Ylidyl 1,2,4-Thiadiphosphetane and 1,2,4-Selenadiphosphetane Sulfides and Selenides

Georg Jochem, Alfred Schmidpeter*, Florian Kulzer, and Stefan Dick[+]

Institut für Anorganische Chemie der Universität München,
Meiserstraße 1, D-80333 München, Germany

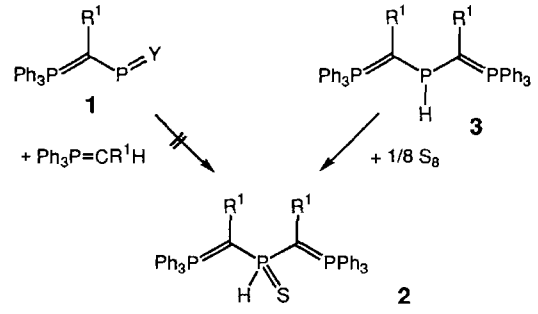
Received April 27, 1995

Key Words: 1,2,4-Thiadiphosphetanes / 1,2,4-Selenadiphosphetanes / Thioxophosphanes / Selenoxophosphanes / Ylides / Phosphane elimination

Phosphoniumylidyl thioxophosphanes and selenoxophosphanes, the only known monomeric chalcogenoxophosphanes, react in a 2:1 ratio with triphenylphosphonium ylides. With loss of PPh_3 the 1,2,4-thia(or selena)diphosphetane monosulfides (or selenides) are formed. Their prominent structural feature are the very different PS bond lengths in the ring. They can be oxidized to the corresponding disulfides or sulfide selenides. The latter rearrange to the isomer in which the selenium atom has become a ring member.

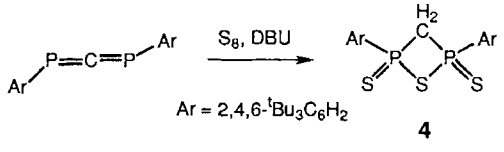
Thioxophosphanes R'P=S with ordinary substituents R' are not known as monomers. They contain a highly electrophilic phosphorus atom which causes them to oligomerize. In fact, up to now only representatives with a phosphonium ylide substituent R' were found to be stable as monomers and could be isolated[1,2]. The fact that they do not oligomerize is obviously due to the electron release of the ylide substituent and to the resulting lower electrophilicity of the two-coordinate phosphorus atom.

Nevertheless we expected a sufficiently strong nucleophile such as a *C*-alkylphosphonium ylide to add to the two-coordinate phosphorus atom of **1** and thus to give a bis(ylidyl)phosphane sulfide **2**, a type of compound which is otherwise readily available by the oxidation of a bis(ylidyl)phosphane **3**[3].



In fact the two components do react, but the reaction turned out to be more complex than expected and led to 1,2,4-thiadiphosphetane derivatives. The elucidation of the structure of these products helped us to understand the secondary reactions observed[1] during the attempted synthesis of *C*-arylylidyl thioxophosphanes **1**, Y = S, R^1 = Ph, 3-MeC_6H_4[4]. The investigations were also extended to 1,2,4-selenadiphosphetane derivatives.

The only representative of the 1,2,4-thiadiphosphetane ring system known so far is the disulfide **4** with bulky 2,4,6-tri-*tert*-butylphenyl substituents Ar[5,6]. It is obtained by base-catalyzed addition of sulfur (and H_2S) to the respective 1,3-diphosphaallene[5]. The corresponding 1,2,4-oxadiphosphetane derivative was prepared analogously[6]. However, the 1,2,4-selenadiphosphetane ring system is not known so far.



Ylidyl Thioxophosphane/Ylide Reaction

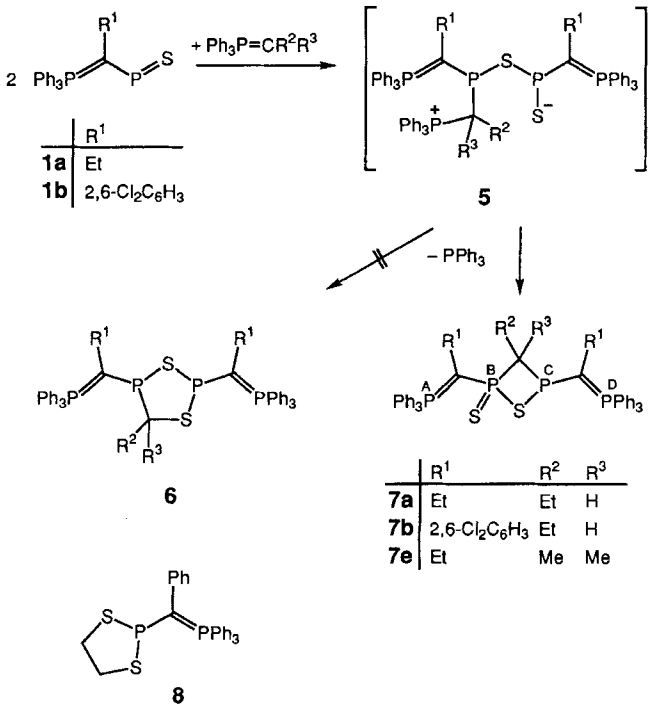
As starting compounds for the intended reaction the thioxophosphanes **1a** and **1b** were used. The former and other *C*-alkylylidyl thioxophosphanes are readily accessible from the respective dichlorophosphanes and sodium sulfide[1] or bis(trimethylsilyl) sulfide. However, as mentioned above this route is in general unsuitable for the preparation of *C*-aryl derivatives due to side reactions involving substitution in the *ortho* position of the aryl substituent (see below). No problems were consequently encountered again in the preparation of the 2,6-dichlorophenyl derivative **1b**[4].

Propylidenetriphenylphosphorane was added to the thioxophosphanes **1a**, **b** in tetrahydrofuran at room temperature or at −78 °C. In both cases the two components reacted in a molar ratio of 1:2. Any excess of the propylidenephosphorane remained unchanged. The $^{31}P\{^1H\}$-NMR spectra of the reaction mixture always indicated a clean re-

[+] X-ray structural investigation.

  0009–2940/95/1010–1015 $ 10.00+.25/0

action. They show the ABCD spin systems of two diastereomeric products and the singlet at $\delta = -5.0$ of an equimolar amount of triphenylphosphane. Thus, the product must have been built up in a non-symmetric fashion from two molecules of **1** and from the propylidene moiety of the phosphorane. The elemental analyses of the isolated products are also in accord with this assumption. The reaction pathway probably starts with the anticipated nucleophilic attack of the propylidenephosphorane on the two-coordinate phosphorus of **1**. (With the less nucleophilic benzylidenephosphorane only a very slow reaction was observed.) Different from our expectation the sulfur atom of the primary adduct then interacts in the same way with a second molecule **1**. The assumed intermediate **5** is finally stabilized by ring closure and elimination of phosphane. Phosphane-eliminating ring closures of other zwitterionic phosphonio intermediates have been observed earlier[7]. The ring closure involves an intramolecular nucleophilic attack on the phosphonio-substituted carbon atom. The nucleophile might be the sulfur atom or the phosphorus atom of the second molecule **1** and would lead to the five- or four-membered product **6** or **7**, respectively.



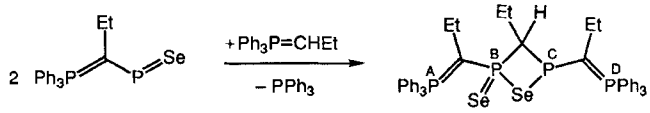
	R^1	R^2	R^3
7a	Et	Et	H
7b	2,6-$Cl_2C_6H_3$	Et	H
7e	Et	Me	Me

Both alternatives **6** and **7** contain the same chain of four non-equivalent phosphorus atoms and are thus both in accord with the observed spin system. However, the two very different $^2J_{PP}$ coupling constants J_{AB} and J_{CD} (Table 1) plead against structure **6**. In particular, J_{CD} is much too small for this structure, as for the closely related compound **8** $^2J_{PP} = 195.6$ Hz was found[3].

Further evidence for structure **7** comes from the fact that the product takes up just one equivalent of sulfur and that it thus becomes a symmetric compound (see below). The final proof results from an X-ray investigation.

The reaction of **1a** with isopropylidenetriphenylphosphorane proceeded nearly analogously but yielded only one diastereomer of **7e**.

The selenoxophosphane **9** reacted analogously. This reaction did, however, not proceed straightforwardly, and the product **10** was not isolated. It was identified on the basis of its ^{31}P-NMR spectral data (Table 1).



9 **10**

With the exception of **7e** three stereocenters are present in **7** and **10**, which would allow four isomers to be distinguished by NMR spectroscopy: two with the ylide substituents lying on the same side of the ring (*cis* isomers) and two with the substituents on opposite sides (*trans* isomers); all of them represent ABCD spin systems. However, only in the case of **7a, b** in THF solution could two diastereomers be detected by ^{31}P-NMR spectroscopy (Table 1). For **7e** and **10** as well as for **7c, d** generated in a different way (see below), just one ^{31}P-NMR spectrum of the ABCD type was obtained. Probably, all observed spectra refer to isomers with a *cis* structure as found in the crystal for **7b** (see below).

The ^{31}P-chemical shifts and the coupling constants determined for compounds **7** and **10** (Table 1) are in agreement with the proposed structure. As usual in phosphanyl-substituted phosphonium ylides[8] $^2J_{PP(III)} = {}^2J_{CD}$ was found to be large; the values of 162–197 Hz indicate a preferred conformation with the lone pair of P_C oriented synperiplanar to the phosphonio group P_D. $^2J_{PP(V)} = {}^2J_{AB}$ is much smaller; the values of 48–60 Hz are characteristic of phosphoryl-substituted phosphonium ylides[8].

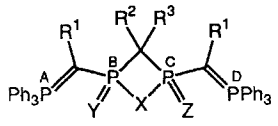
For **7a** and less pronounced also for **7b** a remarkable solvent dependence of δ_C was found: In more polar solvents the signal is shifted to lower field (Table 1), indicating a ring-opened zwitterion **7'** to be involved in a mobile equilibrium.

Molecular Structure of Thiadiphosphetane Sulfide 7b

Figure 1 shows the molecular structure of **7b** as resulting from a single-crystal X-ray structural analysis. It confirms the four-membered ring structure as inferred from the ^{31}P-NMR data. The ring is nonplanar and folded along the C1···S1 diagonal by 29.4° and along the P1···P2 diagonal by 30.3°. The ylide substituents both occupy the equatorial position at P1 and P2, leaving the axial positions for the exocyclic sulfur S2 and for the lone pair at P2. Due to the conformation at P1–C5 and at P2–C4, they are both roughly synperiplanar with regard to the phosphonio groups P3 and P4, respectively. This orientation has in general been found also for acyclic phosphanyl- and thiophosphoryl-substituted phosphonium ylides[8] as well as for a cyclic phosphanyl ylide[9].

The molecule allows a direct structural comparison of P(III) and P(V) in an otherwise alike situation: As expected,

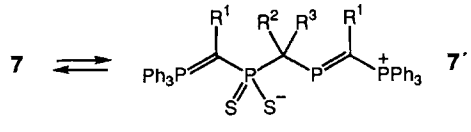
Table 1. ^{31}P-NMR data of compounds **7** and **10**–**13**. Coupling constants J are given in Hz; where signs are given they originate from a simulation of the spectrum by LAOCOON[12] and refer to $J_{AB} = {}^2J_{PP}$ taken as positive



	R^1	R^2	R^3	X	Y	Z	Solvent	δ_A	δ_B	δ_C	δ_D	J_{AB}	J_{AC} AB'	J_{AD} AA'	J_{BC} BB'	J_{BD}	J_{CD}
7a[a]	Et	Et	H	S	S	-	C_6D_6	23.0	61.4	51.8	27.2	50.9	<3	<3	39.7	6.1	168.9
	Et	Et	H	S	S	-	THF	23.0	60.7	51.6	27.8	50.9	<3	<3	39.7	6.1	168.9
	Et	Et	H	S	S	-	CD_2Cl_2	23.3	60.9	60.8	28.1	51.1	+2.0	+1.5	+43.0	+6.6	+168.6
	Et	Et	H	S	S	-	$CDCl_3$	23.0	60.9	62.8	27.8	50.4	<3	<3	41.2	9.5	165.6
7a[b]	Et	Et	H	S	S	-	THF	22.1	84.7	40.6	30.6	63.0	<3	<3	46.8	<3	197.3
7b[a]	2,6-$Cl_2C_6H_3$	Et	H	S	S	-	THF	16.6	58.7	34.0	18.2	50.8	<3	<3	44.7	6.1	166.9
	2,6-$Cl_2C_6H_3$	Et	H	S	S	-	CD_2Cl_2	17.1	59.2	37.5	18.8	52.1	1.0	1.3	47.1	6.7	166.4
	2,6-$Cl_2C_6H_3$	Et	H	S	S	-	$CDCl_3$	17.1	59.5	37.6	18.5	51.8	<3	<3	46.0	6.7	165.2
7b[b]	2,6-$Cl_2C_6H_3$	Et	H	S	S	-	THF	15.6	78.5	40.7	22.1	47.8	<3	<3	64.1	<3	193.3
7c	Ph	Ph	H	S	S	-	THF	20.1	60.0	52.0	23.1	59.5	<3	<3	65.6	<3	179.3
7d	3-MeC_6H_4	3-MeC_6H_4	H	S	S	-	THF	19.7	59.6	52.0	22.6	59.5	4.6	<3	64.6	<3	177.1
7e	Et	Me	Me	S	S	-	THF	22.6	88.9	62.9	29.1	49.8	<3	<3	37.7	<3	197.0
10	Et	Et	H	Se	Se	-	THF	23.8	29.0	76.4	27.4	52.6	<3	<3	62.1	<3	162.5
11a *cis*	Et	Et	H	S	S	S	CD_2Cl_2	25.5	56.6			53.1	+6.7	-1.2	+1.2		
11a *trans*	Et	Et	H	S	S	S	CD_2Cl_2	25.8	55.3	51.6	26.9	51.5	5.0	<3	14.5	<3	58.0
11b *cis*	2,6-$Cl_2H_6H_3$	Et	H	S	S	S	CD_2Cl_2	20.0	53.5			55.6	+7.7	-2.0	+1.5		
11c *cis*	Ph	Ph	H	S	S	S	CD_2Cl_2	21.0	54.8			61.3	+7.3	0.0	+8.8		
11d *cis*	3-MeC_6H_4	3-MeC_6H_4	H	S	S	S	CD_2Cl_2	25.5	56.5			61.9	+7.6	0.0	+8.9		
11e *cis*	Et	Me	Me	S	S	S	CH_2Cl_2	25.6	71.5			64.1	+7.4	+0.2	+3.7		
12 *cis*	Et	Et	H	S	Se[c]	S	CH_2Cl_2	26.5	37.6	56.8	25.7	57.7	6.7	1.0	<1	6.4	52.5
12 *trans*	Et	Et	H	S	Se[d]	S	CH_2Cl_2	26.7	36.9	53.1	27.0	55.8	6.1	0.7	14.2	1.7	58.8
12 *trans*	Et	Et	H	S	Se	S	CH_2Cl_2	[e]		59.0			<5		17.5		51.4
13 *cis*	Et	Et	H	Se[f]	S	S	CH_2Cl_2	25.3	49.9			51.5	+9.5	+0.5	+11.4		
13 *trans*	Et	Et	H	Se[g]	S	S	CH_2Cl_2	25.2	45.1	41.3	26.2	46.9	6.1	1.0	5.8	1.5	53.2

[a] Major isomer. – [b] Minor isomer. – [c] δ^{77}Se = –42.5, $^1J_{SeP}$ = 732.7 Hz. – [d] δ^{77}Se = –63.2, $^1J_{SeP}$ = 721.8 Hz. – [e] Data are not obtained because of superpositions. – [f] δ^{77}Se = 661.5, $^1J_{SeP}$ = 233.3 Hz. – [g] $^1J_{SeP(B)}$ = 232.4, $^1J_{SeP(C)}$ = 241.6 Hz.

the pyramid of P2 (sum of angles 302°) becomes less steep on oxidation at P1 (sum of the same angles 314°) and both PC bonds (P2–C4 173, P2–C1 188 pm) become shorter (P1–C5 173, P1–C1 183 pm). The largest difference was found, however, for the two PS bond lengths (P2–S1 220, P1–S1 210 pm). The former seems to be the longest P(III)–S bond reported so far[10] and should indeed be prone to dissociation and formation of the zwitterion **7′** (see above). As a result, the dihedral angle P4–C4–P2–S1 is relatively small (116°) and thus allows an electron transfer from the p orbital of the ylidic C4 to the antibonding orbital of the P2–S1 bond (negative hyperconjugation). This effect has been discussed in detail in a previous paper[8].



The bond lengths of P1–S1 and P1–S2 (210 and 195 pm) are typical of bonds of phosphorus(V) to two- and one-coordinate sulfur[10]. The bonds are somewhat shorter and longer, respectively, than the corresponding ones in **4** (212 and 192 pm)[5].

From the larger solvent effect in the ^{31}P-NMR spectra (see above) we would expect **7a** to approach structure **7′** even further than **7b**, unfortunately no suitable crystals could be grown of it, however.

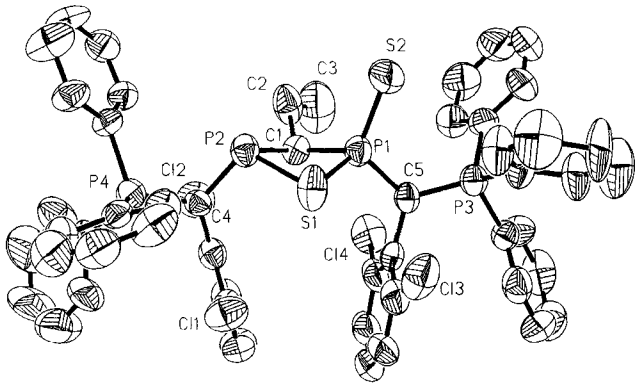
Oxidation of Thiadiphosphetane Sulfides 7 by Sulfur and Selenium

Compounds **7** are readily oxidized with one equivalent of sulfur to form the 1,2,4-thiadiphosphetane 2,4-disulfides **11**.

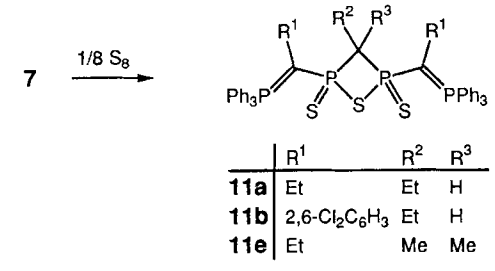
In the case of **11a** the presence of two isomers was detected by the ^{31}P-NMR spectrum which shows an AA′BB′ and an ABCD spin system. These isomers were consequently identified as a *cis* and a *trans* isomer. For **11b** and **11e** (as well as for **11c**, **d**, see below) only a *cis* isomer was found.

If selenium is used to oxidize **7a** besides a *cis* and two *trans* isomers **12**, which result from the oxidation, immedi-

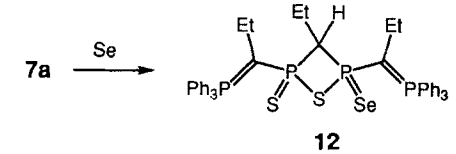
Figure 1. Molecular structure of **7b**; selected bond lengths [pm], bond angles and dihedral angles [°]:



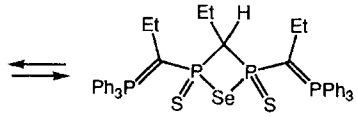
P1-S1	210.3(3)	S1-P1-S2	115.0(2)	P1-S1-P2	80.9(1)	P3-C5-P1-S1	-126.7
P1-S2	195.2(4)	S1-P1-C1	88.8(3)	P1-C1-P2	97.5(4)	P3-C5-P1-S2	2.7
P1-C1	183.3(9)	S2-P1-C1	111.5(3)	P1-C1-C2	119.5(7)	P4-C4-P2-S1	115.9
P1-C5	173.3(10)	S1-P1-C5	108.3(3)	P2-C1-C2	112.2(7)	P4-C4-P2-C1	-153.4
P2-S1	219.9(4)	S2-P1-C5	114.0(3)	P2-C4-P4	115.9(5)		
P2-C1	188.0(8)	C1-P1-C5	116.7(4)	P2-C4-C6	123.6(7)		
P2-C4	174.9(9)	S1-P2-C1	84.9(3)	P4-C4-C6	120.1(7)		
P3-C5	172.7(9)	S1-P2-C4	108.5(3)	P1-C5-P3	122.9(6)		
P4-C4	171.3(9)	C1-P2-C4	108.4(4)	P1-C5-C12	119.1(7)		
C4-C6	148.9(14)			P3-C5-C12	117.2(7)		
C5-C12	150.8						



	R^1	R^2	R^3
11a	Et	Et	H
11b	2,6-$Cl_2C_6H_3$	Et	H
11e	Et	Me	Me



12



13

ately (and which all possess ABCD spin systems of ^{31}P) two more isomers **13** are observed. They contain the selenium atom as a ring member. Their ^{31}P-NMR spectra exhibit an AA'BB' spin system which must be attributed to a *cis* isomer and an ABCD system ascribed *trans* isomer.

Furthermore, the *cis*-to-*trans* ratio of **11a** depends on the polarity of the solvent; in dichloromethane it was about 4:1, whereas in chloroform a 1:2 ratio was determined by ^{31}P-NMR spectroscopy. These observations are readily explained by opening of the four-membered ring of **11**–**13** at a PS or a PSe bond to give a zwitterionic intermediate which may close the ring again with formation of a PS or PSe bond. A similar mechanism was discussed earlier by Yoshifuji et al. for the base-induced *cis/trans* isomerization of **4**[6].

The chemical shifts and the PP coupling constants are in good agreement with the proposed strucutures. As compared to those of **7** and **10** J_{CD} and $J_{BC(BB')}$ are found much smaller in **11**–**13** due to the oxidation of P_C (Table 1).

Decomposition of *C*-Arylylidyl Thioxophosphanes

As mentioned in the introduction and as reported earlier[1] no thioxophosphanes **1c**, **d**, R = Ph, 3 MeC_6H_4, could be prepared. The reaction of the respective chlorophosphanes with sodium or bis(trimethylsilyl) sulfide yielded a complex mixture of products, instead[1,4]. By ^{31}P-NMR spectroscopy the desired thioxophosphanes **1** could be detected for a short time. Other prominent, but relatively stable products are the 3-(triphenylphosphonio)-1,2-diphosphaindenides **14**[11], triphenylphosphane sulfide, the dithioxophosphoranes **15**[1], as well as the 1,2,4-thiadiphosphetane monosulfides **7** and disulfides **11**. The latter two compounds were identified by their characteristic ABCD and AA'BB' spectra (Table 1) which are known from the above-described authentic samples of **7a, b** and **11a, b**. They may arise from the transient thioxophosphane according to the reactions shown in Scheme 1.

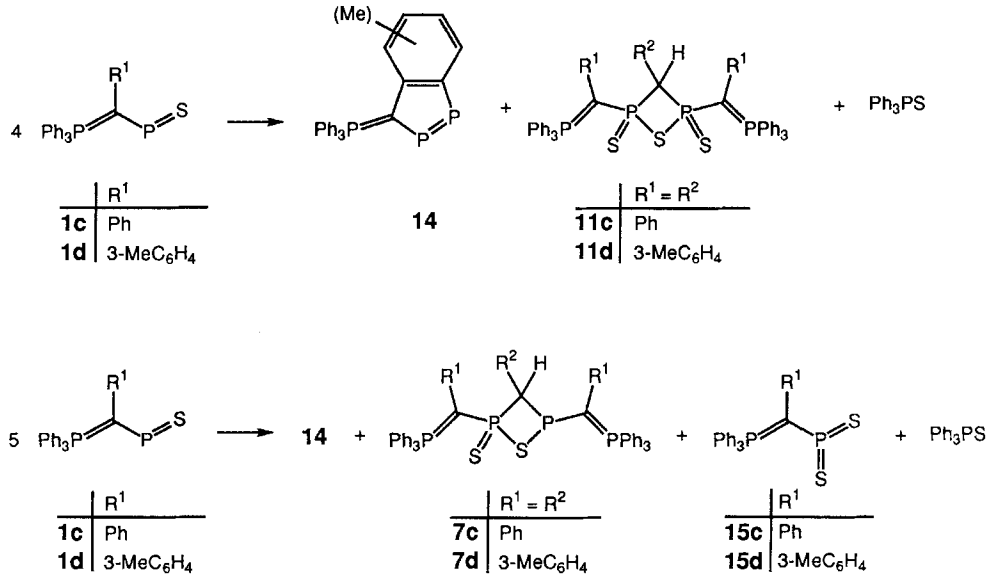
The initial step of the decomposition seems to be an electrophilic *ortho* substitution of the *C*-aryl substituent of one molecule **1** by the two-coordinate phosphorus atom of the other. While this phosphorus atom becomes part of the diphosphaindenide ring its ylide substituent is split off. With two more molecules **1** it forms the 1,2,4-thiadiphosphetane ring in a way similar to that described above. All the sulfur is eliminated from the diphosphaindenide and is contained in the sulfides which constitute the rest of the products.

Another route to ylidyl thioxophosphanes **1** should be the reduction of ylidyl dithioxophosphoranes **15**. The *C*-ethyl derivative **15a** can in fact be converted to **1a** by reaction with triphenylphosphane[4]. In contrast, the reaction of the *meta*-tolyl derivative **1d** with triphenyl- or tributylphosphane mainly yielded the products of the first of the above equations. Compound **11d** could be isolated from this reaction.

Experimental

All operations were carried out in flame-dried glassware under dry argon by using Schlenk technique. Tetrahydrofuran was dried by refluxing with sodium/benzophenone and subsequent distillation. Pentane was dried with molecular sieves (4 Å). Dry dichloromethane and benzene were used as obtained (Fluka). – Melting points were determined in sealed capillaries and are uncorrected. – NMR: Jeol GSX 270 (^{31}P, ^{77}Se), Jeol EX 400 (^{1}H) with Me_4Si (int.), 85% H_3PO_4 (ext.) and Me_2Se (ext.) as standards. ^{31}P-NMR data are compiled in Table 1. The aromatic hydrogen atoms in *ortho, meta* and *para* position of R^1 are identified as 2,3,4-H, those of R^2 as 6,7,8-H and those of Ph_3P as *o,m,p*-H. – The methylenephosphoranes $Ph_3P{=}CHEt$, $Ph_3P{=}CMe_2$ and $Ph_3P{=}CHPh$

Scheme 1



were prepared by reaction of the corresponding phosphonium bromides with $NaN(SiMe_3)_2$[7] in benzene. The triphenylphosphoniumylidyl thioxophosphanes **1**[1,4], dithioxophosphoranes **15**[1,4] and dichlorophanes[8] were prepared as described in the literature.

3-Ethyl-2,4-bis[1-(triphenylphosphoranyliden)propyl]-1,2,4-thiadiphosphetane 2-Sulfide (**7a**): To a magnetically stirred suspension of 1.93 g (5.3 mmol) of **1a** in 20 ml of THF a solution of 0.81 g (2.7 mmol) of propylidenetriphenylphosphorane in 10 ml THF was added dropwise at −78 °C within 30 min. The resulting orange-red solution was warmed up to ambient temp. during 2 h, then concentrated in vacuo to 50% of its original volume. After addition of 5 ml of benzene and cooling of the solution to −30 °C for 15 h the yellow precipitate formed was filtered off, washed twice with a small quantity of benzene and dried in vacuo. Compound **7a** was recrystallized by addition of benzene to a solution of it in dichloromethane until precipitation started. Yield 1.50 g (72%) of **7a** as yellow needles, m.p. 135−136 °C. − ^{1}H NMR ($CDCl_3$): δ = 0.73 (t, $^3J_{HH}$ = 7.3 Hz, 3H, CH_3), 0.76 (t, $^3J_{HH}$ = 7.3 Hz, 3H, CH_3), 1.05 (t, $^3J_{HH}$ = 7.5 Hz, 3H, CH_3), 1.95 (m, 2H, CH_2), 2.18 (m, 2H, CH_2), 2.53−2.72 (m, 2H, CH_2), 4.37 (ddt, $^2J_{PH}$ = $^2J_{PH}$ = $^3J_{HH}$ = 7.2 Hz, 1H, CH), 7.27−7.34 (m, 15H, arom. H), 7.38−7.47 (m, 9H, arom. H), 7.58−7.63 (m, 6H, arom. H). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 14.1 (dd, $^3J_{PC}$ = 10.0, 10.9 Hz, CH_3), 18.6 (s, CH_3), 19.7 (s, CH_3), 21.9 (dd, $^2J_{PC}$ = 10.9, 1.9 Hz, CH_2), 23.5 (dd, $^2J_{PC}$ = 9.0, 5.2 Hz, CH_2), 24.6 (d, $^2J_{PC}$ = 19.5 Hz, CH_2), 34.3 (ddd, $^1J_{PC}$ = 120.4, 73.0, $^3J_{PC}$ = 3.3 Hz, C=PPh_3), 39.2 (ddd, $^1J_{PC}$ = 95.7, 61.1, $^3J_{PC}$ = 8.5 Hz, C=PPh_3), 62.6 (m, C-3), 128.0 (d, $^3J_{PC}$ = 11.8 Hz, *m*-C), 128.6 (d, $^3J_{PC}$ = 11.4 Hz, *m*-C), 128.7 (dd, $^1J_{PC}$ = 85.8, $^3J_{PC}$ = 5.6 Hz, *i*-C), 130.8 (d, $^1J_{PC}$ = 90.0 Hz, *i*-C), 131.1 (d, $^4J_{PC}$ = 2.9 Hz, *p*-C), 132.0 (d, ^4J = 2.4 Hz, *p*-C), 134.1 (dd, $^2J_{PC}$ = 8.8, $^4J_{PC}$ = 1.4 Hz, *o*-C), 134.4 (d, $^2J_{PC}$ = 9.5 Hz, *o*-C). − $C_{45}H_{46}P_4S_2$ (774.9): calcd. C 69.75, H 5.96, S 8.27; found C 70.22, H 6.10, S 8.26.

2,4-Bis[(2,6-dichlorophenyl)(triphenylphosphoranyliden)methyl]-3-ethyl-1,2,4-thiadiphosphetane 2-Sulfide (**7b**): Prepared as described above from 600 mg (1.2 mmol) of **1b** in 30 ml of THF and 190 mg (0.6 mmol) of propylidenetriphenylphosphorane in 10 ml of THF. Yield 375 mg (53%) of **7b** · 2 CH_2Cl_2, pale yellow crystals, suitable for single-crystal X-ray structural determination, m.p. 171−172 °C. − ^{1}H NMR ($CDCl_3$): δ = 1.28 (t, $^3J_{HH}$ = 7.3 Hz, 3H, CH_3), 2.02 (m, 1H, CH_2), 2.45 (m, 1H, CH_2), 3.91 (m, 1H, CH), 5.33 (s, 4H, CH_2Cl_2), 6.61−6.69 (m, 4H, arom. H), 6.95−7.18 (m, 7H, arom. H), 7.29−7.46 (m, 21H, arom. H), 8.13 (m, 4H, arom. H). − $C_{53}H_{42}Cl_4P_4S_2$ · 2 CH_2Cl_2 (1178.6): calcd. C 56.05, H 3.93, S 5.44; found C 56.48, H 3.90, S 6.17.

3-Ethyl-2,4-bis[1-(triphenylphosphoranyliden)propyl]-1,2,4-thiadiphosphetane 2,4-Disulfide (**11a**): 52 mg (1.6 mmol) of sulfur was added to a magnetically stirred solution of 1.26 g (1.6 mmol) of **7a** in 10 ml of dichloromethane at ambient temperature. After cooling the dark yellow solution for 2 d to −30 °C, the pale yellow crystals were filtered off, washed once with cold dichloromethane and dried in vacuo. By concentration of the filtrate to about 20% of its original volume a second crop could be obtained. Yield 1.15 g (85%) of **11a** as pale yellow crystals, m.p. 192−193 °C (dec.). − ^{1}H NMR (CD_2Cl_2): *cis* δ = 0.88 (t, $^3J_{HH}$ = 6.8 Hz, 6H, CH_3), 1.18 (t, $^3J_{HH}$ = 6.8 Hz, 3H, CH_3), 1.93−2.16 (m, 4H, CH_2), 2.50−2.67 (m, 2H, CH_2), 4.70 (m, 1H, CH), 7.47 (m, 12H, *m*-H), 7.54−7.56 (m, 6H, *p*-H), 7.66−7.71 (m, 12H, *o*-H); *trans* δ = 0.66 (t, $^3J_{HH}$ = 7.3 Hz, 3H, CH_3), 0.83 (t, $^3J_{HH}$ = 6.8 Hz, 3H, CH_3), 1.20 (t, $^3J_{HH}$ = 6.8 Hz, 3H, CH_3), other signals could not be detected without doubt because of superpositions. − $C_{45}H_{46}P_4S_3$ · 0.5 CH_2Cl_2 (849.4): calcd. C 64.34, H 5.58, S 11.32; found C 64.37, H 5.61, S 11.12.

2,4-Bis[(2,6-dichlorophenyl)(triphenylphosphoranyliden)methyl]-3-ethyl-1,2,4-thiadiphosphetane 2,4-Disulfide (**11b**): To a magnetically stirred solution of 1.06 g (2.2 mmol) of **1b** in 100 ml of THF 0.50 g (1.6 mmol) of propylidenephosphorane in 10 ml of THF was added dropwise at −78 °C within 10 min. The resulting orange-red solution was warmed up to ambient temp. during 2 h. After additional 15 h at room temp. all volatile components were removed in vacuo, the yellow residue was dissolved in 40 ml of dichloromethane, and 51 mg (1.6 mmol) of sulfur was added. The yellow solution was stirred for 2 h at room temp., then concentrated in vacuo to 25% of its original volume. After addition of 5 ml of benzene a colorless precipitate formed, which was filtered

off after 15 h at room temp., washed once with dichloromethane/benzene (1:1) and dried in vacuo. Concentration of the filtrate to 20% of its volume afforded a second crop. Yield 0.60 mg (52%) of **11b** as colorless crystals, m.p. 279–281 °C (dec.). – ^{1}H NMR ($CDCl_3$): δ = 1.24 (t, $^3J_{HH}$ = 7.8 Hz, 3H, CH_3), 2.24 (dqt, $^3J_{HH}$ = 7.8, 7.0, $^3J_{PH}$ = 23.4 Hz, 2H, CH_2), 4.47 (tt, $^3J_{HH}$ = 7.0, $^2J_{PH}$ = 14.0 Hz, 1H, CH), 5.33 (s, CH_2Cl_2), 6.57 (m, 2H, 4-H), 6.75 (m, 4H, 3,5-H), 6.93–7.00 (m, 8H, arom. H), 7.13 (m, 2H, arom. H), 7.46–7.57 (m, 12H, arom. H), 8.02–8.08 (m, 8H, arom. H). – $C_{53}H_{42}Cl_4P_4S_3 \cdot 0.5\ CH_2Cl_2$ (1083.3): calcd. C 59.31, H 4.00, S 8.88; found C 59.21, H 3.99, S 8.57.

3-Phenyl-2,4-bis[phenyl(triphenylphosphoranyliden)methyl]-1,2,3-thiadiphosphetane 2,4-Disulfide (**11c**): A suspension of 9.28 g (20.5 mmol) of [(dichlorophosphanyl)phenylmethylene]triphenylphosphorane and 1.60 g (20.5 mmol) of Na_2S in 100 ml of THF was stirred at ambient temp. for 10 d. The precipitate formed was filtered off, and 0.33 g (10.3 mmol) of sulfur was added to the orange-red filtrate, which immediately turned brown-red while the sulfur dissolved. After standing at room temp. for 36 h, yellow crystals were filtered off, washed twice with THF and dried in vacuo. – $C_{57}H_{46}P_4S_3 \cdot 0.5$ THF (987.1): calcd. C 71.79, H 5.11, S 9.74; found C 71.06, H 5.23, S 10.11. – The product was recrystallized from chloroform. Yield 3.20 g, colorless crystals, which turned yellow on drying in vacuo, m.p. 226–228 °C. – ^{1}H NMR (CD_2Cl_2): δ = 5.62 (t, $^2J_{PH}$ = 16.1 Hz, 1H, CH), 6.69 (m, 4H, 3-H), 6.77–6.79 (m, 6H, 2,4-H), 7.16 (m, 12H, *m*-H), 7.31–7.37 (m, 18H, *o,p*-H), 7.48 (m, 2H, 7-H), 7.53–7.55 (m, 1H, 8-H), 7.86–7.88 (m, 2H, 6-H). – $C_{57}H_{46}P_4S_3 \cdot 1.5\ CHCl_3$ (1130.1): calcd. C 62.17, H 4.24, S 8.51; found C 61.53, H 3.78, S 8.82.

3-(3-Methylphenyl)-2,4-bis[(3-methylphenyl)(triphenylphosphoranyliden)methyl]-1,2,4-thiadiphosphetane 2,4-Disulfide (**11d**): 875 mg (1.7 mmol) of **15d** and 314 mg (1.7 mmol) of tri-*n*-butylphosphane were refluxed in 10 ml of THF for 36 h. The orange-red solution was concentrated in vacuo to 50% of its original volume. After cooling to −30 °C for 15 h the yellow precipitate was filtered off, washed twice with THF/benzene (1:1) and dried in vacuo. It was recrystallized from chloroform/pentane. Yield 295 mg (70%) of **11d** as pale yellow needles, m.p. 206–208 °C. – ^{1}H NMR ($CDCl_3$): δ = 1.94 (s, 6H, CH_3), 2.46 (s, 3H, CH_3), 5.53 (t, J_{PH} = 16.4 Hz, 1H, CH), 6.48–6.50 (m, 4H, arom. H), 6.55 (m, 2H, arom. H), 6.63 (b, 2H, arom. H), 7.08 (m, 12H, *m*-H), 7.24–7.38 (m, 20H, arom. H), 7.58 (b, 1H, arom. H), 7.86 (m, 1H, arom. H). – $C_{60}H_{52}P_4S_3$ (993.2): calcd. C 72.56, H 5.28, S 9.68; found C 72.44, H 5.30, S 9.82.

3-Ethyl-2,4-bis[1-(triphenylphosphoranyliden)propyl]-1,2,4-thiadiphosphetane 2-Sulfide 4-Selenide (**12**) *and 3-Ethyl-2,4-bis[1-(triphenylphosphoranyliden)propyl]-1,2,4-selenadiphosphetane 2,4-Disulfide* (**13**): 38 mg (0.5 mmol) of grey selenium was added to a stirred solution of 370 mg (0.5 mmol) of **7a** in 5 ml of dichloromethane. The reaction mixture was stirred until all selenium had dissolved. On standing at ambient temp. for 3 d, yellow crystals precipitated. They were filtered off, washed once with a small amount of dichloromethane/benzene (1:1) and dried in a stream of argon. Yield 218 mg (51%), yellow crystals, m.p. 156–158 °C (dec.). – $C_{45}H_{46}P_4S_2Se$ (853.8): calcd. C 63.30, H 5.43, S 7.51; found C 62.17, H 5.21, S 7.90.

Crystal Structure Determination of **7b** · 2 CH_2Cl_2: X-ray scattering intensities of a colorless, block-shaped crystal (size 0.24 × 0.24 × 0.54 mm^3) were measured with a Siemens R3m/V four-circle diffractometer (Mo-K_α, graphite monochromator) at 295 K. The data of 10937 reflections (ω scan, width 1.2°, $5 \leq 2\Theta \leq 50°$) were collected ($0 \leq h \leq 20$, $0 \leq k \leq 17$, $-27 \leq l \leq 27$) of which 10085 were unique and 6366 observed ($|F_o| \geq 3\sigma|F_o|$). The data were corrected for Lorentz and polarization effects and also for absorption (face-indexed numerical) and secondary extinction (empirical). The structure was solved by direct methods and refined by full-matrix least-squares methods. All non-hydrogen atoms were refined with anisotropic displacement parameters, whereas hydrogen atoms were positioned with idealized parameters (riding model) and refined with common isotropic displacement parameters for groups of atoms. Some phenyl groups are slightly disordered, the included solvent molecules (CH_2Cl_2) exhibit strong disorder which could not be resolved by a split model. The final residuals for 628 parameters were R = 0.1123, R_w = 0.0897 and R_g = 0.0852 for weights $1/\sigma^2|F_o|$ (GOOF = 4.40). – Crystallographic data: $C_{55}H_{46}Cl_8P_4S_2$, M = 1178.6, monoclinic, space group $P2_1/a$ (Nr. 14), a = 1735.2(4), b = 1457.1(4), c = 2341.7(6) pm, β = 103.62(2)°, V = 5754(2) · 10^6 pm^3, ρ_{calc} = 1.36 g cm^{-3}, μ(Mo-K_α) = 0.61 mm^{-1}, F(000) = 2.416. – Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen (Germany), on quoting the depository number CSD-58955, the names of the authors, and the journal citation.

[1] G. Jochem, H. Nöth, A. Schmidpeter, *Angew. Chem.* **1993**, *105*, 1117–1119; *Angew. Chem. Int. Ed. Engl.* **1993**, *32*, 1089–1091.

[2] The 2,4-di-*tert*-butyl-6-(dimethylamino)phenyl-substituted thioxophosphane and selenoxophosphane were observed but not isolated. They are stabilized by the interaction between the lone pair of the *ortho*-dimethylamino group and the phosphorus atom, which thus, strictly speaking, loses its two-coordination. M. Yoshifuji, S. Sangu, M. Hirano, K. Toyota, *Chem. Lett.* **1993**, 1715–1718; M. Yoshifuji, M. Hirano, K. Toyota, *Tetrahedron Lett.* **1993**, *34*, 1043–1046.

[3] G. Jochem, A. Schmidpeter, unpublished results.

[4] G. Jochem, K. Karaghiosoff, S. Dick, A. Schmidpeter, *Chem. Ber.*, in press.

[5] K. Toyota, M. Yoshifuji, K. Hiratsu, *Chem. Lett.* **1990**, 643–646.

[6] K. Toyota, Y. Ishikawa, K. Shivabe, M. Yoshifuji, *Heteroatom Chem.* **1993**, *4*, 279–285.

[7] H.-J. Bestmann, R. Zimmermann in *Methoden der Organischen Chemie (Houben-Weyl)* (Ed.: M. Regitz), vol. E1, Thieme, Stuttgart, **1982**.

[8] A. Schmidpeter, H. Nöth, G. Jochem, H.-P. Schrödel, K. Karaghiosoff, *Chem. Ber.* **1995**, *128*, 379–393, and references therein.

[9] A. Schmidpeter, S. Plank, K. Polborn, *Z. Naturforsch., Teil B*, in press.

[10] D. E. C. Corbridge, *The Structural Chemistry of Phosphorus*, Elsevier, Amsterdam, **1974**, sowie Cambridge Structural Database, Recherche: F. H. Allen, O. Kennard, R. Taylor, *Acc. Chem. Res.* **1983**, *16*, 146.

[11] G. Jochem, A. Schmidpeter, M. Thomann, H. Nöth, *Angew. Chem.* **1994**, *106*, 708–711; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 663–665.

[12] L. Cassidei, O. Sciacovelli, *QCPE* program No. 440.

[95063]