Insertion of α-Phosphorylcarbene Moiety into S–S and Se–Se Bonds: Synthesis of Dithio- and Diselenoacetals of Formylphosphonates

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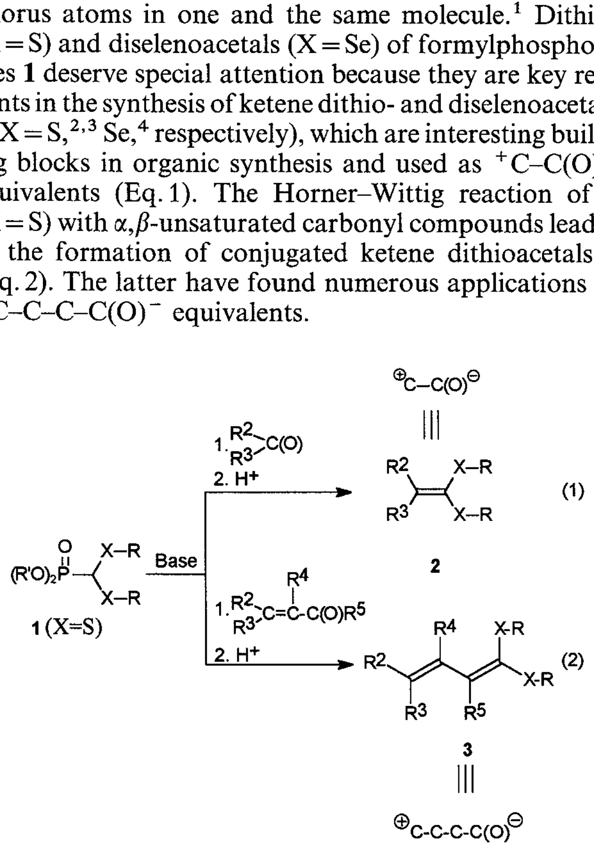
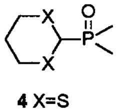
Reaction between diazomethanephosphonates and disulfides or diselenides catalyzed by boron trifluoride – diethyl ether complex leads to insertion of the $(RO)_2P(O)$–CH(:) moiety into S–S and Se–Se bonds, respectively. The proposed method makes it possible to synthesize 2-phosphoryl-substituted 1,3-diselenanes, not available by other means. The yield depends on the reaction conditions. Stereoselectivity of insertion into cyclic systems is discussed. Reactions catalyzed by rhodium(II) acetate or anhydrous copper(II) sulfate afford the relevant sulfides, $(RO)_2P(O)$–CH_2SR. The possible ionic and free radical mechanistic pathways are presented.

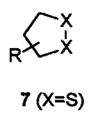
Extensive studies have been carried out in our laboratory on the synthesis, properties, and synthetic applications of organic compounds containing both sulfur and phosphorus atoms in one and the same molecule.[1] Dithio- (X = S) and diselenoacetals (X = Se) of formylphosphonates **1** deserve special attention because they are key reagents in the synthesis of ketene dithio- and diselenoacetals **2** (X = S,[2,3] Se,[4] respectively), which are interesting building blocks in organic synthesis and used as $^+$C–C(O)$^-$ equivalents (Eq. 1). The Horner–Wittig reaction of **1** (X = S) with α,β-unsaturated carbonyl compounds leads[5] to the formation of conjugated ketene dithioacetals **3** (Eq. 2). The latter have found numerous applications as $^+$C–C–C–C(O)$^-$ equivalents.



Diselenoacetal group has been used for protection and umpolung of the carbonyl group.[6–8] Recently, the cyclic dithio-, **4**, and diselenoacetals **5** have also been the subject of intensive conformational studies in connection with the anomeric effect operating in these systems.[9,10]

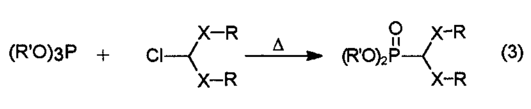


4 X=S
5 X=Se

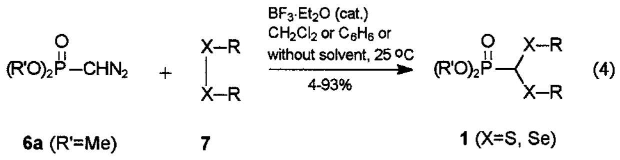


7 (X=S)
8 (X=Se)

Dithioacetals of formylphosphonates **1** (X = S) were first prepared by the Arbuzov reaction of trialkyl phosphites with chlorodithioacetals (Eq. 3)[11] Since then, other syntheses[12–16] of **1** (X = S) have been developed. Several methods for the synthesis of diselenoacetals are also available,[17,18] including a recent preparation[4] of diselenoacetals of formylphosphonates **1** (X = Se). However, these methods could not be applied for the synthesis of 1,3-diselenane derivatives **5**, which were our target structures for the studies on the anomeric effect in C–Se–C–P system.[9,19] Therefore, we decided to examine the possibility of the preparation of the title compounds by the insertion of the dialkoxyphosphorylcarbene moiety into the S–S or Se–Se bonds of disulfides (X = S) or diselenides (X = Se) as shown in Eq. 4.



1 (X=S)

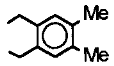
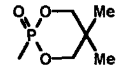
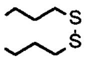
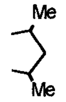
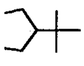
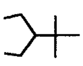
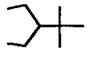
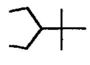
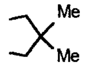
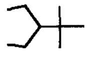


6a (R'=Me) **7** **1** (X=S, Se)
6b (R'=Et)

Several insertions of carbenes or carbenoids generated from diazo compounds into the S–S bond have been reported in the literature.[20–23] The insertion process was initiated photochemically[22] or using a catalytic amount of boron trifluoride – diethyl ether complex,[21] anhydrous copper(II) sulfate,[21] copper(I) chloride or rhodium(II) acetate.[22]

Our preliminary experiments were performed with diethyl diazomethanephosphonate (**6b**) and methyl disulfide (**7a**). We found that the reaction can be carried out in the disulfide as a solvent, and that the use of a catalytic amount (13 %) of boron trifluoride–diethyl ether complex and 3 equivalents of the disulfide **7a** led to the desired diethyl bis(methylthio)methanephosphonate (**1a**) in a good yield (85 %, Table 1, Run 1, method A). A decrease in the excess of the disulfide **7a** from 3 to 2 equivalents (Run 2) resulted in an apparent decrease in yield of **1a** to 63 %. On the other hand, the reaction between **6a** (1 equiv) and **7a** (2 equiv) in dichloromethane, according to a modified procedure (Run 3, method B), afforded acetal **1b** in 88 % yield, which seems to reflect the optimum conditions of the reaction.

Table 1. Results of Synthesis of Acetals **1**, $(R'O)_2P(O)CH(XR)_2$, via the Reaction Between **6** and **7** Catalyzed by $BF_3{\cdot}Et_2O$

Run	$(RX)_2$	Product	R′	X	R	Method	Solvent	n[a]	x[b]	Yield (%)[c]
1	**7a**	**1a**	Et	S	Me	A	none	3	0.13	85
2	**7a**	**1a**	Et	S	Me	A	none	2	0.13	63
3	**7a**	**1b**	Me	S	Me	B	CH_2Cl_2	2	0.10	88
4	**7b**	**1c**	Me	S	Et	B	CH_2Cl_2	2	0.25	78
5	**7c**	**1d**	Me	S	Pr	B	CH_2Cl_2	2	0.25	61
6	**7d**	**1e**	Me	S	*i*-Pr	C	CH_2Cl_2	2	0.50	49
7	**7e**	**1f**	Me	S	$PhCH_2$	C	CH_2Cl_2	2	0.50	35
8	**7f**	**1g**	Me	S	Ph	B	CH_2Cl_2	2	0.25	78
9	**7g**	**1h**	Me	S	*p*-Tol	B	CH_2Cl_2	2	0.10	93
10	**7h**	**1i**	Me	S		C	CH_2Cl_2	2	0.50	27
11	**7i**	**1j**	Me	S	$P(O)(OMe)_2$	C	CH_2Cl_2	2	0.50	50
12	**7j**	**1k**	Me	S		C	CH_2Cl_2	2	0.50	42
13	**7k**	**1l**	Me	S		C	CH_2Cl_2	2	0.50	42
14	**7l**	**1l**	Me	S	$-(CH_2)_3-$	D	CH_2Cl_2	2.7	0.50	30
15	**7l**	**1l**	Me	S	$-(CH_2)_3-$	D[d]	CH_2Cl_2	2.7	0.50	18
16	**7m**	**1m**	Me	S		D	CH_2Cl_2	2.7	0.50	*cis*: 6 *trans*: 4
17	**7m**	**1m**	Me	S		D	C_6H_6	2.7	0.50	*cis*: 7 *trans*: 5
18	**7n**	**1n**	Me	S		D	CH_2Cl_2	2.7	0.50	*cis*: 13 *trans*: 17
19	**7n**	**1n**	Me	S		D[e]	CH_2Cl_2	2.7	0.50	*cis*: 10 *trans*: 10
20	**7n**	**1n**	Me	S		D	C_6H_6	2.7	0.50	*cis*: 7 *trans*: 2
21	**7o**	**1o**	Me	Se	Ph	C	CH_2Cl_2	2	0.50	64
22	**7p**	**1p**	Me	Se		B	CH_2Cl_2	2	0.20	18
23	**7q**	**1q**	Me	Se		B	CH_2Cl_2	2	0.20	*cis*: 4 *trans*: 7

[a] Moles of **7** per mole of **6**.

[b] Moles of catalyst per one mole of **6**.

[c] All products gave satisfactory microanalyses: C ± 0.3, H ± 0.2, P ± 0.3.

[d] Solution of 1,2-dithiolane was concentrated to a volume of about 2 mL prior to the addition of **6a**.

[e] Without removal of PbS.

Nevertheless, for higher alkyl disulfides, it was necessary to optimize the conditions by increasing the amount of the catalyst (up to 50 % for isopropyl derivative **7d**; Run 6, Table 1). It is clear from the data in Table 1 that the yield of the reaction strongly depends on the steric environment of the S–S bond, and decreases with the increase in steric hindrance. Interestingly, the yield of insertion into the Se–Se bond in diphenyl diselenide (**7o**, Run 21) is comparable with that into the S–S bond of diphenyl disulfide (**7f**, Run 8).

Steric factors are important not only for the yield but also for the stereochemical outcome of the reaction as we found based on the insertion into the S–S and Se–Se bonds of the cyclic systems **8** (X = S, Se). 2-Phosphoryl-substituted 1,3-dithianes **4** that are the desired products of this reaction (for X = S) have also been accessible via various other methods.[9] However, the relevant 1,3-diselenanes **5** were unknown. Ando et al. reported[22] a number of insertions into stable cyclic disulfides. Unfortunately, 1,2-dithiolanes **8** (X = S) in which we were interested, were known to polymerize readily.[25] Several methods for the preparation of **8** (X = S) are available.[25–27] Although the experimental details were not published, we selected the method[26] that consisted of the reaction between the appropriate lead dithiolate and elemental sulfur. Lead sulfide as the ballast byproduct could easily be separated, and a solution of the relevant 1,2-dithiolane (**8**, X = S, 2.7 equiv) was used for the reaction with 1 equivalent of dimethyl diazomethanephosphonate (**6a**). The results are collected in Table 1.

It is clear that the yield of the insertion considerably depends on the steric hindrance around the S–S bond, as it was also observed in the acyclic series (*vide supra*). For the least crowded, unsubstituted 1,2-dithiolane (**7l**), the desired **11** could be obtained in almost 30% yield (Run 14), while *cis*-3,5-dimethyl-1,3-dithiolane (**7m**, Run 16) afforded products in 10% overall yield only. However, in contrast to acyclic disulfides, the use of solvent was necessary, otherwise the yield decreased almost by half (cf. Runs 14 and 15). This observation can, perhaps, be attributed to the presence of boron trifluoride – diethyl ether complex, which as Lewis acid is able[25] to promote polymerization of 1,2-dithiolane over the insertion. The reaction between **6a** and 4-*tert*-butyl-1,2-dithiolane (**7n**) in dichloromethane (Run 18) occurred in 30% overall yield, thus suggesting that the 4-*tert*-butyl group does not hinder markedly the S–S bond. Indeed, while two diastereomeric products were formed from **7n**, the selectivity of the insertion was low (*cis* : *trans* = 13 : 17). Interestingly, the isomers containing the equatorial phosphoryl group were preferred (Runs 16–18; e.g. *trans*-**7n** over *cis*-**7n**), though they are thermodynamically less stable.[9] The origin of this selectivity stems, most probably, from repulsive interactions between the phosphorus-containing substituent and axial hydrogens H(3) and H(5) in the transition state leading from the intermediate ylide **9** to axial 1,3-dithiane derivative, as shown in the Figure. The corresponding destabilizing interactions in the transition state derived from **10** are avoided due to different conformation about the exocyclic S(1)–CP bond. Run 20 is the only exception to the rule, however, the overall yield (9%) is so low that it does not seem reasonable to discuss the observed selectivity.

The choice of solvent for the insertion reaction may be important, while in the case of **7m** the replacement of dichloromethane with benzene did not influence the overall yield (Runs 16 and 17), and for the *tert*-butyl derivative **7n** the yield decreased (Runs 18 and 20). Finally, we found it necessary to remove lead sulfide from 1,2-dithiolane solution; otherwise the yield decreased by 10% (Runs 18 and 19).

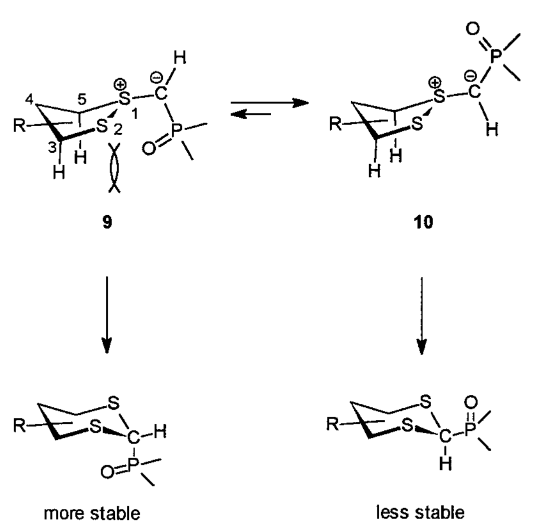
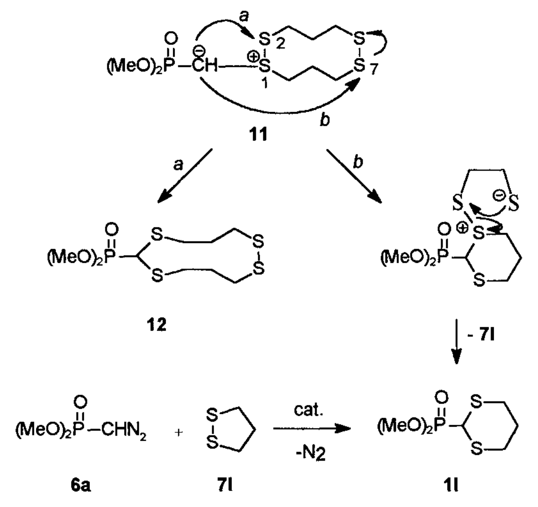


Figure. Interactions During the Insertion into the S–S Bond of Cyclic Disulfides

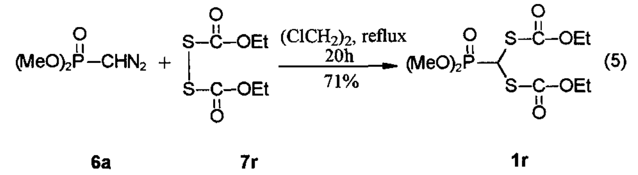
An analogous approach enabled us to prepare the desired, unknown, 2-dimethoxyphosphoryl-1,3-diselenanes **5**. The insertion reaction was carried out in dichloromethane solution by adding dimethyl diazomethanephosphonate (**6a**) to a mixture of the appropriate 1,2-diselenolane **8** (X = Se) used in one molar excess, and boron trifluoride–diethyl ether complex as a catalyst. From 4,4-dimethyl-1,2-diselenolane (**7p**), 2-dimethoxyphosphoryl-1,3-diselenane (**1p**) was obtained as a pale yellow oil in 18% yield. As expected, 4-*tert*-butyl-1,2-diselenolane (**7q**) afforded a mixture of the two isomeric 2-dimethoxyphosphoryl-1,3-diselenanes *cis*-**1q** (yield 4%; mp 109.5–110 °C) and *trans*-**1q** (yield 7%; mp 83.0–83.5 °C), which were separated by flash chromatography on silica gel and crystallized from hexane. By analogy to 1,3-dithianes, *cis*-**1n** and *trans*-**1n**, the preference for the formation of *trans*-**1q** (the less thermodynamically stable isomer)[19] over *cis*-**1q** could be explained on steric grounds (Figure 1, Se instead of S). Apart from NMR evidence the identity of *cis*-**1q** and *trans*-**1q** was also confirmed by X-ray crystallography.[19]

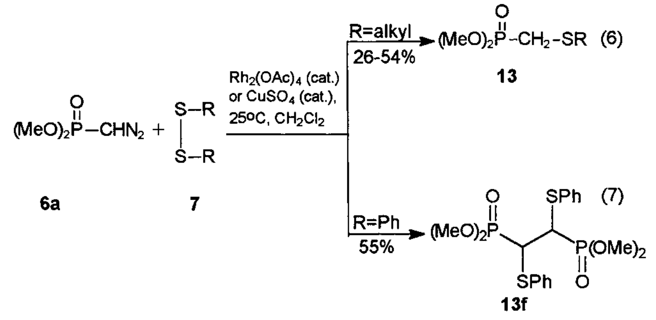
It is interesting that the same products and identical yields were obtained in Runs 13 and 14, though the substrates were different. This observation could be rationalized based on the mechanisms shown in Scheme 1. The size of the ring in the final products is established at the stage of a nucleophilic attack of the phosphonate carbon atom at S(2) or S(7) (pathway *a* or *b*). Presumably, due to a small distance between proanomeric carbon and sulfur S(7) in **11** (X-ray structure of **7k** shows[28] that S(1) and S(2) are located very closely to S(7) and S(6), respectively), such an attack may occur at S(2) and S(7). Because the six-membered derivative **11** should be more stable than the nine-membered one **12**, the relevant transition state in pathway *b* has, probably, lower energy, and this pathway is preferred. The dithiolane **7l** which is formed as a byproduct in pathway *b* may react with **6a** to afford additional portions of **11**.

We were also able to promote thermally the insertion of dialkoxyphosphorylcarbene moiety into the S–S disulfide bond (Eq. 5). However, we found that neither rhodium(II) acetate nor anhydrous copper(II) sulfate led to the formation of the desired dithioacetals **1**. On the other hand, these catalysts promoted the formation of the appropriate sulfides **13** (Eq. 6). Thus, according to Method B and in the presence of 5% mol of rhodium(II) acetate, **7a, 7c, 7d** and *tert*-butyl disulfide (**7s**) were converted into the relevant sulfides **13a, 13c, 13d**, and **13s** in 54, 36, 45, and 26% isolated yield, respectively.

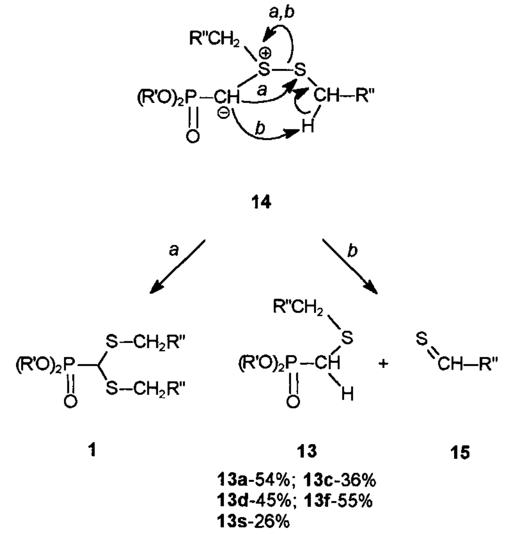


Scheme 1

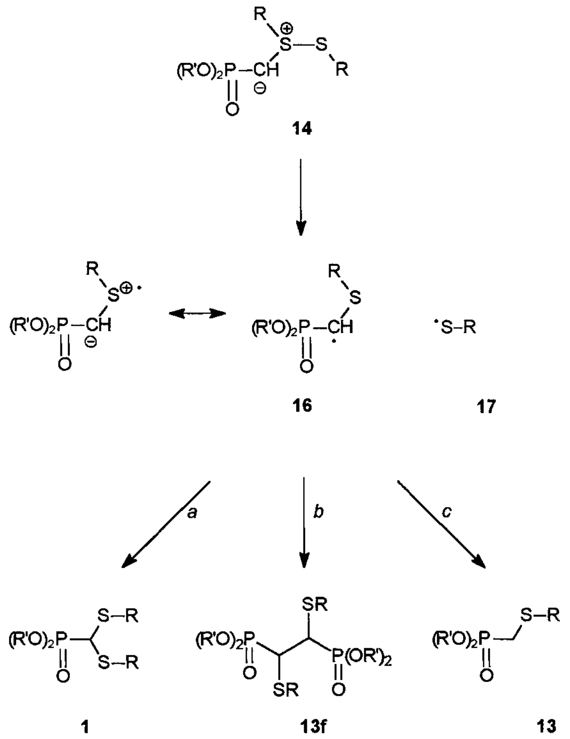




The results obtained for **7a**, **7c**, and **7d** could be rationalized in terms of variable reactivity of the intermediate ylide **14** (Scheme 2; cf. **11**, Scheme 1). Pathway *a* involves a nucleophilic attack at the sulfur atom to afford the expected dithioacetal **1**, which may be related to the ionic Stevens rearrangement.[22,29–31] This kind of reactivity is observed if insertion reactions are catalyzed by boron trifluoride–diethyl ether complex. However, under the influence of rhodium(II) acetate or anhydrous copper(II) sulfate the nucleophilic attack might occur at the geminally bound hydrogen atom (pathway *b*) to afford the sulfide **13** and the thioaldehyde **15** (not isolated). It should be noted that an analogous pathway has been suggested by Ando et al.[22] for the reaction between other disulfides and carbenes. However, the mechanism proposed above cannot operate for *tert*-butyl disulfide (**7s**) because the necessary hydrogen atom is absent. Interestingly, the relevant rhodium(II) acetate catalyzed reaction of phenyl disulfide (**7f**) that does not have hydrogen atoms that could participate in this mechanism either, gave unexpected dimeric sulfide **13f** in 55% yield (Eq. 7). Formation of dimeric structure suggests that a free radical pathway shown in Scheme 3 may be involved, which is in agreement with a possible radical pair pathway in the Stevens rearrangement.[29,30]



Scheme 2



Scheme 3

According to the proposed mechanism, the S–S bond in the ylide **14** may undergo homolytic cleavage to give the radicals **16** and **17**. Their recombination would afford dithioacetal **1** (pathway *a*). Recombination of two radicals **16** would account for the formation of **13f** (pathway *b*). Free radical mechanism would also explain the formation of the sulfide **13** (e.g. **13s**), as it would arise by abstraction of a hydrogen atom from the medium by the radical **16** (pathway *c*). Nevertheless, the exact role of a catalyst for the discussed mechanisms is not clear.

Table 2. ^{1}H, ^{13}C and ^{31}P NMR Data for Acetals **1**, $(MeO)_2P(O)CH(XR)_2$

Compound	n_D^{20} or mp (°C)	^{1}H NMR ($CDCl_3$/TMS), δ, *J* (Hz)			^{13}C NMR ($CDCl_3$/TMS), δ			^{31}P NMR ($CDCl_3$/ 80% H_3PO_4) δ
		CH_3O	CHP	R	CH_3O	CHP	R	
1b	1.5145	3.88 (10.8)	3.76 (18.0)	2.29 (1.2)	54.1 (7.1)	46.6 (156)	14.1 (4.2)	22.0
1c	1.5044	3.88 (10.7)	3.88 (17.3)	CH_3: 1.29 (7.4),^{b} CH_2: 2.84 (7.4)^{c}	54.3 (7.1)	43.2 (157)	CH_3 13.9, CH_2: 25.6 (3.9)	22.7
1d	1.4998	3.88 (10.7)	3.84 (17.3)	CH_3: 1.02 (7.3),^{b} CCH_2C: 1.65 (7.3),^{d} CH_2S 2.76–2.82^{f}	54.3 (7.5)	43.8 (157)	CH_3 13.4, $C\mathit{C}H_2C$: 22.4, CH_2S: 33.6 (3.0)	22.7
1e	1.4951	3.89 (10.7)	3.91 (15.5)	CH_3: 1.31 (6.7), CH_3: 1.33 (6.7), CH: 3.39 (6.7)^{e}	54.0 (7.0)	41.1 (158)	CH_3: 26.6, CH_3: 22.8, CH: 35.5 (3.0)	23.0
1f	1.5889	3.74 (10.7)	3.50 (15.2)	$C\mathit{H}H$: 3.82 (13.1), $CH\mathit{H}$: 13.1 (2.5), C_6H_5, 7.2–7.4^{f}	54.8 (6.8)	41.5 (156)	CH_2: 36.7 (3.6), Ar: 128.0, 129.3, 129.9, 137.7	22.8
1g	1.6038	3.84 (10.8)	4.43 (16.4)	7.2–7.5^{f}	55.0 (7.1)	54.1 (153)	129.1, 129.7, 133.9, 134.1	21.6
1h	1.5894	3.83 (10.8)	4.31 (16.3)	CH_3: 2.33, Ar: 7.1–7.4^{f}	54.9 (6.8)	54.8 (152)	CH_3: 21.8, Ar: 130.4, 130.6, 134.4, 139.4	21.9
1i	155–156	3.92 (10.7)	5.05 (14.8)	CH_3: 2.21, $C\mathit{H}H$: 3.50, $CH\mathit{H}$ 3.55, Ar: 6.94	54.6 (6.8)	41.0 (157)	CH_3: 19.2, CH_2: 34.0, Ar: 130.5, 136.1, 136.6	19.8
1j	1.4500^{g}	3.85 (10.9)	4.90 (14.9, 16.9^{b})	CH_3: 3.83 (12.9), CH_3: 3.84 (12.9)	54.8 (6.8)	42.6 (159, 5^{b})	CH_3: 54.5 (4.8)	19.8 (19.5^{b}), 25.0 (19.5)
1k	glassy solid	2.37 (11.2, 1.4)	3.84 (13.2)	CH_3: 0.92, CH_3: 1.30, $C\mathit{H}H$: 3.95 (10.9, 1.4), $CH\mathit{H}$: 4.14 (10.9, 4.2)	63.8 (7.0, 1.4)	29.1 (128)	CH_3: 21.2, CH_3: 22.6, $Me_2\mathit{C}$: 33.2, CH_2: 78.5 (7.1)	7.0 (17.1^{b}), 16.9 (17.1)
1o	1.6258	3.78 (10.8)	4.30 (11.5)	7.2–7.6^{f}	54.9 (6.5)	33.0 (151)	129.3, 129.7, 131.0, 135.6	24.1
1p	1.5583	3.88 (10.6)	3.67 (12.7)	CH_3: 1.25, CH_3: 1.27, $C\mathit{H}H$ 2.35 (12.8), $CH\mathit{H}$: 3.42 (12.8, 1.8)	54.4 (6.9)	8.95 (155)	$Me_2\mathit{C}$: 25.84, CH_3: 25.84, CH_3: 29.95, CH_2: 34.64	22.9
cis-**1q**	109.5–110	3.89 (10.6)	3.48 (13.9)	CH_3: 0.93, CH: 1.84 (11.4^{b} 2.1^{b}), $C\mathit{H}_{eq}H$: 2.68 (12.6, 2.1), $C\mathit{H}_{ax}H$: 3.47 (12.6, 11.4)	54.5 (7.3)	6.66 (155)	CH_2: 21.9, CH_3 27.4, $Me_3\mathit{C}$: 34.9, *t*-Bu*C*: 47.25	23.0
trans-**1q**	83–83.6	3.86 (10.9)	4.54 (13.1)	CH_3: 0.94, CH: 1.96 (10.2,^{b} 3.2^{b}), $C\mathit{H}_{ax}H$: 2.84 (12.9, 10.2), $C\mathit{H}_{eq}H$: 3.02 (12.9, 3.4, 3.2)	54.0 (6.9)	13.7 (150)	CH_2: 25.0 (4.5), CH_3: 27.3, $Me_3\mathit{C}$: 35.0, *t*-Bu*C*: 45.8	25.0
1r	1.5714	3.85 (11.0)	6.11 (16.6)	CH_3: 1.45 (7.2^{b}), CH_2: 4.70 (7.2^{c})	55.3 (6.6)	50.1 (156)	CH_3: 14.4, CH_2: 71.9, C=S: 209.8 (6.3)	19.8

[a] The *J* values are given in parenthesis. Multiplets are doublets, except otherwise stated.
[b] Triplet.
[c] Quartet.
[d] Sextet.
[e] Septet.
[f] Multiplet.
[g] n_D^{23}.

General experimental procedures were the same as described previously.[32]

Dimethyl diazomethanephosphonate (**6a**),[33] diethyl diazomethanephosphonate (**6b**),[34] disulfides **7b**,[35] **7c**,[35] **7d**,[35] **7h**,[26] **7i**,[36] **7j**,[36] **7k**,[28] diselenides **7p**,[37] **7q**,[37] 2-*tert*-butylpropane-1,3-dithiol[38,39] and *meso*-pentane-2,4-dithiol[38] were prepared according to known procedures.

Dithio- and Diselenoacetals of Formylphosphonates 1; General Procedures:

Method A (for **1a**): To a solution of **6b** (178 mg, 1.0 mmol) in Me_2S (**7a**; *n* mmol, see Table 1) was added $BF_3 \cdot Et_2O$ (19 mg, 0.13 mmol). Vigorous evolution of a gas occurred. After 16 h, a TLC ($CHCl_3$/MeOH, 50 : 1, v/v) of the mixture showed the absence of **6b**. Products **1a** and **1l** were isolated by means of column chromatography on silica gel and were found to be indistinguishable (TLC, ^{1}H NMR, ^{31}P NMR, ^{13}C NMR) from original samples[11] (Table 1, 2).

Method B (for **1b–d, g, h, p, q** and **13a, c, d, f, s**): To a magnetically stirred solution of appropriate disulfide or diselenide **7** (2.0 mmol) and $BF_3 \cdot Et_2O$ [0.10–0.25 mmol, see Table 1; for **13**, rhodium(II) acetate (0.05 mmol) or anhydrous copper(II) sulfate (0.1 mmol)] in the appropriate solvent (0.5 mL) was added dropwise a solution of **6a** (150 mg, 1 mmol) in the same solvent (0.5 mL). Vigorous

Table 3. ^1H, ^{13}C and ^{31}P NMR Data for Sulfides **13** $[(MeO)_2P(O)CH_nSR]_{3-n}$[a]

Compound[b]	^1H NMR ($CDCl_3$/TMS), δ, *J* (Hz)			^{13}C NMR ($CDCl_3$/TMS), δ			^{31}P NMR ($CDCl_3$/ 80% H_3PO_4) δ
	CH_3O	CH_nP	R	CH_3O	CHP	R	
13a	3.79 (10.7)	2.70 (12.8)	2.28 (1.1)	53.9 (6.8)	27.4 (151)	18.0	26.7
13c	3.75 (10.9)	2.68 (13.3)	CH_3: 0.93 (7.3[c]), CCH_2C: 1.57 (7.3[d]), CH_2S: 2.64 (7.3[c])	53.3 (6.7)	24.5 (150)	CH_3: 22.3, C*C*H_2C: 13.3, CH_2S: 35.7 (3.0)	27.0
13d	3.64 (10.9)	2.63 (14.3)	CH_3: 1.12 (6.7), 3.01 (6.7, 0.6[e])	53.3 (6.5)	23.4 (150)	CH_3: 22.8, CH: 36.3 (4.2)	26.9
13f	3.46 (10.7), 3.73 (10.8)	5.23 (21.1)	7.1–7.4[f]	53.9 (6.9), 54.2 (7.2)	45.5 (147)	127.6, 127.9, 128.7, 129.0, 129.1, 130.0, 130.5, 132.3	23.2
13s	3.78 (10.6)	3.85 (15.4)	CH_3: 1.36	54.6 (7.5)	39.0 (162)	CH_3: 31.3, C: 46.7, (2.5)	27.5

[a] The *J* values are given in parenthesis. Multiplets are doublets, except otherwise stated; for **13a, c, d, s** (n = 2), for **13f** (n = 1).

[b] Satisfactory microanalyses obtained: C ± 0.2, H ± 0.1, P ± 0.3.

[c] Triplet.

[d] Sextet.

[e] Septet.

[f] Multiplet.

evolution of a gas occurred. After stirring for 12 h, the product was isolated by means of column chromatography on silica gel with Et_2O (for **1o–1q**) or with benzene/acetone, 4 : 1 (v/v, for others) as eluent (Tables 1–3).

Method C (for **1e, f, i–l, o**): To a magnetically stirred solution of appropriate disulfide or diselenide **7** (2.0 mmol) and **6a** (150 mg, 1 mmol) in the appropriate solvent (1.0 mL) was added dropwise a solution of a catalyst (0.5 mmol, see Table 1) in the same solvent (0.5 mL). Vigorous evolution of a gas occurred. After stirring for 12 h, the product was isolated by means of column chromatography as described in Method B (Tables 1 and 2).

Method D (for **1l–n**): To a magnetically stirred and light protected suspension of the appropriate lead dithiolate **18** (*vide infra*, 4.0 mmol) in the solvent given in Table 1 (15 mL), was added elemental sulfur (128 mg, 0.50 mmol) in one portion, and the suspension was stirred for 0.5 h in the dark. The black precipitate of PbS was removed by centrifugation. To the remaining yellow solution of 1,2-dithiolane **8** (X = S) were added **6a** (224 mg, 1.49 mmol) and $BF_3 \cdot Et_2O$ (88 μL, 0.70 mmol). Immediate evolution of a gas occurred. After 30 min of additional stirring, the mixture was evaporated and submitted to chromatographic resolution on silica gel with Et_2O as eluent to give pure product(s). They were identified by comparison with original samples[32] prepared by the Arbuzov reaction (Eq. 3) (Tables 1, 2).

Method E (for **1r**): A solution of **6a** (1.0 mmol) and **7r** (2.0 mmol) in 1,2-dichloroethane (4.0 mL) was refluxed for 20 h. The product **1r** was isolated in 71 % yield by means of column chromatography, as described in Procedure B (Table 2).

Lead(II) Propane-1,3-dithiolate (18a); Typical Procedure:

To a magnetically stirred solution of propane-1,3-dithiol (3.51 g, 32.4 mmol) in H_2O (60 mL)/MeOH (120 mL) mixture was added a solution of $Pb(OAc)_2 \cdot 3H_2O$ (12.5 g, 33.0 mmol) in H_2O (60 mL). A yellow precipitate appeared immediately. The suspension was stirred for 15 min, and then it was centrifugated. The precipitate was washed with H_2O (3 x 100 mL), and dried (P_2O_5) to afford **18a** (8.5 g, 84 %) as a yellow powder.

Anal. Calcd for $C_3H_6PbS_2$ (313.4): C, 11.50; H, 1.93. Found: C, 11.79; H, 1.93.

Lead(II) 2-tert-Butylpropane-1,3-dithiolate (**18b**):

The procedure applied for **18a** was followed to convert 2-*tert*-butylpropane-1,3-dithiol (5.30 g, 32.5 mmol) and $Pb(OAc)_2 \cdot 3H_2O$ (12.5 g, 33.0 mmol) into **18b** (9.8 g, 82 %); yellow powder.

Anal. Calcd for $C_7H_{14}PbS_2$ (369.5): C, 22.75; H, 3.82. Found: C, 22.48; H, 3.82.

Lead(II) meso-Pentane-2,4-dithiolate (**18c**):

The method applied for **18a** was used to convert *meso*-pentane-2,4-dithiol (3.50 g, 25.7 mmol) and $PbOAc_2 \cdot 3H_2O$ (10.2 g, 26.9 mmol) into **18c** (4.2 g, 48 %); yellow powder.

Anal. Calcd for $C_5H_{10}PbS_2$: C, 17.59; H, 2.95. Found: C, 17.65; H, 2.87.

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