Endo- and Exocyclic Substitutions in α-$P_4S_3I_2$

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Dedicated to Prof. Dr. *Frank Seela* on the occasion of his 60th birthday

Two isomers each of α-$P_4S_2SeX_2$ and α-$P_4SSe_2X_2$ (X = Cl, Br) have been identified by ^{31}P-NMR spectroscopy in mixtures obtained from thermal reaction of PX_3 and $P_4S_{1.4}Se_{1.6}$. Systematic changes in chemical shifts and coupling constants with electronegativity of the ligand by exocyclic substitution and with alteration of the molecular geometry by the replacement of sulfur by selenium are reported.

Introduction. – Systematic changes in the ^{31}P-NMR parameters with endocyclic substitution have been reported for the bicyclic α-$P_4S_3I_2$ [1] and β-$P_4E_3I_2$ [2], α-$P_4E_3R_2$ [3] (E = S, Se; R = carboxylate) and β-$P_4E_3I(CHI_2)$ [4], as well as for the tricyclic P_5E_2X (X = Cl, Br, I) [5]. The influence of an exocyclic ligand exchange was investigated for α-P_4E_3XY [6] and P_5E_2X [5] (X, Y = Cl, Br, I). In contrast to exocyclic substitution in which changes of ^{31}P-NMR data are mainly determined by the differences in electronegativities of the ligands, endocyclic replacements of S- by Se-atoms causes changes in geometry.

Molecules α-$P_4E_3X_2$ are interesting because the symmetric position of their ligands X and their $[AB]_2$ and $[ABCD]$ spin systems make them suitable probes for investigating the influence of such replacements. In both spin systems, the couplings between all P-atoms can be determined and, from these data, changes in the geometry of the P_4E_3 skeleton by the S/Se replacement can be qualitatively predicted. For the six-membered ring in α-$P_4S_3I_2$, exists an optimum distance $P_A \cdots P_C$ (*Fig.*). Replacement of S by the larger Se-atom as the bridge E_a between P_A and P_C has a pronounced effect on the relative stability of the different isomers of $P_4S_{3-n}Se_nX_2$ and their ^{31}P-NMR parameters [3].

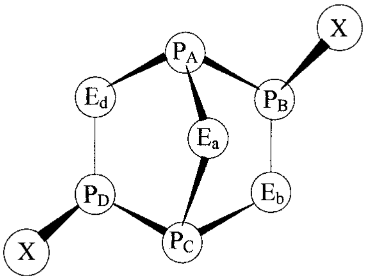


Figure. *Ring-position labels for* α-$P_4E_3X_2$

In this paper, a detailed ^{31}P-NMR investigation of α-$\mathrm{P_4S_nSe_{3-n}X_2}$ ($n = 1,2$) was performed. The findings support statements made in previous papers regarding changes in geometry of the skeleton resulting from S/Se replacement [2–4].

Results and Discussion. – 1. *Spectral Assignment*. The spectra of α-$\mathrm{P_4S_3X_2}$ [7] and α-$\mathrm{P_4Se_3X_2}$ [8] have been assigned previously. The ^{31}P-NMR spectra of α-$\mathrm{P_4E_3X_2}$ (E = S and Se) were of two types: those having symmetric spin systems $[AB]_2$ and those having unsymmetric spin systems $[ABCD]$.

The A and B parts of the spin systems $[AB]_2$ were identified in the spectra with the aid of their relation by mirror symmetry. The *multiplets* due to the P-atoms $\mathrm{P_B}$ and $\mathrm{P_D}$ carrying the ligand were distinguished from the bridgehead nuclei $\mathrm{P_C}$ by the large downfield shift. The shift in the range 162–171 ppm can be assigned to the P-atom carrying Cl in the dichloride, and that in the range 151–157 ppm can similarly be assigned to the dibromide. The signals of the bridgehead atoms $\mathrm{P_A}$ are typically found below 135 ppm.

In the unsymmetric compounds, the shift of a P-nucleus bearing a halogen ligand can be assigned as above. The assignment of the shift for the bridgehead P-atom, to which it is coupled with a large ^1J constant, follows consequently. The decision whether the *multiplets* belong to $\mathrm{P_A/P_C}$ or $\mathrm{P_B/P_D}$ was made according to the sizes of couplings they shared, as described for other α-$\mathrm{P_4S_3X_2}$ compounds [7][8].

Further discrimination was achieved on the basis of the value of the ^2J bridge coupling constants. Previous investigations have shown that the values of $^2J(\mathrm{P{-}S{-}P})$ constants are larger by *ca.* 10 Hz than those of the respective $^2J(\mathrm{P{-}Se{-}P})$ coupling constants and values of $^2J_{AD}$ and $^2J_{BC}$ for the S-compounds are larger by *ca.* 6 Hz compared to those of the corresponding Se-derivatives [7][8]. For each compound initial analysis was followed by iterative fitting with the program NUMARIT [9]. Simulation and comparison of the calculated and measured spectra were performed with the programs 1D Win NMR and Win Daisy [10][11].

Though some *multiplets* were overlapping, most of the transitions (*Table 1*) were found *via* the observed splittings measured in the readily visible part of the spectrum of each compound. The interpretation of the spectra of α-$\mathrm{P_4E_3Cl_2}$ was complicated by the low concentrations of its isomers in the sample.

Table 1. *Iterative Fitting of NMR Data of* α-$\mathrm{P_4E_3Br_2}$ *and* α-$\mathrm{P_4E_3Cl_2}$ (E = S, Se)

	Fraction of transitions observed					
Compound	$\delta(\mathrm{P_A})$	$\delta(\mathrm{P}_{\mathrm{B})}$	$\delta(\mathrm{P_C})$	$\delta(\mathrm{P_D})$	Total	r.m.s. [Hz]
α-$\mathrm{P_4S_3Br_2}$	12/12	12/12	$=\delta(\mathrm{P_A})$	$=\delta(\mathrm{P_B})$	24/24	0.08259
α-$\mathrm{P_4S_2Se_aBr_2}$	10/12	10/12	$=\delta(\mathrm{P_A})$	$=\delta(\mathrm{P_B})$	20/24	0.43645
α-$\mathrm{P_4S_2Se_bBr_2}$	8/8	8/8	8/12	8/12	32/40	0.04521
α-$\mathrm{P_4S_dSe_2Br_2}$	6/8	7/8	8/10	8/9	29/35	0.03460
α-$\mathrm{P_4S_aSe_2Br_2}$	8/12	8/12	$=\delta(\mathrm{P_A})$	$=\delta(\mathrm{P_B})$	16/24	0.10693
α-$\mathrm{P_4Se_3Br_2}$	7/12	8/12	$=\delta(\mathrm{P_A})$	$=\delta(\mathrm{P_B})$	15/24	0.10645
α-$\mathrm{P_4S_3Cl_2}$	9/12	8/12	$=\delta(\mathrm{P_A})$	$=\delta(\mathrm{P_B})$	17/24	0.22458
α-$\mathrm{P_4S_2Se_aCl_2}$	11/12	10/12	$=\delta(\mathrm{P_A})$	$=\delta(\mathrm{P_B})$	21/24	0.54224
α-$\mathrm{P_4S_2Se_bCl_2}$	4/8	7/8	6/8	6/8	27/32	0.07506
α-$\mathrm{P_4S_dSe_2Cl_2}$	6/8	6/8	8/8	8/8	28/32	0.11900
α-$\mathrm{P_4S_aSe_2Cl_2}$	11/12	11/12	$=\delta(\mathrm{P_A})$	$=\delta(\mathrm{P_B})$	22/24	0.39403
α-$\mathrm{P_4Se_3Cl_2}$	12/12	12/12	$=\delta(\mathrm{P_A})$	$=\delta(\mathrm{P_B})$	24/24	0.42537

2. *Relative Yields of the Compounds*. Relative amounts (in mol-%) of the different compounds, estimated by integration of the NMR signals, were: 15.3% PBr_3, 29.0% α-$P_4E_3Br_2$, and 50.1% P_4E_3 for α-$P_4E_3Br_2$ and 2.6% PCl_3, 11.5% α-$P_4E_3Cl_2$, and 85.6% P_4E_3 for α-$P_4E_3Br_2$.

In the same way the amount of P_4E_3 could be separated into different contributions of the different $P_4S_{3-n}Se_n$ species. The molar ratios P_4E_3/P_4Se_3 found for X = Br were $P_4S_3/P_4S_2Se/P_4SSe_2$ 5.0 : 8.3 : 4.5, and for X = Cl, $P_4S_3/P_4S_2Se/P_4SSe_2$ 3.5 : 6.9 : 4.4. These values show that the solutions contain more sulfur than the educts. The change in Se content is due to the tendency to form insoluble products in the reactions in which P and Se are involved.

Table 2 gives the NMR-spectral parameter of α-$P_4E_3Br_2$ and α-$P_4E_3Cl_2$. The labelling of the atomic positions used in the *Tables* is shown in the *Figure*.

Table 2. *^{31}P-NMR-Data of Isomers of α-$P_4E_3X_2$*

	Chemical shifts δ[ppm]				Coupling constants J [Hz]					
α-$P_4E_3X_2$	P_A	P_B	P_C	P_D	$^1J_{AB}$	$^1J_{CD}$	$^2J_{AC}$	$^2J_{AD}$	$^2J_{BC}$	$^3J_{BD}$
Bromides										
α-$P_4S_3Br_2$	132.64	151.69	132.64	151.69	– 254.31 (3)	– 254.31 (3)	70.19 (5)	19.77 (2)	19.77 (2)	11.66 (5)
α-$P_4S_2Se_aBr_2$	119.98	151.91	119.98	151.91	– 255.1 (2)	– 255.1 (2)	60.1 (3)	24.0 (1)	24.0 (1)	8.0 (3)
α-$P_4S_2Se_bBr_2$	138.19	154.37	121.82	155.04	– 254.86 (3)	– 252.23 (3)	82.01 (3)	20.19 (3)	14.72 (3)	11.22 (3)
α-$P_4S_dSe_2Br_2$	124.72	154.76	106.38	155.67	– 255.34 (2)	– 252.65 (2)	71.36 (2)	24.93 (2)	18.60 (3)	7.95 (2)
α-$P_4S_aSe_2Br_2$	127.19	156.74	127.19	156.74	– 252.5 (9)	– 252.5 (9)	94.54 (7)	15.16 (4)	15.16 (4)	10.30 (6)
α-$P_4Se_3Br_2$	110.93	157.54	110.93	157.54	– 251 (1)	– 251 (1)	83.57 (7)	20.12 (4)	20.12 (4)	7.13 (7)
Chlorides										
α-$P_4S_3Cl_2$	133.55	162.34	133.55	162.34	– 261.3 (3)	– 261.3 (3)	66.6 (1)	20.51 (7)	20.51 (7)	10.0 (1)
α-$P_4S_2Se_aCl_2$	121.19	162.10	121.19	162.10	– 263.0 (2)	– 263.0 (2)	56.9 (4)	24.3 (2)	24.3 (2)	6.3 (3)
α-$P_4S_2Se_bCl_2$	139.32	167.84	123.55	166.21	– 263.47 (7)	– 259.86 (5)	78.21 (5)	20.02 (5)	14.93 (5)	9.25 (6)
α-$P_4S_dSe_2Cl_2$	126.17	167.65	108.43	166.43	– 264.19 (7)	– 260.54 (7)	68.06 (7)	24.79 (8)	18.97 (9)	6.5 (1)
α-$P_4S_aSe_2Cl_2$	129.19	170.84	129.19	170.84	– 261.0 (2)	– 261.0 (2)	90.5 (2)	15.4 (1)	15.4 (1)	7.8 (3)
α-$P_4Se_3Cl_2$	113.27	171.11	113.27	171.11	– 261.5 (2)	– 261.5 (2)	80.0 (2)	19.4 (1)	19.4 (1)	4.4 (2)

The total number of P–S, P–Se, and P–X bonds does not change in compounds with equal numbers of S- and Se-atoms. The ratio of α-$P_4S_3X_2$/α-$P_4S_2SeX_2$/α-$P_4SSe_2X_2$/α-$P_4Se_3X_2$ should, therefore, correspond to a statistical distribution 1 : 3 : 3 : 1. The experimental ratios (*Table 3*) were 12 : 37 : 40 : 12 in α-$P_4E_3I_2$ [1], 11 : 36 : 38 : 17 in α-$P_4E_3Br_2$ and 6 : 27 : 47 : 20 in α-$P_4E_3Cl_2$, approximately as expected. The relief of ring strain achieved by increasing the size of the six-membered ring *via* substitution of S by Se in position E_b or E_d may account for the preferential generation of Se-rich isomers.

Table 3. *Relative Yields of Isomers of α-$P_4E_3X_2$* (mol-%)

X	α-$P_4S_3X_2$	α-$P_4S_2Se_aX_2$	α-$P_4S_2Se_bX_2$	α-$P_4S_dSe_2X_2$	α-$P_4S_aSe_2X_2$	α-$P_4Se_3X_2$
I	11.9	3.0	33.5	11.0	28.8	11.9
Br	10.5	3.9	31.3	13.7	23.8	16.8
Cl	6.0	5.0	22.4	17.4	29.4	19.9

Within one pair of isomers the ratio of unsymmetric/symmetric isomers should be 2 : 1, because in the unsymmetric α-$P_4E_3X_2$ two permutations are possible instead of one in the symmetric compound.

The relation between unsymmetric and symmetric α-$P_4E_3X_2$ is determined mainly by the bond angle at E_a. Substitution of S by Se decreases the strained bond angle in α-$P_4S_3X_2$, and substitution of Se by S increases it in α-$P_4Se_3X_2$. The first substitution is unfavorable, whereas the second one is favorable; therefore, the ratio of symmetric/unsymmetric isomer is small in α-$P_4S_2SeX_2$ (*ca.* 0.2) and large in α-$P_4SSe_2X_2$ (*ca.* 1.6). A detailed discussion of this phenomenon was given by *Blachnik et al.* [1].

3. *^{31}P-NMR Parameters.* As reported in preceding papers [12][13], the ^{31}P-NMR data of α-$P_4E_3Br_2$ and α-$P_4E_3Cl_2$ are compared with those of α-$P_4E_3I_2$.

3.1. *Halogen Substitution.* The changes in chemical shifts of all P-atoms and some coupling constants are determined by the change in electronegativity differences in going from I to Cl.

The effects of these replacements on the values of the ^{31}P chemical shifts and P,P coupling constants are presented in *Table 4*. These values are obtained by substracting each of the ^{31}P-NMR data of α-$P_4E_3I_2$ from those of the corresponding data of α-$P_4E_3X_2$ (X = Cl, Br). The changes in chemical shifts and coupling constants of bromides and chlorides caused by substitution of I can be divided for each in two groups, one in which P-atoms carrying the halogen have a sulfur neighbor and the other with P-atoms with a Se-neighbor. In both groups, the changes in NMR parameters in the different isomers are remarkably constant for each of their parameters. The changes of the ^1J coupling constant in a five-membered ring of α-$P_4E_3X_2$ with S in position E_b or E_d is contained in the column ^1J(P−PS) of this table, those with Se in this position in the column ^1J(P−Se).

Table 4. *Averaged Changes in NMR Parameters of α-$P_4E_3X_2$ on Halogen Substitution*

	$\Delta\delta$ [ppm]				ΔJ [Hz]	
	$P_{(B/D)-S}$	$P_{(B/D)-Se}$	$P_{(A/C)-S}$	$P_{(A/C)-Se}$	$^1J_{P-PS}$	$^1J_{P-PSe}$
Br	26.2	32.1	4.3	5.4	– 11.1	– 12.4
Cl	36.8	45.7	5.4	7.5	– 18.6	– 21.3

All chemical shifts increase nearly linearly with increasing electronegativity of the ligand (I → Cl). The chemical shifts of the P-nuclei bound to S are approximately given by

$$\delta_{P(B,D-S)} = 74.6\ \chi_X - 70.7$$

those bound to Se by

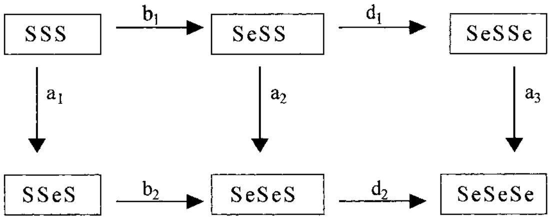
$$\delta_{P(B,D-Se)} = 92.7\ \chi_X - 121.2$$

where χ is *Pauling*'s electronegativity. The coupling constants ^1J become more negative when the substituent is changed from I to Cl, *i.e.*, with increasing electronegativity of the substituent. This behavior of the ^1J coupling constants is expected from *Walsh* rules [14] and was previously observed for other ^1J(P−P) couplings [15–17]. The value of the bridge coupling $^2J_{AC}$ decreases with increase in halogen electronegativity. Such an influence of electronegativity on ^2J coupling constants was also reported by *Verkade* [18], and *Schuhmann* and *Kroth* [19].

In chemical shifts and in ^1J and $^2J_{AC}$ couplings, the changes of NMR parameters are larger for the I/Cl substitution than for the I/Br replacements. The changes in couplings $^2J_{AD}$, $^2J_{BC}$, and $^3J_{BD}$ do not correlate with electronegativity. The change in the bridge coupling $^2J_{AC}$ is mainly due to the change in electronegativity of the halogen and is thus nearly constant within bromides (–4.2 Hz) or chlorides (–7.8 Hz).

3.2. *Chalcogen Substitution.* As shown in the *Scheme*, the replacement of sulfur by selenium may be classified in three groups: *i*) $a_1 - a_3$ substitution in the bridging position E_a, *ii*) b_1 or b_2 (at E_b) as the first, *iii*) and d_1 or d_2 (at E_d) as the second replacement, respectively, in the six-membered ring.

Scheme. *Sequence of Replacement of S by Se in* α-$P_4S_nSe_{3-n}X_2$ ($a_1 - a_3$ at position E_a, $b_1 - b_2$ at E_b, $d_1 - d_2$ at E_d)



The effects of these substitutions are given in *Table 5*. It is completed by corresponding data of $P_4E_3I_2$ [1]. The values in these tables are obtained by subtracting each of the ^{31}P-NMR data of the Se-rich isomers from those of the corresponding S-rich isomers. Changes in each of the measured chemical shifts and coupling constants were remarkably constant within each of these groups, independent of the character of the halogen ligand.

In accord with the C_2 symmetry of the molecules, changes in one parameter caused by a b_1 or b_2 replacement are very similar to changes in the corresponding parameter caused by a d_1 or d_2 replacement, *e.g.*, as revealed by the changes in $^1J_{AB}$ compared with $^1J_{CD}$ caused by these substitutions. This effect was already observed in α-$P_4E_3I_2$ [1].

The bond angles at the chalcogen bridge E_a are smaller for E = S than for E = Se. This is reflected by the changes in $^2J_{AC}$ to less positive values for all substitutions $a_1 - a_3$. Like $^2J_{AC}$, the coupling constants $^2J_{BC}$ and $^2J_{AD}$ become less positive by almost the same amount as the chalcogen transmitting the coupling is changed from S to Se, and the bond angle at the chalcogen atom consequently decreases (b_1/b_2 and d_1/d_2 replacements, respectively).

A second effect of the chalcogen substitution at E_b and E_d is an enlargement of the bond angle at E_a by introducing Se in the six-membered ring. This replacement is reflected in changes in $^2J_{AC}$ of a nearly equal order of magnitude as those for the replacements $a_1 - a_3$, however, in the opposite sense. Thus, the bond angle at E_a has a larger influence on the value of $^2J_{AC}$ than does the nature of the chalcogen atom (S or Se).

The increase in bond angle at a P-atom as a S-atom is replaced by a Se-atom in a non-adjacent position leads to a shift of its NMR signal to lower field. Such shifts are

Table 5. *Changes in NMR Parameters by Chalcogen Substitution in* α-$P_4S_{3-n}Se_nX_2$

		a1	a2	a3	b1	b2	d1	d2
$\Delta\delta$ [ppm]								
P_A	Cl	– 12.4	– 13.2	– 15.9	5.8	5.0	– 10.1	– 12.9
	Br	– 12.7	– 13.5	– 16.3	5.6	4.7	– 11.0	– 13.8
	I	– 13.4	– 16.1	– 16.8	5.6	4.9	– 12.2	– 15.0
P_B	Cl	– 0.2	– 0.2	0.3	5.5	5.6	3.0	3.5
	Br	0.2	0.4	0.8	2.7	2.9	2.4	2.8
	I	1.3	1.9	2.4	– 3.5	– 2.9	2.2	2.6
P_C	Cl	– 12.4	– 15.1	– 15.9	– 10.0	– 12.8	5.6	4.8
	Br	– 12.7	– 15.4	– 16.3	– 10.8	– 13.6	5.4	4.6
	I	– 13.4	– 16.1	– 16.8	– 12.3	– 15.0	5.6	4.9
P_D	Cl	– 0.2	0.2	0.3	3.9	4.3	4.6	4.7
	Br	0.2	0.6	0.8	3.4	3.8	1.7	1.9
	I	1.3	1.9	2.4	3.0	3.5	– 4.2	– 3.8
ΔJ [Hz]								
$^1J_{AB}$	Cl	– 1.7	– 0.7	– 0.5	– 2.2	– 1.2	2.5	2.7
	Br	– 0.8	– 0.5	0.8	– 0.6	– 0.2	2.4	3.6
	I	– 0.1	0.1	0.2	1.0	1.1	2.8	3.0
$^1J_{CD}$	Cl	– 1.7	– 0.7	– 0.5	1.4	2.4	– 1.1	– 0.9
	Br	– 0.8	– 0.4	0.8	2.1	2.5	– 0.3	0.9
	I	– 0.1	0.0	0.2	2.5	2.6	1.3	1.5
$^2J_{AC}$	Cl – 9.6	– 10.2	– 10.5	11.7	11.1	12.3	12.0	
	Br	– 10.1	– 10.7	– 11.0	11.8	11.3	12.5	12.2
	I	– 10.3	– 11.1	– 11.7	11.5	10.8	12.6	11.9
$^2J_{AD}$	Cl	3.8	4.8	4.0	– 0.5	0.5	– 4.6	– 5.4
	Br	4.2	4.7	5.0	0.4	0.9	– 5.0	– 4.8
	I	4.2	4.7	3.9	1.0	1.5	– 5.2	– 6.0
$^2J_{BC}$	Cl	3.8	4.0	4.0	– 5.6	– 5.3	0.5	0.5
	Br	4.2	3.9	5.0	– 5.0	– 5.4	0.4	1.5
	I	4.2	3.8	3.9	– 4.9	– 5.3	0.8	0.9
$^3J_{BD}$	Cl	– 3.7	– 2.8	– 3.4	– 0.8	0.2	– 1.4	– 2.0
	Br	– 3.6	– 3.3	– 3.2	– 0.4	– 0.1	– 0.9	– 0.8
	I	– 4.2	– 3.4	– 3.7	0.2	1.0	– 0.5	– 0.8

observed for $\delta(P_A)$ or $\delta(P_C)$ in the b_1/b_2 or d_1/d_2 substitutions, and for $\delta(P_B)$ or $\delta(P_D)$ in the a_2/a_3 or d_1/d_2 replacements, respectively. This effect can be masked by the effect of the electronegativity difference between S and Se. A replacement of S by Se at E_b causes similar changes of the angles $P_B-P_A-E_a$ and $E_b-P_C-E_a$. An effect on $\delta(P)$ is observed only for P_A (b_1 or b_2), and is compensated for P_C by the shielding effect of Se_b. The same shielding accounts also for the high-field shift of $\delta(P_A)$ and $\delta(P_C)$ for all S/Se substitutions in position E_a.

Experimental Part

All operations for the synthesis were carried out under Ar by *Schlenk* methods. CS_2 was dried by distillation from P_4O_{10}.

The conventional method for the syntheses of α-$P_4E_3X_2$ (E = S, Se; X = Cl, Br) is the replacement of I in α-$P_4E_3I_2$ with organometallic or metal halides [6][20] in CS_2 solution. This method has a disadvantage: when the reaction is finished the soln. contains the desired product together with α-P_4E_3IX and unreacted α-$P_4E_3I_2$, which complicate interpretation of the ^{31}P-NMR spectra. A more useful route to α-$P_4E_3X_2$ is the high-temp. synthesis from P_4E_3 and PX_3. Thus, $P_4S_{1.4}Se_{1.6}$ was prepared by heating the elements in this stoichiometric ratio at 250° in an evacuated and sealed quartz ampoule. The reaction product was recrystallized from CS_2. In a typical experiment, 1.5 g of $P_4S_{1.4}Se_{1.6}$ and the stoichiometric amount of PX_3 were filled into a quartz ampoule, which was evacuated and sealed. The sample was subjected to a slow heating program, first annealed for 24 h at 120°, then the temp. was increased at a rate of 10°/h to 250°, the sample was annealed at this temp. for 48 h, heated slowly to 350°, and annealed at 350° for two weeks. The reaction was judged complete when no droplets condensed on the walls of the ampoules on cooling. Soluble products were extracted by stirring in CS_2 at r.t. for 6 h. After filtration, the ^{31}P-NMR spectra of the solns. were measured.

^{31}P-NMR Spectra: *Bruker AC-250* spectrometer, 101.5 MHZ, in 5-mm diameter tubes with precision capillaries containing C_6D_6 for locking; chemical shifts δ in ppm relative to 85% aq. H_3PO_4.

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