[17] and their reactivity toward various nucleophiles[18] and dienes[7,19] has been studied, they have never been used as dipolarophiles. According to general rules, the presence of the electron-withdrawing phosphonyl group should enhance the dipolarophilicity of the C=S group toward electron-rich thiocarbonyl ylides compared with that of other dithioesters.

The reactions of **3b** and **3c** with **8b** occurred similarly, and ^{1}H NMR analyses of the crude mixtures confirmed the formation of only one 1:1 cycloadduct in each case. The



Scheme 4. Reactions of thioester **7** with thiocarbonyl ylides **3a**–**c**.



Scheme 5. Reactions of dithioesters **8** with thiocarbonyl ylides **3a**–**d**.

evidence for the regioselective formation of the product was the presence of only one MeS signal, at ca. 2.40 ppm. In contrast to the reactions of **3b** with **6a** and **7**, no thiirane **15** was formed. This observation fits well with our expectation that the phosphonyl group increases the dipolarophilic properties of the dithioester. Chromatographic workup gave the pure 1,3-dithiolanes **19** and **20** (Scheme 5), respectively, and these were characterized spectroscopically. In the ^{13}C NMR spectra, the signals for the CH_2 group of the 1,3-dithiolane ring were found at δ = 46.0 ppm for **19** and at δ = 44.5 ppm for **20**.[9] These values suggest that the cycloaliphatic thiocarbonyl *S*-methylides again afford the sterically less hindered products (i.e., the "5-CH_2 1,3-dithiolanes"). In the case of **20**, the structure was unambiguously confirmed by X-ray crystallography (Figure 3).

As already reported, the formation of 1,3-dithiolanes from aromatic thioketone *S*-methylides and C=S dipolarophiles occurs with inverse regioselectivity in relation to that obtained from aliphatic thiocarbonyl ylides.[12] This difference is a result of the stepwise mechanism in the case of the aromatic thiocarbonyl ylides, and diradical species are postulated as intermediates.[20] In view of this consideration, aromatic thiocarbonyl *S*-methylides **3a** and **3d**, generated in situ at low temperature from **2a** and **2d**, respectively,[8,21] were treated with **8a** and **8b**. Although the reaction partners **2** and **8** were used in equimolar amounts, the dithioesters **8** were not completely consumed. In each case, only one cycloadduct was formed, as evidenced by the presence of only one *singlet* for MeS in the ^1H NMR spectra. Chromatographic separation gave the 1,3-dithiolanes **21** and **22** in good yields.[22] The determination of the structures of the cycloadducts was based on their spectroscopic data. As mentioned above, the ^{13}C chemical shifts of the CH_2 group of the 1,3-dithiolane ring are most indicative. In all products, this signal appeared at 32.4–31.8 ppm and exhibited coupling with the P atom [^3J(C,P) = ca. 5.6 Hz

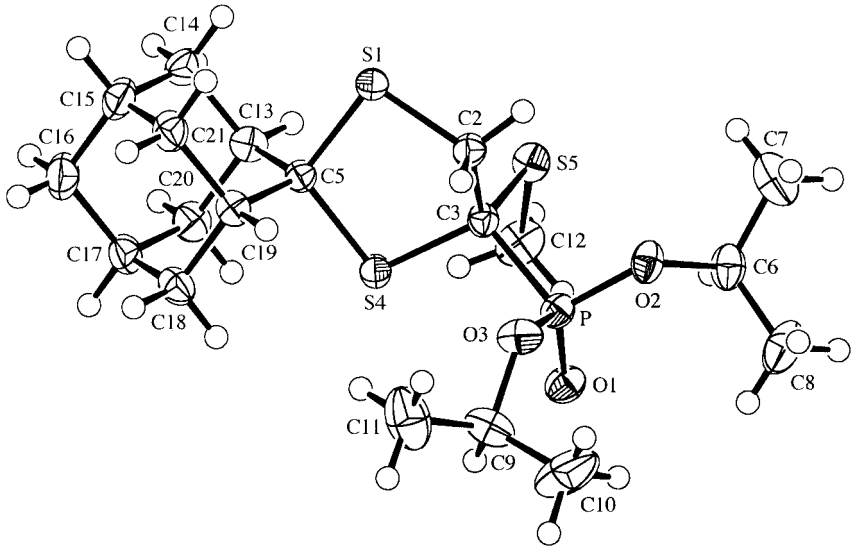


Figure 3. ORTEP plot[11] of the molecular structure of **20** (50% probability ellipsoids).

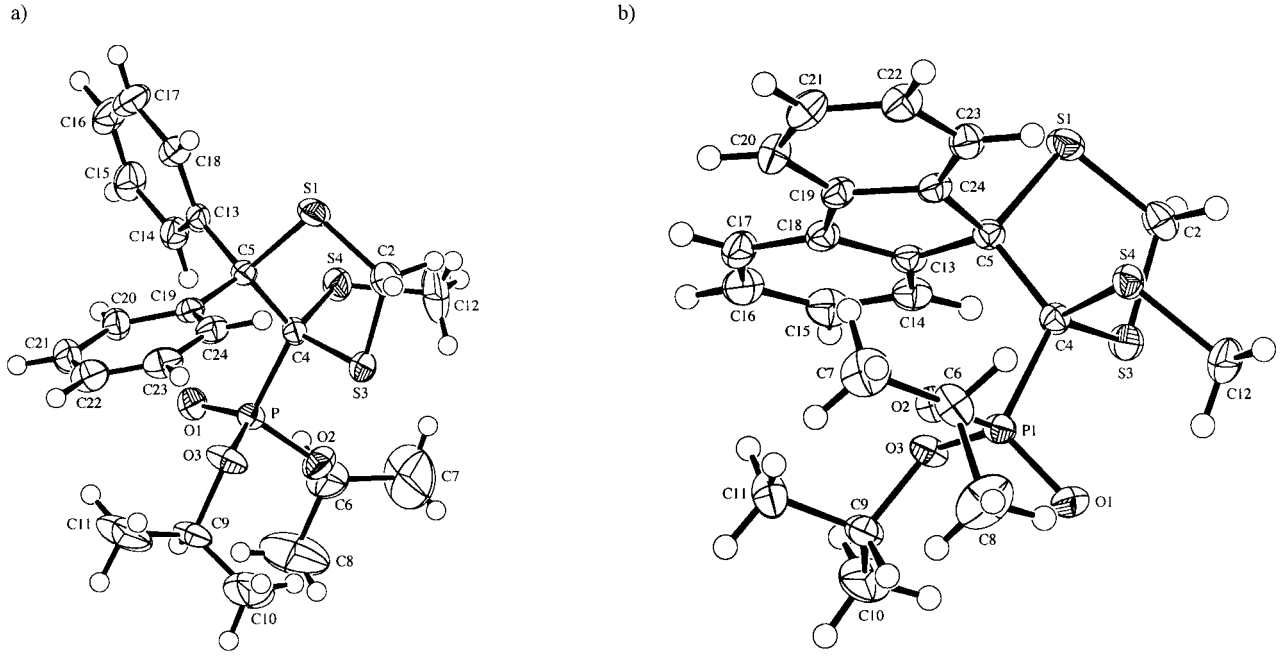


Figure 4. ORTEP plots[11] of the molecular structures of: a) **21b** and b) one of the two symmetry-independent molecules of **22b** (50% probability ellipsoids).

for **21** and ca. 10.6 Hz for **22**]. Finally, the suggested structures of **21b** and **22b** were confirmed by X-ray crystal structure determinations (Figure 4).[23]

Conclusions

In summary, the presented results show that thiocarbonyl ylides, in contrast to other 1,3-dipoles such as nitrilium ylides,[25] imides, and oxides,[26] undergo cycloadditions only with trithiocarbonates and dithioesters, and not with their O-substituted analogues. In the light of these and previously reported results, the successful formation of **16** from a thionolactone must be considered an exception. Furthermore, the phosphonylated dithioesters **8** are better dipolarophiles toward thiocarbonyl *S*-methylides. The corresponding [3+2] cycloadducts were obtained in good yields both with aliphatic (**3b**, **3c**) and with aromatic thiocarbonyl ylides (**3a**, **3d**). The regioselectivity of the reaction is reversed in the two series (i.e., the sterically more crowded "2-CH_2 1,3-dithiolanes" are formed in the cases of **3a** and **3d**, whereas **3b** and **3c** afford the "5-CH_2 1,3-dithiolanes"). The results obtained with **3a** and **3d** are in agreement with those reported for nonactivated dithioesters.[3] However, the reactions with **3b** and **3c**, which each give a single regioisomer, clearly differ from those found in the case of aromatic dithioesters.

Experimental Section

General Remarks: M.p.s were determined in a capillary with a Melt-Point apparatus (Aldrich) and are uncorrected. IR spectra: Perkin–Elmer, Spectrum One FT-IR; in KBr. ^{1}H and ^{13}C NMR spectra: Tesla BS-80 (80 and 20 MHz, respectively) or Bruker ARX 300 (300 and 75 MHz, respectively). Chemical shifts are given in ppm relative to tetramethylsilane (TMS) as the internal standard. ^{13}C Signal multiplicities were derived from DEPT spectra. EI- and CI-MS: Finnigan TSQ-700 triple quadrupole instrument. Elemental analyses were carried out in the analytical sections of the Institute of Organic Chemistry, University of Zurich, and the Polish Academy of Sciences (CBMiM) in Lodz.

Starting Materials: Thiobenzophenone (**1a**),[27] 2,2,4,4-tetramethyl-3-thioxocyclobutanone (**1b**),[28] adamantanethione (**1c**),[29] and 9*H*-fluorene-9-thione (**1d**)[30] were prepared by thionation of the corresponding commercially available ketones by literature procedures. Diphenyl trithiocarbonate (**5a**)[31] and diphenyl thiocarbonate (**5b**)[32] were synthesized from thiophosgene and sodium thiophenolate and sodium phenolate, respectively, by known procedures. Methyl dithiobenzoate (**6a**) was conveniently prepared from benzoic acid by treatment with Davy's reagent,[33] and *O*-methyl thiobenzoate (**6b**) as well as *O*-benzyl thiobenzoate (**6c**) were available by thionation of the corresponding benzoates with Lawesson's reagent.[34] Thiophthalide (**7**) was prepared from commercially available phthalide by treatment with Lawesson's reagent according to ref.[16] The phosphonylated *S*-methyl dithioformates **8a** and **8b** were synthesized by the procedure described by Grisley.[17] The stable, crystalline 2,5-dihydro-1,3,4-thiadiazoles **2b** and **2c** were prepared from **1b** and **1c**, respectively, by treatment with diazomethane in pentane solution at 0 °C.[35,36] Because of their known instability, the aromatic substituted 2,5-dihydro-1,3,4-thiadiazoles **2a** and **2d** were prepared at –65 °C from **1a** and **1d**, respectively, and decomposed at –30 °C without isolation.[21]

Reactions of Cycloaliphatic Thiocarbonyl *S*-Methylides 3b and 3c with Thio- and Dithioesters. General Procedure: A solution of freshly recrystallized **2b** or **2c** (1.0 mmol) and an excess of the corresponding thioester **5**, **6**, **7**, or **8** in abs. THF (2 mL) was stirred at 45 °C (oil bath). The reaction flask was connected to a gas burette, which enabled continuous monitoring of nitrogen evolution. After 6 h, the gas evolution ceased. In all experiments, the expected amount of nitrogen (ca. 24 mL) was evolved. The solvent was evaporated and the residue was examined by ^{1}H NMR spectroscopy. Reported yields refer to isolated purified products.

Reaction between 2b and 5a (molar ratio of 1:2.5): The solid residue was treated with small amounts of methanol and any remaining **5a** was filtered off. The filtrate was separated chromatographically (SiO_2 column) with use of petroleum ether and increasing amounts of dichloromethane as the eluent. With a 1:1 mixture of the solvents, a colorless thick oil was obtained, and was identified as **9**. Recrystallization afforded an analytically pure sample of 1,1,3,3-tetramethyl-6,6-bis(phenylsulfanyl)-5,8-dithiaspiro[3.4]octan-2-one (**9**). Yield: 180 mg (41.6%), m.p. 98–100 °C (methanol/dichloromethane). ^{1}H NMR: δ = 1.14, 1.17 (2 s, 4 Me), 3.03 (br. s, CH_2), 7.25–7.83 (m, 10 arom. H) ppm. ^{13}C NMR: δ = 22.5, 25.1 (2 q, 4 Me), 49.2 (t, CH_2), 68.3 (s, 2 C_q), 83.8 (s, C_q), 131.7, 132.0, 140.2 (3 d, 10 arom. CH), 135.2 (s, 2 arom C_q), 224.3 (s, C=O) ppm. IR (KBr): $\tilde{\nu}$ = 2980 m, 1770 vs (C=O), 1470 m, 1440 s, 1015 m, 940 m, 750 s, 695 s, 690 s cm^{-1}. $C_{22}H_{24}OS_4$ (432.70): calcd. C 61.07, H 5.59, S 29.64; found C 60.83, H 5.65, S 29.74.

Attempted Reaction between 2b and 5b: A solution of **2b** (1.0 mmol) and **5b** (2.5 mmol) in abs. THF (2 mL) was heated until the gas evolution ceased. Workup of the crude mixture was performed analogously to the experiment with **5a**. The ^{1}H NMR analysis of the residue indicated that neither of the expected 1,3-dithiolanes had been formed (no signal between 2.0 and 5.0 ppm).

Decomposition of 2b in the Presence of 6a: A solution of **2b** (1.0 mmol) and **6a** (1.1 mmol) in abs. THF (2 mL) was heated until the gas evolution ceased. ^{1}H NMR analysis of the crude mixture revealed the formation of a mixture of two regioisomeric products in a ratio of ca. 1:3 (comparison of the intensities of the MeS signals). The crude mixture was dissolved in hexane and crystallized at –76 °C (dry ice). The colorless crystals were separated by filtration; m.p. 100–105 °C. Repeated crystallization afforded an analytically pure sample of the major product. Attempts to separate the filtrate, both on a SiO_2 column and on SiO_2-coated prep. TLC plates, were in vain. The minor cycloadduct could be characterized by NMR spectroscopy of a mixture with the major product. 1,1,3,3-Tetramethyl-8-(methylsulfanyl)-8-phenyl-5,7-dithiaspiro-[3.4]octan-2-one (**13**). Yield: 105 mg (31.0%), m.p. 102–104 °C (hexane). ^{1}H NMR: δ = 1.24, 1.46, 1.48, 1.74 (4 s, 4 Me), 1.86 (s, MeS), 3.70, 3.79 (AB system, J = 8.4 Hz, CH_2), 7.24–7.35, 8.02–8.05 (2 m, 5 arom. H) ppm . ^{13}C NMR (one C_q not found): δ = 15.2 (q, MeS), 24.6, 24.7, 25.1, 25.6 (4 q, 4 Me), 27.6 (t, CH_2), 66.9, 68.2 (2 s, 2 C_q), 83.3 (s, C_q), 127.6, 128.1, 132.0 (3 d, 5 arom. CH), 136.3 (s, arom. C_q), 219.0 (s, C=O) ppm. IR (KBr): $\tilde{\nu}$ = 1771 vs (C=O), 1458 m, 1441 m, 1375 m, 1165 m, 1133 m, 1026 m, 896 m, 831 m, 733 s, 710 s cm^{-1}. MS (EI): *m*/*z* (%) = 338 (3) $[M]^{+\cdot}$, 245 (42), 221 (100), 175 (31), 150 (22), 143 (25), 77 (12). $C_{17}H_{22}OS_3$ (338.56): calcd. C 60.31, H 6.55, S 28.41; found C 60.25, H 6.63, S 28.39. 1,1,3,3-Tetramethyl-6-(methylsulfanyl)-6-phenyl-5,8-dithiaspiro[3.4]octan-2-one (**14**) (isolated as a 3:2 mixture with **13**). Colorless oil. ^{1}H NMR: δ = 1.41, 1.45, 1.57, 1.62 (4 s, 4 Me), 2.12 (s, MeS), 3.86, 3.95 (AB system, J = 8.4 Hz, CH_2), 7.75–7.79, 8.18–8.21 (2 m, 5 arom. H) ppm. ^{13}C NMR: δ = 15.3 (q, MeS), 49.3 (t, CH_2) ppm.

Decomposition of 2b in the Presence of 7: A solution of **2b** (1.0 mmol) and **7** (2.0 mmol) in abs. THF (2 mL) was heated until the gas evolution ceased. The ^{1}H NMR spectrum of the crude mixture showed that **16** had been formed regioselectively along with the earlier described thiirane **15**[12,36] in a ratio of ca. 3:2 (comparison of the intensities of CH_2 signals). Separation on a SiO_2 column with chloroform/petroleum ether 4:1 afforded the 9,10-benzo-annulated 1,1,3,3-tetramethyl-7-oxa-5,12-dithiadispiro[3.1.4.2]dodecan-2-one **16**, which was subsequently purified by recrystallization from hexane at 0 °C. Yield: 160 mg (49.9%), m.p. 51–53 °C (hexane). ^{1}H NMR: δ = 1.37, 1.42, 1.44, 1.48 (4 s, 4 Me), 3.46, 3.67 (AB system, J = 11.9 Hz, CH_2), 5.09, 5.16 (AB system, J = 12.8 Hz, CH_2), 7.23–7.44 (2 m, 4 arom. H) ppm. ^{13}C NMR: δ = 22.4, 23.1, 24.1, 24.8 (4 q, 4 Me), 50.8 (t, CH_2S), 66.1, 67.0 (2 s, 2 C_q), 71.6 (t, CH_2O), 76.4 (s, C_q), 110.4 (s, C_q), 121.2, 122.0, 128.0, 129.1 (4 d, 4 arom. CH), 138.5, 139.4 (2 s, 2 arom. C_q), 220.2 (s, C=O) ppm . IR (KBr): $\tilde{\nu}$ = 2967 s, 1786 vs (C=O), 1463 s, 1165 m, 1029 m, 1012 s, 1002 vs, 934 m, 761 s, 745 m, 700 m cm^{-1}. $C_{17}H_{20}O_2S_2$ (320.48): calcd. C 63.71, H 6.29, S 20.01; found C 63.60, H 6.26, S 19.96.

Attempted Reaction between 3c and 7 (molar ratio of 1:3): When the evolution of nitrogen ceased, excess **7** was removed by crystallization from methanol. The filtrate, after evaporation of the solvent, was analyzed by ^{1}H NMR spectroscopy. The spectrum indicated the formation of the known thiirane **18**[37] as the only product. No signal for an AB system appeared in the 3.0–4.0 ppm range.

Decomposition of 2b in the Presence of 8b: A solution of **2b** (1.1 mmol) and **8b** (1.0 mmol) in abs. THF (2 mL) was heated to 45 °C until the gas evolution ceased. The ^{1}H NMR spectrum of

the crude mixture showed only one AB signal between 3.0 and 4.0 ppm, confirming the regioselective course of the reaction. Separation on PLC plates (SiO_2, dichloromethane/ethyl acetate 96:4) yielded a thick, colorless oil, which solidified at room temperature. Purification by crystallization gave analytically pure diisopropyl-1,1,3,3-tetramethyl-6-(methylsulfanyl)-5,8-dithiaspiro[3.4]octane-6-phosphonate (**19**). Yield: 290 mg (68.0%), colorless crystals, m.p. 48–50 °C (pentane, dry ice). ^{1}H NMR: δ = 1.39, 1.40 (2 d, J = 6.6 Hz, 2 Me_2CH), 1.34, 1.41, 1.45 (3 s, 4 Me), 2.43 (s, MeS), 3.18–3.24, 3.57–3.65 (dd, J(H,H) = 12.9, J(H,P) = 3.6 and 9.1 Hz, respectively, CH_2), 4.81–4.90 (m, 2 Me_2CH) ppm. ^{13}C NMR: δ = 16.6 (q, MeS), 21.6, 21.7, 23.6, 23.7, 23.8, 24.2, 24.3, 24.6 (8 q, 8 Me), 46.0 (t, CH_2), 68.5 (d, J(C,P) = 156.9 Hz, C_q), 65.1, 67.7 (2 s, 2 C_q), 72.9,73.0 (2 dd, J(C,P) = 7.4 Hz, 2 Me_2CH), 78.1 (d, J(C,P) = 7.0 Hz, C_q), 218.9 (s, C=O) ppm . IR (KBr): $\tilde{\nu}$ = 2978 s, 2930 m, 1783 s (C=O), 1460 m, 1383 m, 1243 s, 1105 m, 996 vs, 568 m cm^{-1}. MS (EI): m/z (%) = 426 (4) $[M]^{+\cdot}$, 356 (31), 309 (20), 267 (30), 238 (100), 225 (81), 196 (41), 154 (61). $C_{17}H_{31}O_4PS_3$ (426.60): calcd. C 47.87, H 7.32, S 22.55; found C 47.96, H 7.35, S 22.32.

Decomposition of 2c in the Presence of 8b: A solution of **2c** (1.1 mmol) and **8b** (1.0 mmol) in abs. THF (2 mL) was heated to 45 °C until the gas evolution ceased. The crude mixture was separated on SiO_2 (column, dichloromethane with increasing amounts of diethyl ether). The main fraction, isolated as a thick, colorless oil, was purified by crystallization, affording diisopropyl 4-(methylsulfanyl)spiro[1,3-dithiolane-2,2′-tricyclo[3.3.1^{1,5}.1^{3,7}]decane]-4-phosphonate (**20**). Yield: 360 mg (82.5%), colorless crystals, m.p. 60–62 °C (hexane, refrigerator). ^{1}H NMR: δ = 1.35, 1.37 (2 d, J = 5.8 Hz, 2 Me_2CH), 1.73–2.45 (m, 14 adamantyl-H), 2.39 (s, MeS), 3.18 (dd, J(H,H) = 13.2, J(H,P) = 2.2 Hz, 1 H of CH_2), 3.81 (dd, J(H,H) = 13.2, J(H,P) = 8.0 Hz, 1 H of CH_2), 4.79–4.87 (m, 2 Me_2CH) ppm. ^{13}C NMR: δ = 16.4 (q, MeS), 23.4, 23.6, 24.2, 24.3 (4 qd, J(C,P) = ca. 7 Hz, 2 Me_2CH), 26.2, 26.4 (2 d, 2 CH), 35.1, 36.8, 37.3, 37.6, 38.1 (5 t, 5 CH_2), 40.9, 42.1 (2 d, 2 CH), 44.5 (t, CH_2S), 68.2 (d, J(C,P) = 157.2 Hz, C_q), 72.9, 73.0 (2 dd, J(C,P) = 7.6 Hz, 2 Me_2CH), 81.6 (d, J(C,P) = 7.3 Hz, C_q) ppm. IR (KBr): $\tilde{\nu}$ = 2978 s, 2917 vs, 2855 s, 1452 s, 1385 m, 1374 m, 1252 vs, 1100 s, 991 vs, 569 s, 541 m cm^{-1}. MS (EI): m/z (%) = 436 (11) $[M]^{+\cdot}$, 389 (32), 305 (100), 271 (80), 225 (520), 224 (70), 105 (78), 91 (68). $C_{19}H_{33}O_3PS_3$ (436.62): calcd. C 52.27, H 7.62, S 22.03; found C 52.54, H 7.98, S 21.66.

Reactions of Aromatic Thiocarbonyl *S*-Methylides 3a and 3d with Dithioformates 8a and 8b – General Procedure: A stirred solution of freshly purified **1a** or **1d** (1.0 mmol) in abs. THF (1 mL) was cooled to –65 °C (acetone/dry ice). Under nitrogen, a solution of diazomethane in petroleum ether was added in small portions until complete decoloration of the solution. Then, solutions of **8a** and **8b**, respectively, were added in one portion. The magnetically stirred mixture was slowly warmed up to room temperature. At ca. –30 °C, vigorous evolution of nitrogen was observed. After 2 h at ambient temperature, the solvents were removed in vacuo and the residue was analyzed by ^{1}H NMR spectroscopy. Products were isolated either by trituration with hexane or by chromatography on a SiO_2 column. Reported yields refer to isolated purified products.

Reaction between 2a and 8a: Diethyl 4-(methylsulfanyl)-5,5-diphenyl-1,3-dithiolane-4-phosphonate (**21a**). Chromatography with hexane and increasing amounts of ethyl acetate. Yield: 140 mg (31.8%), m.p. 188–191 °C (hexane/dichloromethane). ^{1}H NMR: δ = 0.97, 1.23 (2 t, J = 6.9 Hz, 2 $MeCH_2$), 2.49 (s, MeS), 3.62–4.22 (m, 2 MeCH_2), 3.88, 3.97 (AB system, J = 9.3 Hz, CH_2), 7.17–7.27, 7.60–7.66, 7.76–7.79 (3 m, 10 arom. H) ppm. ^{13}C NMR: δ = 15.9, 16.3 (2 dd, J(C,P) = 5.6 Hz, 2 $MeCH_2$), 18.5 (q, MeS), 31.7 (td, J(C, P) = 5.7 Hz, CH_2), 63.7, 64.1 (2 td, J(C,P) = 8.2 Hz, 2 MeCH_2), 73.5 (d, J(C,P) = ca. 180 Hz, C(4)), 80.0 (d, J(C,P) = ca. 10 Hz, C(5)), 126.8, 127.6, 130.4, 131.0 (4 d, 10 arom. CH), 141.6, 142.9 (2 s, 2 arom. C_q) ppm. IR (KBr): $\tilde{\nu}$ = 2985 w, 1443 w, 1249 s, 1055 vs, 1023 vs, 971 s, 700 s, 560 s cm^{-1}. MS (CI, NH_3): m/z (%) = 441 (30) $[M + H]^+$, 393 (100). $C_{20}H_{25}O_3PS_3$ (440.57): calcd. C 54.52, H 5.72, S 21.83; found C 54.11, H 5.84, S 21.39.

Reaction between 2a and 8b: Diisopropyl 4-(methylsulfanyl)-5,5-diphenyl-1,3-dithiolane-4-phosphonate (**21b**). Treatment of the crude product with petroleum ether and recrystallization. Yield: 150 mg (32.0%), m.p. 170–172 °C (hexane/dichloromethane). ^{1}H NMR: δ = 1.05, 1.13, 1.19, 1.21 (4 d, J = ca. 6 Hz, 2 Me_2CH), 2.45 (d, J(H,P) = 0.5 Hz, MeS), 3.86, 3.94 (AB system, J = 16.0 Hz, CH_2), 4.50, 4.63 (2 m, Me_2CH), 7.01–7.76 (m, 10 arom. H) ppm. ^{13}C NMR: δ = 18.9 (q, MeS), 23.3, 23.5 (2 qd, J(C,P) = 6.8 and 6.0 Hz, respectively, 2 Me_2CH), 31.8 (td, J(C,P) = 5.6 Hz, CH_2), 72.7 (d, J(C,P) = 8.5 Hz, Me_2CH), 126.68, 126.73, 126.8, 127.4, 130.6, 131.3 (6 d, 10 arom. CH), 141.0 (d, J(C,P) = 60.3 Hz, arom. C_q), 145.0 (d, J(C,P) = ca. 10 Hz, arom. C_q) ppm. C(4) and C(5) could not be detected. IR (KBr): $\tilde{\nu}$ = 2979 m, 1443 w, 1244 s, 1105 m, 1005 vs, 699 s, 559 s cm^{-1}. MS (CI, NH_3): m/z (%) = 469 (43) $[M + H]^+$, 421 (100), 391 (57), 377 (98).

Reaction between 2d and 8a. Diethyl 5-(methylsulfanyl)spiro[1,3-dithiolane-4,9′-[9*H*]fluorene]-5-phosphonate (**22a**). Chromatography with hexane and increasing amounts of ethyl acetate and crystallization. Yield: 350 mg (79.8%), colorless crystals, m.p. 83–85 °C (hexane/diethyl ether). ^{1}H NMR: δ = 0.86 (dt, J(H,H) = 7.0, J(H,P) = 0.5 Hz, $MeCH_2$), 0.92 (t, J(H,H) = 7.0 Hz, $MeCH_2$), 2.47 (s, MeS), 3.41–3.87 (m, 2 MeCH_2), 4.23, 4.44 (AB system, J = 8.7 Hz, 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) ppm. ^{13}C NMR: δ = 15.8, 15.9 (2 qd, J(C,P) = 5.5 Hz, 2 $MeCH_2$), 16.9 (q, MeS), 32.4 (td, J(C,P) = 10.8 Hz, CH_2), 63.0, 64.9 (2 td, J(C,P) = 7.6 Hz, 2 MeCH_2), 73.3 (d, J(C,P) = 151 Hz, C_q), 75.5 (s, C_q), 118.9, 119.4, 126.1, 126.8, 128.6, 128.9, 129.2 (7 d, 8 arom. CH), 139.2, 140.9, 142.2, 149.1 (4 s, 4 arom. C_q) ppm. IR (KBr): $\tilde{\nu}$ = 2977 m, 1447 s, 1243 vs, 1055 vs, 1023 vs, 981 s, 743 s, 556 s, 543 s cm^{-1}. MS (CI, NH_3): m/z (%) = 456 (9) $[M + NH_4]^+$, 439 (21) $[M + H]^+$, 391 (100), 361 (30). $C_{20}H_{23}O_3PS_3$ (438.55): calcd. C 54.77, H 5.29, S 21.93; found C 54.54, H 5.39, S 21.70.

Reaction between 2d and 8b: Diisopropyl 5-(methylsulfanyl)-spiro[1,3-dithiolane-4,9′-[9*H*]fluorene]-5-phosphonate (**22b**). Chromatographic purification on a SiO_2 column with hexane and increasing amounts of ethyl acetate followed by recrystallization. Yield: 180 mg (38.6%), colorless crystals, m.p. 117–119 °C (hexane/dichloromethane). ^{1}H NMR: δ = 0.64, 0.78, 0.99, 1.04 (4 d, J = 6.2 Hz, 2 Me_2CH), 2.46 (d, J(H,P) = 0.5 Hz, MeS), 4.22, 4.42 (AB system, J = 8.7 Hz, CH_2), 4.30–4.53 (m, 2 Me_2CH), 7.18–7.61 (m, 6 arom. H), 8.16–8.19 (m, 2 arom. H) ppm. ^{13}C NMR: δ = 17.0 (q, MeS), 22.2, 23.1, 23.5, 24.0 (4 qd, J(C,P) = 6.7 and 2.5 Hz, 2 Me_2CH), 32.2 (td, J(C,P) = 10.6 Hz, CH_2), 71.1, 73.2 (2 dd, J(C,P) = 8.3 Hz, 2 Me_2CH), 73.0 (d, J(C,P) = ca. 160 Hz, C_q), 75.0 (s, C_q), 118.8, 119.4, 126.1, 126.8, 128.5, 128.9, 129.0, 129.6 (8 d, 8 arom. CH), 139.3, 141.4, 142.4, 149.0 (4 s, 4 arom. C_q) ppm . IR (KBr): $\tilde{\nu}$ = 2978 s, 2919 m, 1447 s, 1384 m, 1373 m, 1241 vs, 1104 s, 1000 vs, 741 s, 582 s cm^{-1}. MS (CI, isobutane): m/z (%) = 467 (3) $[M + H]^+$, 419 (100), 389 (5), 377 (6). $C_{22}H_{27}O_3PS_3$ (466.61): calcd. C 56.63, H 5.83, S 20.62; found C 56.75, H 5.92, S 20.36.

X-ray Crystal Structure Determinations of Compounds 9, 20, 21b, and 22b: See Figs. 2–4.[37] In the case of **9**, all measurements were made on a Rigaku AFC5R diffractometer with use of graphite-monochromated Mo-K_α radiation (λ, 0.71073 Å) and a 12 kW rot-

ating anode generator. Data reduction was performed with teXsan.[38] All measurements for **20, 21b,** and **22b** were made at low temperature on a Nonius KappaCCD area-detector diffractometer[39] with use of graphite-monochromated Mo-K_α radiation (λ, 0.71073 Å) and an Oxford Cryosystems Cryostream 700 cooler. Data reductions were performed with HKL Denzo and Scalepack.[40] The intensities were corrected for Lorentz and polarization effects, and, except in the case of **9**, an absorption correction based on the multi-scan method[41] was applied. Equivalent reflections were merged. Each structure was solved by direct methods by use of SIR92,[42] which revealed the positions of all non-H atoms. In the case of **22b**, there were two symmetry-independent molecules in the asymmetric unit. The atomic coordinates of the two molecules were tested carefully for a relationship from a higher symmetry space group by use of the program PLATON,[43] but none could be found. The non-H atoms were refined anisotropically. For each structure, all of the H atoms were placed in geometrically calculated positions and refined by use of a riding model in which each H atom was assigned a fixed isotropic displacement parameter with a value equal to $1.2U_{eq}$ of its parent atom ($1.5U_{eq}$ for methyl groups). The refinement of each structure was carried out on F^2 by full-matrix least-squares procedures, which minimized the function $\Sigma w(F_o^2 - F_c^2)^2$. No corrections for secondary extinction were applied. In **20** and **22b**, three and two reflections, respectively, the intensities of which were considered to be extreme outliers, were omitted from the final refinement. Neutral atom scattering factors for non-H atoms were taken from ref.[44a] and the scattering factors for H atoms were taken from ref.[45] Anomalous dispersion effects were included in F_c;[46] the values for f' and f'' were those of ref.[44b] The values of the mass attenuation coefficients are those of ref.[44c] All calculations were performed with the aid of the SHELXL97[47] program.

Crystal Data for 9: $C_{22}H_{24}OS_4$, M = 432.67, colorless, prism, crystal dimensions 0.21×0.32×0.41 mm, triclinic, space group $P\bar{1}$, Z = 2, reflections for cell determination 25, 2θ range for cell determination 39–40°, a = 6.328(1), b = 12.845(3), c = 13.710(3) Å, α = 84.29(2), β = 78.88(2), γ = 81.14(2)°, V = 1077.6(4) Å^3, D_X = 1.333 g·cm^{-3}, μ(Mo-K_α) = 0.451 mm^{-1}, T = 173 K, ω/2θ scans, $2\theta_{(max.)}$ = 55°, total reflections measured 5175, symmetry independent reflections 4953 (used in refinement), reflections with $I > 2\sigma(I)$ 4232, parameters refined 248, R [on F; $I > 2\sigma(I)$ reflections] = 0.0334, $wR(F^2)$ [all reflections] = 0.0962 ($w = [\sigma^2(F_o^2) + (0.0511P)^2 + 0.2872P]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$), goodness of fit 1.056, final $\Delta_{max.}/\sigma$ 0.001, $\Delta\rho$ (max./min.) = 0.35/–0.28 e·Å^{-3}.

Crystal Data for 20: $C_{19}H_{33}O_3PS_3$, M = 436.62, colorless, tablet, crystal dimensions 0.08×0.15×0.30 mm, monoclinic, space group $P2_1/n$, Z = 4, reflections for cell determination 73999, 2θ range for cell determination 4–60°, a = 12.6113(2), b = 9.5466(1), c = 19.4271(3) Å, β = 105.6553(6)°, V = 2252.16(6) Å^3, D_X = 1.288 g·cm^{-3}, μ(Mo-K_α) = 0.416 mm^{-1}, T = 160 K, φ and ω scans, transmission factors (min./max.) 0.907/0.969, $2\theta_{(max.)}$ = 60°, total reflections measured 66087, symmetry independent reflections 6586, reflections with $I > 2\sigma(I)$ 4911, reflections used in refinement 6583, parameters refined 240, R [on F; $I > 2\sigma(I)$ reflections] = 0.0391, $wR(F^2)$ [all reflections] = 0.1037 ($w = [\sigma^2(F_o^2) + (0.049P)^2 + 0.6677P]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$), goodness of fit 1.047, final $\Delta_{max.}/\sigma$ 0.001, $\Delta\rho$ (max./min.) = 0.40/–0.41 e·Å^{-3}.

Crystal Data for 21b: $C_{22}H_{29}O_3PS_3$, M = 468.62, colorless, plate, crystal dimensions 0.05×0.28×0.32 mm, monoclinic, space group $P2_1/c$, Z = 4, reflections for cell determination 23352, 2θ range for cell determination 4–55°, a = 17.3416(4), b = 13.7696(2), c = 9.8350(2) Å, β = 97.5728(6)°, V = 2327.99(8) Å^3, D_X = 1.337 g·cm^{-3}, μ(Mo-K_α) = 0.0.408 mm^{-1}, T = 200 K, φ and ω scans, transmission factors (min./max.) 0.868/0.981, $2\theta_{(max.)}$ = 55°, total reflections measured 52311, symmetry independent reflections 5342 (used in refinement), reflections with $I > 2\sigma(I)$ 3414, parameters refined 267, R [on F; $I > 2\sigma(I)$ reflections] = 0.0470, $wR(F^2)$ [all reflections] = 0.1294 ($w = [\sigma^2(F_o^2) + (0.0684P)^2 + 0.2581P]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$), goodness of fit 1.025, final $\Delta_{max.}/\sigma$ 0.001, $\Delta\rho$ (max./min.) = 0.35/–0.46 e·Å^{-3}.

Crystal Data for 22b: $C_{22}H_{27}O_3PS_3$, M = 466.61, colorless, prism, crystal dimensions 0.22×0.28×0.30 mm, monoclinic, space group $P2_1/c$, Z = 8, reflections for cell determination 61664, 2θ range for cell determination 4–55°, a = 28.6621(3), b = 10.2839(1), c = 15.5655(1) Å, β = 98.0275(4), V = 4543.10(7) Å^3, D_X = 1.364 g·cm^{-3}, μ(Mo-K_α) = 0.418 mm^{-1}, T = 160 K, φ and ω scans, transmission factors (min./max.) 0.835/0.915, $2\theta_{(max.)}$ = 55°, total reflections measured 79006, symmetry independent reflections 10419, reflections with $I > 2\sigma(I)$ 7239, reflections used in refinement 10417, parameters refined 533, R [on F; $I > 2\sigma(I)$ reflections] = 0.0423, $wR(F^2)$ [all reflections] = 0.1078 ($w = [\sigma^2(F_o^2) + (0.0499P)^2 + 1.2088P]^{-1}$, where $P = (F_o^2 + 2F_c^2)/3$), goodness of fit 1.038, final $\Delta_{max.}/\sigma$ 0.001, $\Delta\rho$ (max./min.) = 0.36/–0.38 e·Å^{-3}.

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