Addition of Diazomethane to Phosphonodithioformates and Reactions of Phosphonylated Thiocarbonyl S-Methylides

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Abstract: The reaction of phosphonodithioformates 14 with diazomethane at –60°C yielded 2,5-dihydro-1,3,4-thiadiazoles 15 as unstable intermediates. Their structure was evidenced by the base-catalyzed elimination of methylsulfane leading to 1,3,4-thiadiazole-2-phosphonates. At ca. –35°C, thermal decomposition of 15 by N2-elimination led to reactive thiocarbonyl S-methylides 17. In the absence of trapping reagents, these 1,3-dipoles undergo a head-to-head dimerization leading to 1,4-dithianes 18. An intermediate zwitterionic dimer 19 was detected by 31P NMR spectroscopy. The initially formed thiocarbonyl S-methylide 17 as well as an open-chain zwitterionic dimer 20 was intercepted by methanol. Stable interception products were also obtained with S- and N-nucleophiles.

Addition of Diazomethane to Phosphonodithioformates and Reactions of Phosphonylated Thiocarbonyl *S*-Methylides

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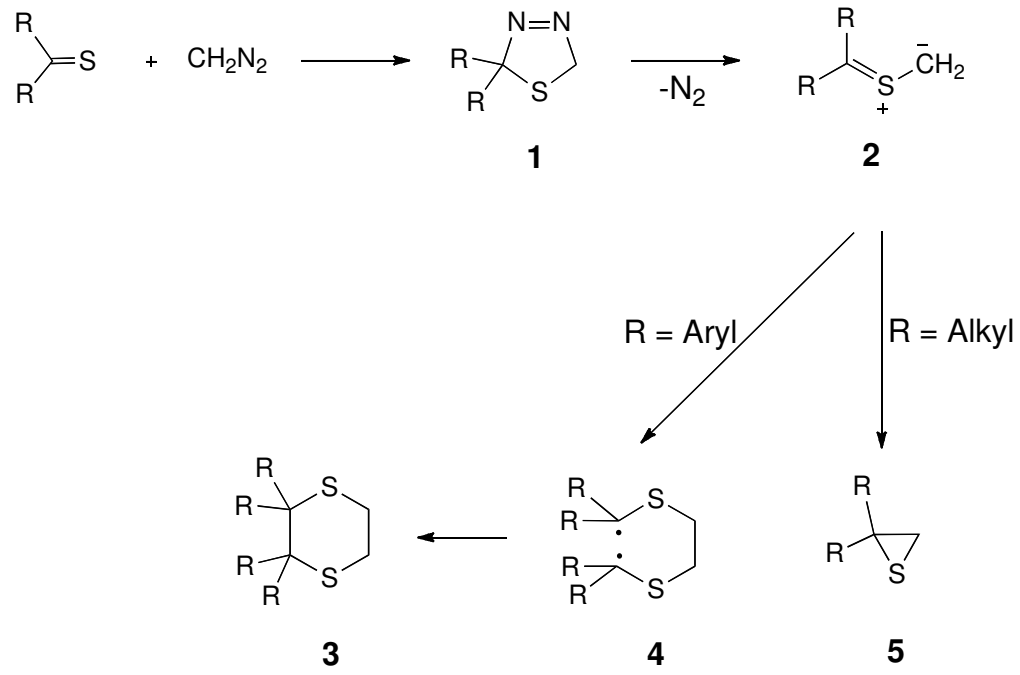
The reaction of phosphonodithioformates **14** with diazomethane at –60°C yielded 2,5-dihydro-1,3,4-thiadiazoles **15** as unstable intermediates. Their structure was evidenced by the base-catalyzed elimination of methylsulfane leading to 1,3,4-thiadiazole-2-phosphonates. At ca. –35°C, thermal decomposition of **15** by N_2-elimination led to reactive thiocarbonyl *S*-methylides **17**. In the absence of trapping reagents, these 1,3-dipoles undergo a head-to-head dimerization leading to 1,4-dithianes **18**. An intermediate zwitterionic dimer **19** was detected by ^{31}P NMR spectroscopy. The initially formed thiocarbonyl *S*-methylide **17** as well as an open-chain zwitterionic dimer **20** was intercepted by methanol. Stable interception products were also obtained with S- and N-nucleophiles.

Key words: addition reactions, dimerization, thiocarbonyl ylides, 1,3-dipoles, sulfur heterocycles

The preferred method for the *in-situ* generation of thiocarbonyl ylides **2** is the thermal decomposition of 2,5-dihydro-1,3,4-thiadiazoles of type **1** *via* elimination of N_2 (Scheme 1) [1,2]. Whereas the formation of **1** from thioketones and diazomethane takes

place already at low temperature, the ease of the extrusion of N_2 depends on the type of the substitutents R. The nature of R also determines the further transformation of **2**. The systems containing aromatic substituents eliminate N_2 below 0°C, and the generated ylides **2** undergo preferentially head-to-head dimerization to give 1,4-dithianes **3**. Recent computational studies show that the dimerization of thiobenzophenone *S*-methylide (**2**, R = Ph) occurs stepwise *via* a 1,6-biradical **4** [3]. However, in the presence of electron-deficient dipolarophiles, they enter [2+3] cycloaddition reactions to yield sulfur containing five-membered heterocycles [4]. On the other hand, aliphatic derivatives of **1** show enhanced stability and extrude N_2 only at elevated temperature. In the presence of dipolarophiles, they also undergo [2+3] cycloadditions, but in the absence of trapping agents, instead of dimerization, a 1,3-dipolar electrocyclization leading to thiiranes **5** is observed [1,2].

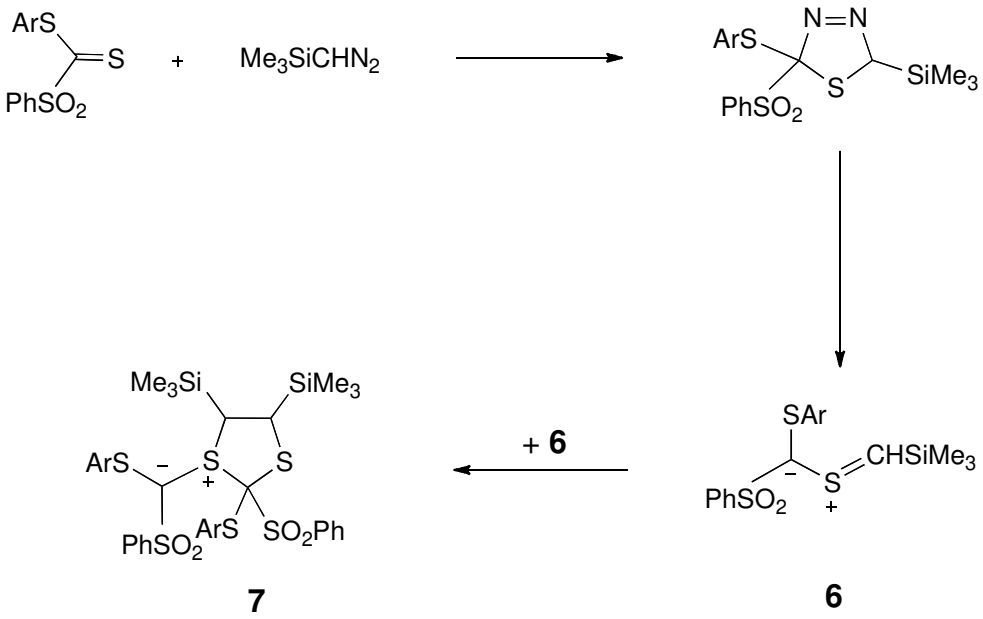
Scheme 1



Thio- and dithioesters show similar reactivity as thioketones and enter [2+3] cycloadditions at low temperature. Reactions of aliphatic and aromatic dithioesters with diazomethane in the absence of dipolarophiles afford 1,4-dithianes and thiiranes [5-7]. At enhanced temperature (>0°C) the reactions occur with spontaneous elimination of N_2, and

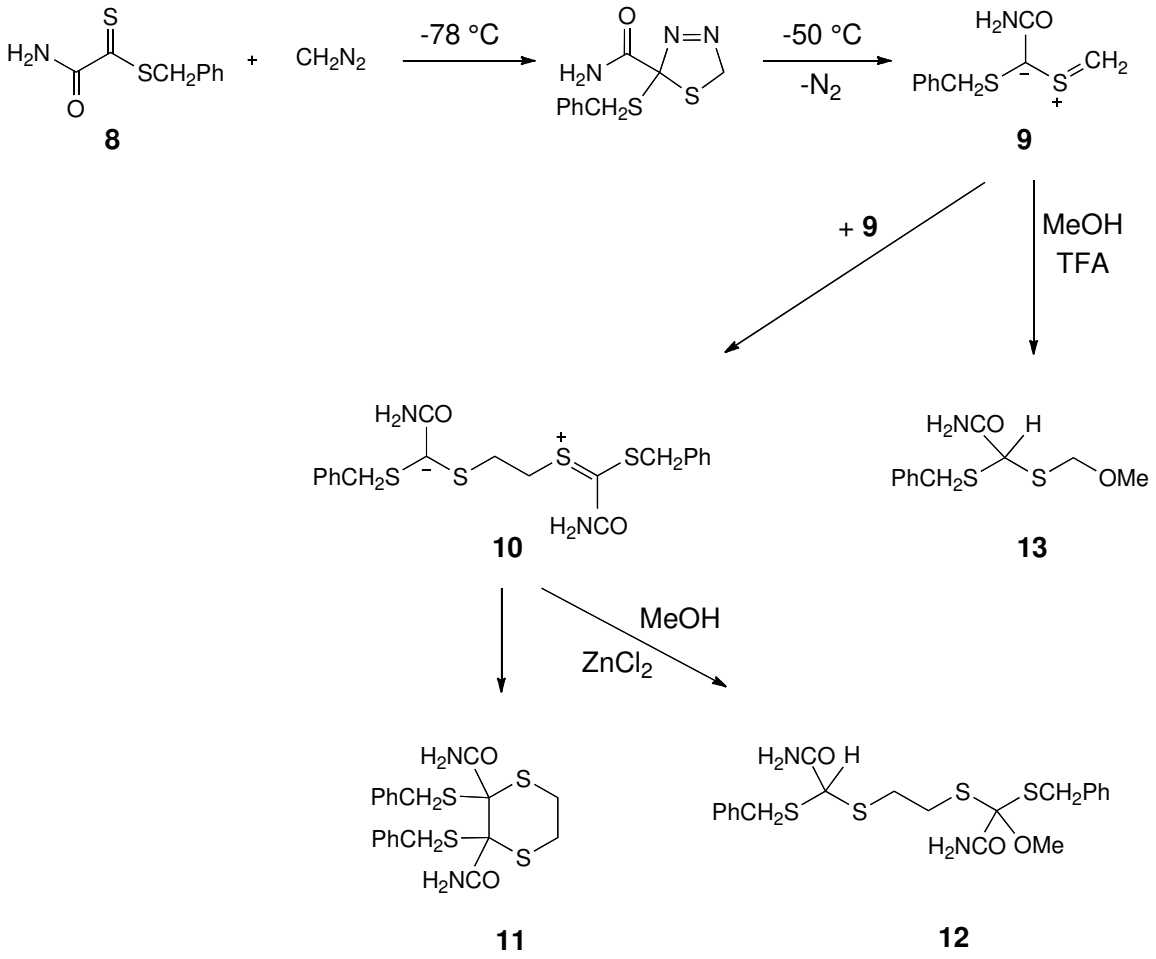
1,3-dithiolanes are formed (so-called Schönberg reaction) [6,8,9]. Furthermore, C-functionalized dithioformates are attractive dienophiles and dipolarophiles. Especially C-sulfonylated dithioformates were explored in reactions with diazoalkanes as well as with dienes [10-12]. In a recent paper, an unprecedented dimerization of the thiocarbonyl ylide **6** via a conceivable [2+3] cycloaddition leading to the zwitterionic 1,3-dithiolane derivative **7**, instead of products of type **3** and/or **5**, has been described [13] (Scheme 2).

Scheme 2



The reaction of diazomethane with the dithiooxamide **8** yielded **11**, *i.e.*, the cyclic dimer of the thiocarbonyl *S*-methylide **9**, *via* a postulated zwitterionic head-to-head dimer **10** [14] (Scheme 3). In the presence of $ZnCl_2$, the intermediate **10** was intercepted by methanol to give product **12**. Surprisingly, the dimerization of **9** could not be supressed completely when it was generated in a mixture of methanol and trifluoroacetic acid (TFA), and only part of **9** was trapped yielding the methanol adduct **13**.

Scheme 3



These results show that the substitution pattern of the C=S compound strongly influences the behavior of the thiocarbonyl ylide. Therefore, we were aimed to investigate C-phosphonylated dithioformates. Although they have been used as phosphonylated building blocks in Diels-Alder reactions [15], there are no reports on their reactions as dipolarophiles. Only recently we reported on efficient [2+3] cycloadditions with thiocarbonyl ylides [16].

In the present paper, the results of our studies on reactions of C-phosphonylated dithioformates **14a**,**b** with diazomethane and on the reactivity of the corresponding thiocarbonyl *S*-methylides with nucleophilic reagents are described. The presence of a phosphonyl group not only activates the dipolarophile but also allows the detection of less stable intermediates by ^{31}P-NMR measurements.

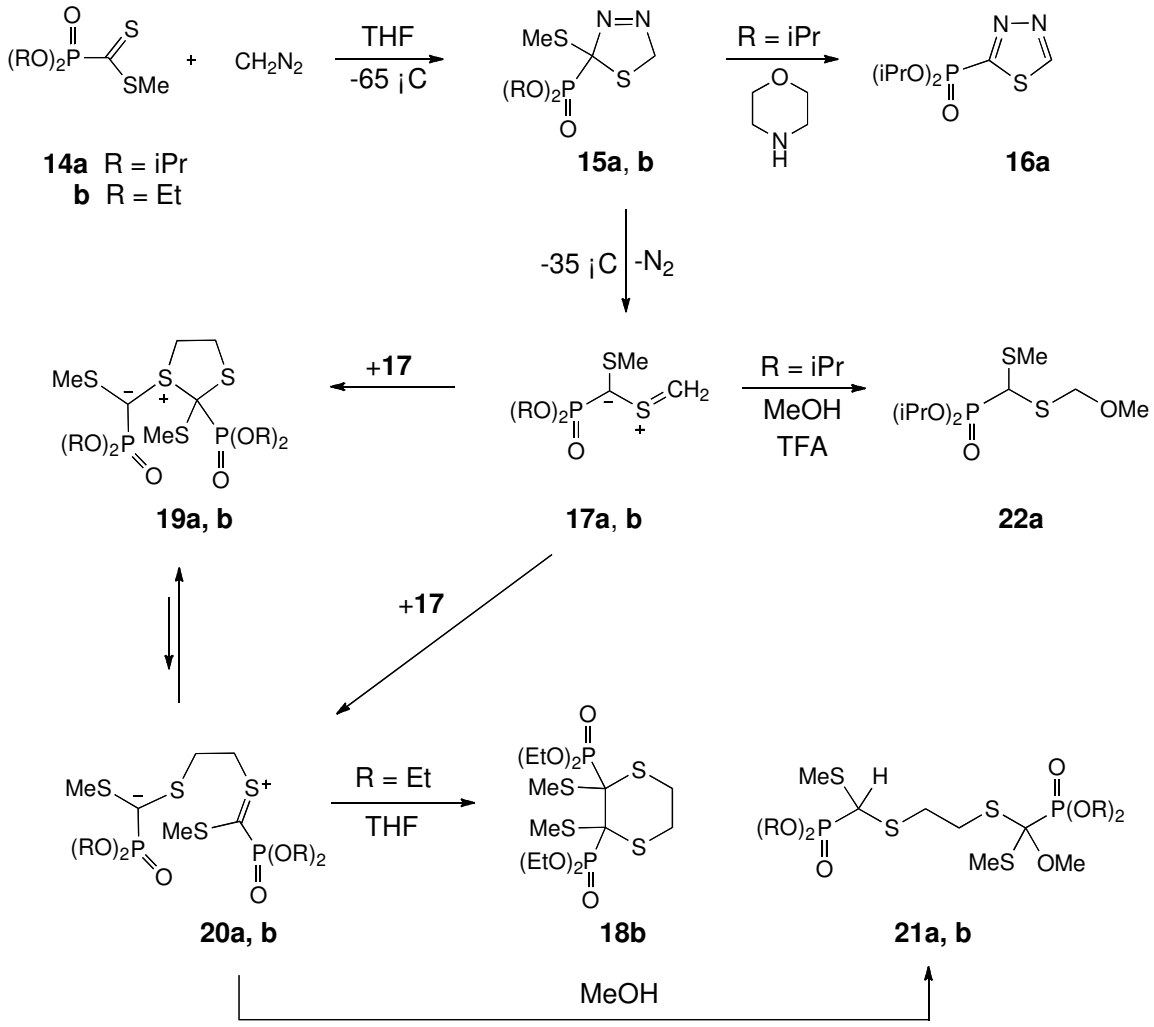
RESULTS AND DISCUSSION

It is well established that [2+3] cycloadditions of diazomethane with dithioesters and aliphatic thioketones can lead to the formation of two regioisomeric cycloadducts, *i.e.*, 1,3,4- and 1,2,3-thiadiazole derivatives [5,17], and only the 1,3,4-isomers are suitable precursors of thiocarbonyl *S*-methylides. The addition of an etheral solution of diazomethane to the orange-red solution of **14** in THF at –65°C resulted in immediate decolorization. In the case of **14a**, the low temperature ^{31}P-NMR spectra showed that only one product, showing a signal at 12.75 ppm, was formed at –60°C. Thus, the cycloaddition took place with complete regioselectivity. The structure of a 1,3,4-thiadiazole derivative **15a** was confirmed by the addition of a ten-fold excess of morpholine to the crude product at –65°C. During slow warming to room temperature, no evolution of N_2 was observed. After workup, 1,3,4-thiadiazole-2-phosphonate **16a**, formed from **15a** by elimination of methylsulfane, was obtained as the only product (Scheme 4).

The decomposition of **15b** at –35°C in the absence of any intercepting agent led to the formation of a crystalline product, which was identified as 1,4-dithiane **18b** (Scheme 4). This product shows a single signal at 17.22 ppm in the ^{31}P-NMR spectrum. When the reaction was monitored at low temperature by ^{31}P-NMR spectroscopy, this signal appeared only at temperatures above +10°C. At –10°C, the spectrum revealed two signals at 28.93 and 18.96 ppm with equal intensity, indicating the existence of an intermediate containing two non-equivalent phosphonyl groups. Based on the reported data [13], we propose that the zwitterionic 1,3-dithiolane ylide **19b** is this intermediate, which probably exists in equilibrium with the open-chain dimer **20b**[*]. The latter could be the precursor of the isolated dimer **18b**.

Scheme 4

* In the light of the recent studies on the dimerization of thiocarbonyl *S*-methylides [3], the intermediate **20** could also be presented as a 1,6-diradical. Furthermore, the structure of **17** can be presented as a 1,3-diradical [1,18].

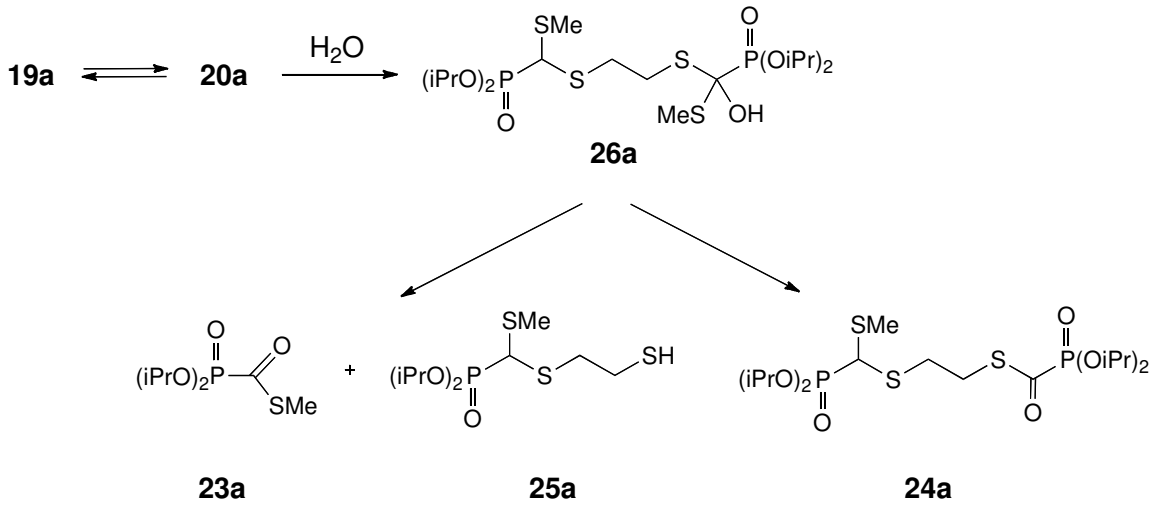


In the case of **15a**, the decomposition in THF in the absence of trapping reagents was also monitored by ^{31}P-NMR spectroscopy. At –40°C, the main component was still **15a** (signal at 12.70 ppm), accompanied by **19a** showing two signals at 28.87 and 17.08 ppm. With increasing temperature, the ratio of **15a/19a** changed in favor of the latter, and at –10°C only the signals of **19a** were present. Further warming led to a mixture of new products, and the major one showed a signal at 17.99 ppm, which can be attributed by analogy with the ethoxy derivative to 1,4-dithiane **18a**. However, all attempts to isolate this product were in vain. After chromatographic workup, many decomposition products were obtained. The first fraction was identified as **23a**, which is the C=O analogue of **14a**, with a ^{31}P absorption at –4.84 ppm. A second fraction, which was obtained as a colorless oil, showed also a C=O absorption (IR, ^{13}C-NMR), and its structure was

determined as **24a**. Its formation can be explained by addition of water to **20a** followed by elimination of methylsulfane.

In another experiment, the reaction mixture in THF, containing a few drops of water, was also analyzed by ^{31}P-NMR spectroscopy. Between –60 and –10°C, the signals of **15a** and **19a** were present in analogy to the experiment carried out in absolute THF. At 0°C, only the signals of **19a** were observed. After warming to room temperature, two ^{31}P absorptions at –4.76 and –18.56 ppm remained. The signal at higher field evidenced the presence of **23a**. The second product of the hydrolytic decomposition is probably the sulfane **25a**. The formation of **23a**–**25a** requires the precursor **26a**, which is formed by interception of **20a** by water (Scheme 5).

Scheme 5

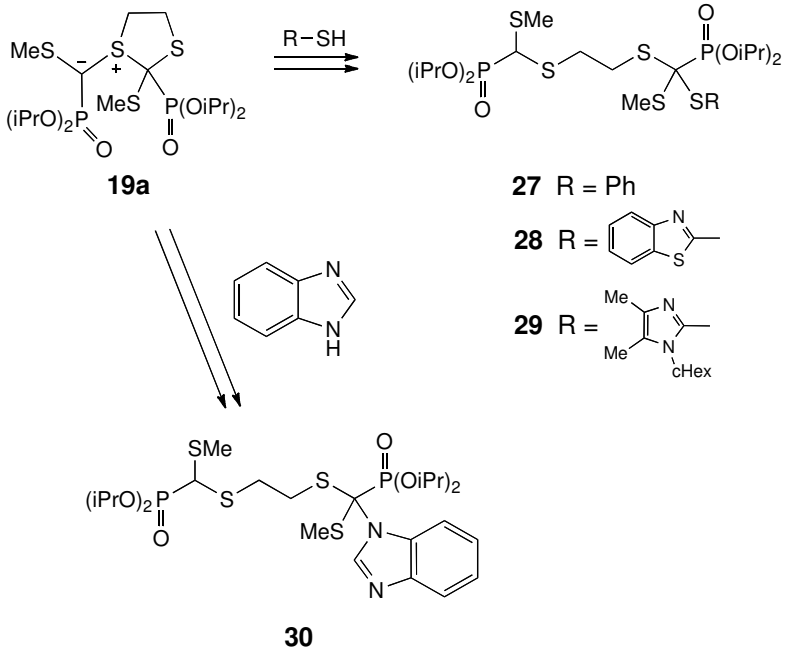


It is well documented that alcohols can be used as trapping agents for thiocarbonyl ylides to yield dialkyl O,S-acetals [2]. With the aim of intercepting **17**, decompositions of **15** were performed in the presence of excess methanol. In the case of **15a**, the ^{31}P-NMR spectrum at –10°C showed the presence of **15a** and **19a** as well as of a new product with two signals at 21.74 and 16.24 ppm. The latter became the only product when the solution was warmed to +10°C. In both reactions (with **15a**, **15b**), stable products were isolated as colorless oils, and the spectroscopic data proved the formation of 2:1 methanol adducts **21** (Scheme 4). In order to accelerate the addition of methanol to **17**, and in

regard to suppress its dimerization, the decomposition of **15a** was carried out in methanol containing trifluoroacetic acid (TFA). Similar to the reaction presented in Scheme 3 [14], 2:1 and 1:1 adducts **21a** and **22a**, respectively, were formed side by side in a slight favor of the first one.

Thiophenol and enolizable heterocyclic thiones are also efficient trapping reagents for thiocarbonyl *S*-methylides [2,19]. Therefore, thiophenol, benzo-1,3-thiazole-2-thione, and 1-cyclohexyl-4,5-dimethylimidazole-2-thione were applied to capture the reactive dipolar intermediates in reactions with **15a**. As in the experiments with methanol, only the 2:1 adducts **27**–**29** were obtained, and no 1:1-adducts could be observed (Scheme 6). Among N-nucleophiles, imidazoles and 1,2,4-triazoles are known to intercept thiocarbonyl *S*-methylides [20]. In the present study, the decomposition of **15a** in the presence of benzimidazole gave the 2:1 adduct **30** as the only product. These results evidence once more that the dimerization of **17** is the fastest process and proceeds prior to the reaction with the trapping agent.

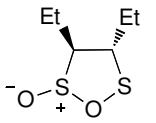
Scheme 6



In conclusion, the presented results show that phosphonylated dithioformates **14** react smoothly and regioselectively with diazomethane to afford 2,5-dihydro-1,3,4-thiadiazole-2-phosphonates **15**, which can conveniently be used as precursors of thiocarbonyl *S*-methylides **17** in a one-pot procedure (Scheme 4). These 1,3-dipoles are able to enter [2+3] cycloadditions with suitable dipolarophiles [21], but generated in the absence of intercepting agents, dimerization to give **20** is the preferred reaction.

Our observations, supported by earlier reports [13,16] clearly indicate that the presence of electron-withdrawing substituents in thiocarbonyl *S*-methylides strongly influence their behavior. Apparently, dimerization reactions are faster then 1,3-dipolar electrocyclization to give thiiranes. Similar to the known formation of tetraaryl-1,4-dithianes [3,8], the primarily formed dimers of **17** are the open-chain compounds **20**. These intermediates exist in equilibrium with the five-membered zwitterionic cycloadducts of type **19**. Their stability is limited, and only in the case described in [13] the isolation of the crystalline product was possible. On the other hand, the formation of **19** can be understood as a [2+3] cycloaddition of thiocarbonyl *S*-methylide **17** as a 1,3-dipole with a second molecule of **17**, in which the C=S bond acts as a dipolarophile. This process shows analogies to the 'Schönberg reaction' [8].

The dimerization of strongly polarized thiocarbonyl *S*-methylides (*e.g.* **6**, **9**, and **17**) to give dipolar products of type **7** and **19** has analogies in other 1,3-dipolar systems. The closest example is the dimerization of some sulfines leading to 1,2,5-oxadithiolane-2-oxides **31** [22] (Figure). Another well established example concerns the formation of 1,2,5-oxadiazole-2-oxides **32** (furoxanes) as dimers of extensively explored nitrile oxides [23,24] Analogous five-membered dimers **33** of nitrile imides are proposed as intermediates, which finally convert into 1,2,3-triazoles by elimination of a nitrene [24,25]. There are also examples known in which two different 1,3-dipoles combine in a formal [2+3] cycloaddition to give five-membered, zwitterionic heterocycles. Sulfines are especially prone to act as electron-deficient dipolarophiles, *e.g.*, the reaction with nitrile imides yields 4,5-dihydro-1,3,4-thiadiazole-1-oxides **34** [26], diazo compounds afford 2,5-dihydro-1,3,4-thiadiazole-1-oxides **35** [28,29], and a thiocarbonyl *S*-methylide combines to give the 1,3-dithiolane *S*-oxide **36** [30].



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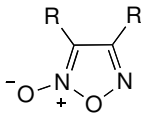

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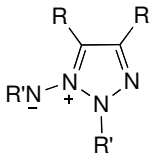

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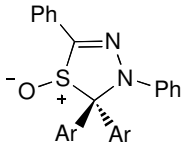

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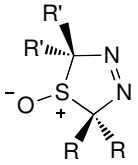

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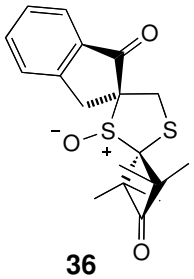

36

EXPERIMENTAL

1. General. For general information on instruments and methods see [15]. ^{31}P-NMR Spectra: Bruker DRX 400, in $CDCl_3$. Chemical shifts are given in ppm relative to H_3PO_4 (85%) as an external standard.

2. Starting materials. Methyl (diisopropoxy)phosphonyldithioformate (**14a**) and methyl (diethoxy)phosphonyldithioformate (**14b**) were prepared from the corresponding phosphites and carbon disulfide following a known protocol [30]. 1-Cyclohexyl-4,5-dimethyl-3*H*-imidazole-2-thione was synthetized from the corresponding imidazole *N*-oxide and 2,2,4,4-tetramethylcyclobutane-1,3-dithione as described in [31]. Other reagents were purchased from Sigma-Aldrich and used without purification.

3 Reactions of dithioformates 14a and 14b with diazomethane. General procedure: A solution of **14a** or **14b** (1 mmol) in abs. THF (1 ml) was placed in a flask equipped with a magnetic stirring bar. The flask was cooled in an aceton/dry ice bath to –65°C. While stirring, a freshly prepared etheral solution of diazomethane was added dropwise until the orange-red color of the starting material vanished. The colorless solution was slowly warmed up, and at –35°C a rapid evolution of nitrogen was observed. The mixture was stirred at room temperature for 1 h and the solvents were evaporated in

vacuum. The thick oily residue was analysed by ^{1}H-NMR spectroscopy and after removal of the solvent, the crude residue was separated chromatographically on preparative plates coated with silica gel. In the case of **14a**, chromatography with diethyl ether as eluent yielded two fractions, which were identified as **23a** and **24a**, respectively, and in the case of **14b**, the main fraction was identified as 1,4-dithiane **18b** (CH_2Cl_2/MeOH 97:3). In this case, the isolated solid was additionally purified by crystallisation.

An analogous experiment carried out with **14a** in a THF solution containing 3% (v/v) of water led to **23a** and **24a** in almost unchanged ratio.

Tetraethyl 2,3-bis(methylsulfanyl)-[1,4]dithian-2,3-diphosphonate (**18b**). Yield: 150 mg (62%), colorless crystals, m.p. 94–96°C (hexane, dry ice cooling). IR (KBr): 2981*s*, 2918*s*, 1475*m*, 1441*s*, 1390*s*, 1244*vs*, 1163*s*, 1028*vs*, 966*vs*, 791*s*, 750*vs*, 663*m*. ^{1}H-NMR: 1.34–1.41 (*m*, 4 *Me*CH_2); 2.36 (*s*, MeS); 2.75–2.95 (*m*, 2 CH_2S); 4.21–4.42 (*m*, 4 MeC*H*$_2$). ^{13}C-NMR: 15.7 (MeS); 16.7, 16.8, 16.9 (4 *Me*CH_2); 28.2, 28.9 (2 CH_2S); 64.2 (*d*, $^2J_{C\text{-}P} \approx 8.0$ Hz, 4 Me*C*H_2); 65.3, 65.4 (2 C_q). ^{31}P-NMR: 17.22. MS (EI): 484 ($M^{+\cdot}$, 22), 390 (23), 365 (51), 256 (35), 228 (58), 181 (63), 94(100). Anal. Calc. for $C_{14}H_{30}O_6P_2S_4$ (484.04): C 34.70, H 6.24, S 26.47. Found: C 34.82, H 6.43, S 26.03.

S-*Methyl [(diisopropoxy)phosphonyl]thioformate* (**23a**). Yield: 50 mg (20%), pale yellow oil, which showed now differences in the IR spectrum when compared with an original sample prepared according to [29]. IR (neat): 2981*s*, 2933*s*, 1647*s* (C=O), 1468*m*, 1454*m*, 1387*s*, 1377*s*, 1261*s*, 1180*m*, 1144*m*, 1103*s*, 993*s*, 881*m*. ^{1}H-NMR: 1.36–1.41 (*m*, 2 *Me*$_2$CH); 2.41 (*d*, $^4J_{H\text{-}P} \approx 1.1$ Hz, MeS); 4.79–4.87 (*m*, 2 Me$_2$C*H*). ^{13}C-NMR: 11.0 (*d*, $^3J_{C\text{-}P} \approx 1.3$ Hz, MeS); 23.7, 23.8, 24.0, 24.1 (2 *Me*$_2$CH); 73.9 (*d*, $^2J_{C\text{-}P} \approx 7.0$ Hz, 2 $(CH_3)_2$*C*H); 199.4 (*d*, $^1J_{C\text{-}P} \approx 209$ Hz, C=O). ^{31}P-NMR: –4.85.

Diisopropyl ({2-[(diisopropoxyphosphonyl)(methylsulfanyl)methylsulfanyl]ethyl-sulfanyl}oxomethanephosphonate (**24a**). Yield: 100 mg (35%), thick, pale yellow oil. IR (neat): 2980*s*, 2933*s*, 1645*s* (C=O), 1468*m*, 1452*m*, 1387*s*, 1375*s*, 1252*vs*, 1178*s*, 1142*s*, 1105*s*, 993*vs*, 887*m*. ^{1}H-NMR: 1.36, 1.39 (2 *d*, *J* = 7.5, 4 *Me*$_2$CH); 2.31 (*d*, $^4J_{H\text{-}P} \approx 1.0$ Hz, MeS); 2.94–3.31 (*m*, 2 CH_2); 3.79 (*d*, $^2J_{H\text{-}P} \approx 17.0$ Hz, CHP); 4.75–4.88 (*m*, 4 Me$_2$C*H*). ^{13}C-NMR: 14.7 (*d*, $^3J_{C\text{-}P} \approx 3.7$ Hz, MeS); 23.6, 23.7, 23.9, 24.0, 24.1 (4 *Me*$_2$CH); 28.1, 30.6 (2 CH_2); 46.2 (*d*, $^1J_{C\text{-}P} \approx 157$ Hz, CHP); 72.4, 73.9 (2 *d*, $^2J_{C\text{-}P} \approx 7.0$ Hz, 4 Me$_2$*C*H); 198.9 (*d*, $^1J_{C\text{-}P} \approx 209$ Hz, C=O). MS (CI, NH_3): 511 (100, $[M+1]^+$), 479 (19), 423 (11).

4. Treatment of 2,5-dihydro-1,3,4-thiadiazole 15a with morpholine. To a cold solution (–65°C) of **15a**, obtained from 1 mmol of **14a** according to the general procedure, was added morpholine (10 mmol) and, while stirring, the mixture was slowly warmed up to room temperature. No evolution of nitrogen was observed. After evaporation of the solvents and removal of excess morpholine by distillation in a Kugel-Rohr, the semisolid residue was separated on preparative plates coated with silica gel (CH_2Cl_2/MeOH 99:1 as eluent). The main fraction was purified by crystallisation.

Diisopropyl 1,3,4-thiadiazol-2-phosphonate (**16a**). Yield: 160 mg (64%), colorless crystals, m.p. 36–38°C (diethyl ether/dry ice cooling). IR (KBr): 3051*m*, 2983*m*, 1377*m*, 1250*s*, 1105*s*, 1005*vs*, 652*m*, 579*s*. ^{1}H-NMR: 1.36, 1.41 (2 *d*, $J_{H\text{-}H} \approx 6.2$ Hz, 2 *Me*$_2$CH); 4.88–4.99 (*m*, 2 Me$_2$C*H*); 9.37 (*d*, $^4J_{H\text{-}P} \approx 1.0$ Hz, CH=N). ^{13}C-NMR: 23.5, 23.6, 23.7, 23.8 (2 *Me*$_2$CH); 73.9 (*d*, $^2J_{C\text{-}P} \approx 6.3$ Hz, 2 Me$_2$*C*H); 154.4 (*d*, $^3J_{C\text{-}P} \approx 3.6$ Hz, *C*H=N); 161.0 (*d*, $^1J_{C\text{-}P} \approx 220$ Hz, C_qP). MS (CI, NH_3): 268 (100, $[M+NH_4]^+$), 251 (32, $[M+1]^+$). Anal. Calc. for $C_8H_{15}N_2O_3PS$ (250.56): C 38.40, H 6.04, N 11.19, S 12.81. Found: C 38.44, H 6.02, N 11.12, S 12.55.

5. Decompositions of 2,5-dihydro-1,3,4-thiadiazoles 15a and 15b in methanol. The reactions were performed according to the general procedure, but instead of abs. THF, MeOH (3 ml) was used as the solvent. The crude mixtures were separated chromatographically on preparative plates coated with silica gel using mixture of CH_2Cl_2/AcOEt (1:1) or CH_2Cl_2/MeOH (98:2) as eluents yielding **21a** and **21b**, respectively.

Diisopropyl ({2-[(diisopropoxyphosphonyl)(methylsulfanyl)methylsulfanyl]ethyl-sulfanyl}(methoxy)(methylsulfanyl)methanephosphonate (**21a**). Yield: 200 mg (70%), thick pale yellow oil. IR (neat): 2980*s*, 2931*s*, 1468*m*, 1452*m*, 1385*s*, 1373*s*, 1248*vs*, 1178*s*, 1142*s*, 1105*s*, 985*vs*, 737*m*. ^{1}H-NMR: 1.38 (*d*, 4 *Me*$_2$CH); 2.23 (*s*, MeS); 2.31 (*d*, $^4J_{H\text{-}P} \approx 0.7$ Hz, MeS); 3.00–3.15 (*m*, 2 CH_2S); 3.42 (*s*, MeO); 3.80 (*d*, $^2J_{H\text{-}P} \approx 18.0$ Hz, CHP); 4.45–5.10 (*m*, 4 Me$_2$*C*H). ^{31}P-NMR: 13.18, 18.23. MS (CI, isobutan): 588 (23, $[M+CH_4]^+$), 587 (100, $[M+CH_3]^+$), 573 (8, $[M+1]^+$). Anal. Calc. for $C_{19}H_{42}O_7P_2S_4$ (572.75): C 39.84, H 7.39, S 22.39. Found: C 39.60, H 7.36, S 22.29.

Diethyl ({2-[(diethoxyphosphonyl)(methylsulfanyl)methylsulfanyl]ethylsulfanyl}-(methoxy)(methylsulfanyl)methanephosphonate (**21b**). Yield: 201 mg (73%), thick, pale

yellow oil. IR (film): 2981*s*, 2927*s*, 1637*w*, 1441*m*, 1390*m*, 1250*s*, 1051*s*, 1022*s*, 970*s*, 793*m*, 744*m*. ^{1}H-NMR: 1.35 (*t*, 4 *Me*CH_2); 2.22 (*s*, MeS); 2.31 (*d*, $^4J_{H\text{-}P} \approx$ Hz, MeS); 3.00–3.15 (*m*, 2 CH_2S); 3.50 (*s*, MeO); 3.95 (*d*, $^2J_{H\text{-}P} \approx 18.5$ Hz, CHP); 4.10–4.50 (*m*, 4 Me*C*H_2). ^{13}C-NMR: 13.8, 14.6 (2 MeS); 16.4, 16.5, 16.6, 16.7 (4 *Me*CH_2); 30.5 (MeO); 31.5, 31.7 (2 CH_2S); 45.7 (*d*, $^1J_{C\text{-}P} \approx 155.1$ Hz, CHP); 63.8, 64.1, 64.4, 64.8 (4 Me*C*H_2). Anal. Calc. for $C_{17}H_{38}O_7P_2S_4$ (544.70): C 37.49, H 7.03, S 23.55. Found: C 37.60, H 7.16, S 23.29.

In an analogous reaction with **15a**, a catalytic amount of TFA (ca. 0.1 vol.%) was added to the solution. After evaporation of the solvent *in vacuo*, the crude residue forming a thick colorless oil was analysed by ^{1}H-NMR spectroscopy. Along with signals of the known **21a**, the presence of characteristic signals at 2.40 (*s*, MeS), 2.90 (*m*, S-CH_2-O), and 3.48 (*d*, $^2J_{H\text{-}P} \approx 0.7$ Hz, MeO), respectively, revealed the formation of a new product, which was identified as **22a**. The comparision of the intensities of MeS-signals for **21a** (2.23 ppm) and **22a** (2.40 ppm) confirmed the ratio of both compounds as *ca.* 3:2. Attempted separations of **21a** and **22a** on silica were unsuccessful, and complete decomposition of **22a** was observed.

6. Interception of the "dimeric" thiocarbonyl ylide 20 with S- and N-nucleophiles. The reactions were performed according to the general procedure. Abs. THF (1 ml) was used as a solvent for all experiments, which were carried out with 1 mmol of **14a**. After decolorization of the dithioester at –65ºC, 1 mmol of corresponding nucleophile was added and the mixture was slowly warmed up to room temperature. Then, the solvent was evaporated, the crude residue was separated on preparative TLC plates coated with silica gel. The isolated solid products were additionally purified by crystallisation.

Reaction with thiophenol. A mixture of CH_2Cl_2 and diethyl ether (9:1) was used as eluent. *Diisopropyl ({2-[(diisopropoxyphosphonyl)(methylsulfanyl)(methylsulfanyl]-ethylsulfanyl}(methylsulfanyl)(phenylsulfanyl)methanephosphonate* (**27**). Yield: 160 mg (49%), thick, colorless oil. IR (neat): 2980*s*, 2931*m*, 2922*m*, 1645*w*, 1468*m*, 1452*m*, 1439*m*, 1385*s*, 1375*s*, 1248*s*, 1178*m*, 1142*m*, 1109*s*, 989*vs*, 889*m*, 750*s*. ^{1}H-NMR: 1.29–1.37 (*m*, 4 *Me*$_2$CH); 2.26, 2.28 (2 *s*, 2 MeS); 2.95–3.26 (*m*, 2 CH_2S); 3.75 (*d*, $^2J_{H\text{-}P} \approx 17.3$

Hz, CHP); 4.72–4.88 (*m*, 4 Me_2CH); 7.24–7.37 (*m*, 3 arom. H); 7.69–7.72 (*m*, 2 arom. H). ^{13}C-NMR: 14.5, 14.8 (2 *d*, $^3J_{C\text{-}P} \approx 3.3$ and ≈ 10.5 Hz, resp., 2 MeS); 23.5, 23.6, 23.8, 23.9, 24.0, 24.1, 24.3 (4 Me_2CH); 31.0, 31.1 (2 CH_2S); 45.9 (*d*, $^1J_{C\text{-}P} \approx 157$ Hz, CHP); 53.4 (SC_qS); 72.3–74.1 (4 Me_2CH); 128.2, 129.9, 137.7 (5 arom. CH); 130.0 (1 arom. C). ^{31}P-NMR: 18.56, 21.42. MS (EI): 651 (12, $M^{+\cdot}$), 269 (100), 225 (20), 183 (33). Anal. Calc. for $C_{24}H_{44}O_6P_2S_5$ (650.89): C 44.29, H 6.81, S 24.63. Found: C 43.14; H 6.82; S 23.82.

Reaction with benzothiazole. A mixture of CH_2Cl_2 and diethyl ether (4:1) was used as the eluent. *Diisopropyl [(benzothiazol-2-yl)sulfanyl]{2-[(diisopropoxyphosphonyl)-(methylsulfanyl)methylsulfanyl]ethylsulfanyl}(methylsulfanyl)methyanephosphonate* (**28**). Yield: 140 mg (40%), thick, pale yellow oil. IR (neat): 2980*s*, 2931*m*, 1458*s*, 1427*s*, 1385*s*, 1375*s*, 1248*s*, 1178*m*, 1142*m*, 1103*s*, 991*s*, 756*s*, 665*m*. ^{1}H-NMR: 1.28–1.30 (*m*, 4 Me_2CH); 2.35, 2.40 (2 *s*, 2 MeS); 2.93–3.04 (*m*, 2 CH_2S); 3.80 (*d*, $^2J_{H\text{-}P} \approx 17.5$ Hz, CHP); 4.78–4.87 (*m*, 4 Me_2CH); 7.13–8.02 (*m*, 4 arom. H). ^{13}C-NMR: 14.5, 15.7 (2 MeS); 23.7, 23.8, 23.9, 24.0, 24.1, 24.2 (4 Me_2CH); 31.0, 32.1 (2 CH_2S); 45.9 (*d*, $^1J_{C\text{-}P} \approx 157$ Hz, CHP); 65.0 (*d*, $^1J_{C\text{-}P} \approx 160$ Hz, SC_qS); 72.5, 74.1 (4 Me_2CH); 112.7 (NCS); 121.0–141.3 (4 arom. CH, 2 arom. C). ^{31}P-NMR: 17.57, 21.45. MS (EI): 269 (100), 255 (40), 167 (76), 123 (35).

*Reaction with 1-cyclohexyl-4,5-dimethyl-(3*H*)-imidazole-2-thione*. A mixture of CH_2Cl_2 and diethyl ether (4:1) was used as eluent. *Diisopropyl [(1-cyclohexyl-4,5-dimethyl-1*H*-imidazol-2-yl)sulfanyl]{2-[(diisopropoxyphosphonyl)(methylsulfanyl)methyl sulfanyl]ethylsulfanyl}(methylsulfanyl)methanephosphonate* (**29**). Yield: 230 mg (61%), thick, pale yellow oil. IR (neat): 2978*s*, 2931*s*, 2858*s*, 1722*w*, 1578*m*, 1450*s*, 1385*s*, 1373*s*, 1252*s*, 1105*s*, 987*s*, 733*s*. ^{1}H-NMR: 1.26–1.35 (*m*, 4 Me_2CH); 1.73–1.99 (*m*, 5 cyclohexyl-CH_2); 2.05, 2.15 (2 *s*, 2 MeS); 2.19, 2.20 (2 *s*, 2 Me); 2.97 (*m*, 1 cyclohexyl-CH); 4.05 (*d*, $^2J_{H\text{-}P} \approx 16.5$ Hz, CHP); 4.20–4.28 (*m*, 2 CH_2S); 4.63–4.91 (*m*, 4 Me_2CH). ^{13}C-NMR: 10.7, 12.5 (2 Me); 14.1. 14.2 (2 MeS); 23.4, 23.6, 23.7, 24.0, 24.1, 24.2, 24.8, 25.2, 26.0, 26.1 (4 Me_2CH, 5 cyclohexyl-CH_2); 30.6, 31.9 (2 CH_2S); 45.2 (*d*, $^1J_{C\text{-}P} \approx 156$ Hz, CHP); 53.3 (SC_qS); 57.2 (cyclohexyl-CH); 72.1, 72.3, 72.4, 72.5 (4 Me_2CH); 126.1, 135.4, 135.8 (3 imidazole-C). ^{31}P-NMR: 21.42. MS (EI): 751 (16, $M^{+\cdot}$), 481 (72), 255 (100), 209 (65), 142 (35).

Reaction with benzimidazole. A mixture of CH_2Cl_2 and MeOH (96:4) was used as eluent. *Diisopropyl (benzimidazol-2-yl){2-[(diisopropoxyphosphonyl)(methylsulfanyl)-methylsulfanyl]ethylsulfanyl}(methylsulfanyl)methanephosphonate* (**30**). Yield: 300 mg (90%), thick, colorless oil. IR (neat): 2981*s*, 2931*m*, 1495*m*, 1450*m*, 1387*s*, 1246*s*, 1103*s*, 993*vs*, 750*s*. ^{1}H-NMR: 1.27–1.35 (*m*, 4 *Me*$_2$CH); 1.91, 2.24 (2 *s*, 2 MeS); 2.58–2.69 (*m*, 2 CH_2S); 3.45 (*d*, $^2J_{H\text{-}P} \approx 17.6$ Hz, CHP); 4.66–4.90 (*m*, 4 Me$_2$C*H*); 7.69–8.44 (*m*, 4 arom. H). ^{13}C-NMR: 14.3, 14.5 (2 *d*, $^3J_{C\text{-}P} \approx 4.3$ and ≈ 8.0 Hz, resp., 2 MeS); 23.6, 23.7, 23.8, 24.1, 24.2, 24.3, 24.4 (4 *Me*$_2$CH); 30.2, 31.5 (2 CH_2S); 45.4 (*d*, $^1J_{C\text{-}P} \approx 155$ Hz, CHP); 69.0 (NC_qS); 72.3–72.5 (4 Me$_2$*C*H); 116.1, 120.4, 123.1, 123.3 (4 arom. CH); 132.4, 143.5, 143.9 (3 arom. C). ^{31}P-NMR: 14.70, 21.45. MS (EI): 659 (<4, $M^{+\cdot}$), 317 (40), 269 (100), 118 (64), 83 (56), 43 (62).

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