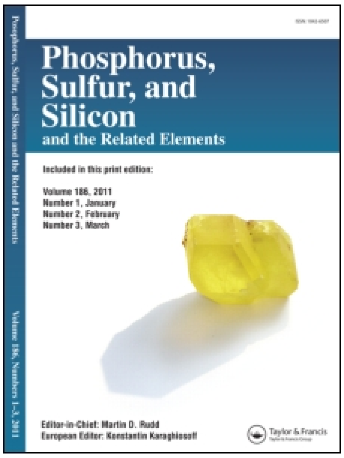

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Substitution Reactions of $A_4B_3X_2$-Compounds (A=P; B=S,Se; X=I,Br,Cl)

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To cite this Article Blachnik, Roger and Hackmann, Kerstin(1992) 'Substitution Reactions of $A_4B_3X_2$-Compounds (A=P; B=S,Se; X=I,Br,Cl)', Phosphorus, Sulfur, and Silicon and the Related Elements, 65: 1, 99 — 102

To link to this Article: DOI: 10.1080/10426509208055328

URL: http://dx.doi.org/10.1080/10426509208055328

Phosphorus, Sulfur, and Silicon, 1992, Vol. 65, pp. 99–102
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SUBSTITUTION REACTIONS OF $A_4B_3X_2$-COMPOUNDS (A=P; B=S,Se; X=I,Br,Cl)

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Abstract Mixed halido compounds of the general formula P_4B_3XY (B=S, Se; X,Y=I, Br, Cl) have been synthesized by reaction of $P_4B_3X_2$ molecules with bismuth- or mercury halides in CS_2 solution. ^{31}P-n.m.r. spectra have been measured and assigned. Predictive relationships were found between n.m.r. parameters for unsymmetric molecules and those for the symmetric ones, showing that the molecules can be composed from parts of the pure $P_4B_3X_2(Y_2)$ compounds.

INTRODUCTION

α-$P_4B_3I_2$ [1,2] and β-$P_4B_3I_2$ [3,4,5,6] (B=S, Se) are well known compounds, produced by the reaction of P_4B_3 with iodine. α-$P_4S_3I_2$ was reacted with AgX (X=Br, Cl, CN,SCN) in CS_2 solution by FLUCK in 1976 [7], who obtained a series of α-$P_4S_3X_2$ compounds. Recently we have synthesized all other molecules of the type $P_4B_3X_2$.[8] By using Bi- or Hg-halides instead of Ag-halide we obtained higher yields in shorter times. With these reagents even the substitution in the β-$P_4B_3I_2$ molecules, which transform easily into the α-form at ambient temperature, was possible. In the case of insufficient amounts of halide being present for total substitution or if the reaction is stopped after a few hours mixed halides of the general formula P_4B_3XY are formed. The molecular structures of the α- and β-forms are shown in Figure 1.

α-$P_4B_3X_2$ compounds belong to an AA'BB' spin-system in the ^{31}P-n.m.r., the β-molecules to an AB_2X spin-system. All P_4B_3XY molecules show an ABCD spin-system.

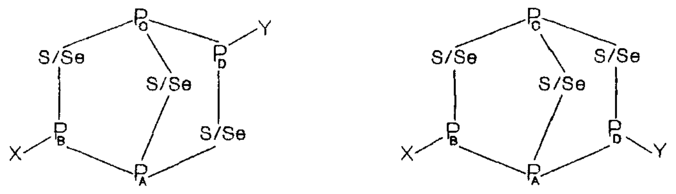

FIGURE 1 α-P_4B_3XY β-P_4B_3XY

RESULTS AND DISCUSSION

The ^{31}P-n.m.r. data of the compounds are summarized in the Tables 1-4.

TABLE 1 ^{31}P-n.m.r. data of α-P_4S_3XY molecules

	X=I, Y=Br Lit[9]		X=Br, Y=Cl	X=I, Y=Cl
Chemical shifts [ppm]				
δ_A	129.05	129.30	131.51	128.31
δ_B	125.12	125.29	151.98	125.38
δ_C	132.26	132.04	134.33	134.13
δ_D	150.78	150.39	162.07	161.15
Coupling constants [Hz]				
J_{AB}	-241.8	-242.1	-253.2	-240.6
J_{AC}	72.1	72.4	68.1	70.6
J_{AD}	21.5	21.7	20.6	22.3
J_{BC}	19.9	20.1	18.7	19.1
J_{BD}	10.5	9.9	10.6	9.5
J_{CD}	-255.9	-256.7	-262.9	-265.3
rms [Hz]	0.38	0.25	0.26	0.22

TABLE 2 ^{31}P-n.m.r. data of α-P_4Se_3XY molecules

	X=I, Y=Br	X=Br, Y=Cl	X=I, Y=Cl
Chemical shifts [ppm]			
δ_A	105.72	109.50	105.11
δ_B	127.79	158.08	128.72
δ_C	109.94	113.06	112.95
δ_D	154.37	169.40	166.71
Coupling constants [Hz]			
J_{AB}	-238.5	-251.7	-237.6
J_{AC}	85.3	81.8	83.6
J_{AD}	21.0	19.9	21.8
J_{BC}	19.6	18.5	18.9
J_{BD}	6.3	5.9	4.9
J_{CD}	-254.1	-262.3	-263.8
rms [Hz]	0.03	0.04	0.07

TABLE 3 ^{31}P-n.m.r. data of β-P_4S_3XY molecules

	X=I, Y=Br	X=Br, Y=Cl	X=I, Y=Cl
Chemical shifts [ppm]			
δ_A	159.77	170.67	163.39
δ_B	94.94	133.65	94.85
δ_C	197.28	198.29	196.36
δ_D	129.29	146.41	142.56
Coupling constants [Hz]			
J_{AB}	-259.9	-282.4	-266.4
J_{AC}	78.4	72.1	76.5
J_{AD}	-267.2	-284.5	-275.0
J_{BC}	56.4	58.4	56.5
J_{BD}	170.3	153.9	165.1
J_{CD}	57.4	58.8	58.2
rms [Hz]	0.36	0.30	0.56

TABLE 4 ^{31}P-n.m.r. data of β-P_4Se_3XY molecules

	X=I, Y=Br	X=Br, Y=Cl	X=I, Y=Cl
Chemical shifts [ppm]			
δ_A	158.12	169.11	161.71
δ_B	93.00	135.52	92.64
δ_C	173.12	174.32	172.15
δ_D	131.66	150.03	146.38
Coupling constants [Hz]			
J_{AB}	-265.6	-290.3	-272.9
J_{AC}	86.6	80.1	83.6
J_{AD}	-272.6	-292.0	-281.4
J_{BC}	53.9	55.9	53.4
J_{BD}	184.1	168.3	178.9
J_{CD}	55.5	57.5	56.9
rms [Hz]	0.17	0.25	0.16

For the interpretation of the ^{31}P-n.m.r. data the unsymmetric α-P_4B_3XY molecule can be considered as being composed of the two parts (P_A+P_B and P_C+P_D), each belonging to the symmetric disubstituted α-$P_4B_3X_2$ and α-$P_4B_3Y_2$ molecule. This simple relationship between the unsymmetric and the symmetric forms has already been discussed by TATTERSHALL [10]. The influence of the parts on each other is low, as shown by the small changes in coupling constants and chemical shifts for the same P-atoms in the unsymmetric and the symmetric molecules. These deviations increase with larger electronegativity difference between the two halogen atoms. Coupling constants between P-atoms belonging to different parts can be calculated from the respective average values of the parent molecules. Generally all rules of averaging found for the iodo-amino compounds [10] are valid. A comparison of the calculated values and the experimental data is given in Table 5.

If the sulphur is substituted with selenium the phosphorus P_A and P_C bonded to two selenium atoms are shifted to lower frequencies, the phosphorus P_B and P_D bonded to the halogen atoms show a small shift to higher frequencies.

The effect of an unsymmetric substitution is different in the β-compounds. The apical P-atom, separated by chalcogen atoms from the halogen bearing P-atoms, behaves like the P-atoms in the α-molecules. Its chemical shift remains nearly constant. The substitution of a halogen X by a more electronegative Y in the basal XP_3X unit has a drastic effect. It can be explained in a simplified

TABLE 5 Relationship between n.m.r. parameters for α-P_4B_3XY compounds and those for α-$P_4B_3X_2$ and α-$P_4B_3Y_2$

B	S	S	S	Se	Se	Se
X	I	Br	I	I	Br	I
Y	Br	Cl	Cl	Br	Cl	Cl
Couplings (Hz) influenced similarly by X and Y						
$^2J_{AC}$ (XY)	72.1	68.1	70.6	85.3	81.8	83.6
Av. $^2J_{AA'}$ (X_2,Y_2)	72.5	68.2	70.5	83.4	79.4	83.8
Diff.	-0.4	-0.1	+0.1	+1.9	+2.4	-0.2
$^3J_{BD}$ (XY)	10.5	10.6	9.5	6.3	5.9	4.9
Av. $^3J_{BB'}$ (X_2,Y_2)	10.7	11.1	9.8	6.3	5.5	5.2
Diff.	-0.2	-0.5	-0.3	0.0	+0.4	-0.3
Couplings (Hz) influenced dissimilarly by X and Y						
$^2J_{AD}$ (XY)	21.5	20.6	22.3	21.0	19.9	21.8
$^2J_{BC}$ (XY)	19.9	18.7	19.1	19.6	18.5	18.9
$^2J_{AB'}$ (X_2)	21.7	19.8	21.7	21.3	17.8	21.3
$^2J_{AB'}$ (Y_2)	19.8	20.1	20.1	17.8	19.5	19.5
Av. $^2J_{AD}$ $^2J_{BC}$ (XY)	20.7	19.7	20.7	20.3	19.2	20.4
Av. $^2J_{AB'}$ (X_2,Y_2)	20.8	20.0	20.9	19.6	18.7	20.4
Diff.	-0.1	-0.3	-0.2	+0.7	+0.5	0.0
$^1J_{AB}$ (XY) - $^1J_{AB}$ (X_2)	+1.8	+0.8	+3.0	+2.1	-0.6	+3.0
$^1J_{CD}$ (XY) - $^1J_{AB}$ (Y_2)	-1.9	-0.9	-3.3	-3.0	-0.7	-2.2
Av. $^1J_{AB}$ $^1J_{CD}$ (XY)	-248.9	-258.1	-253.0	-246.3	-257.0	-250.7
Av. $^1J_{AB}$ (X_2,Y_2)	-248.8	-258.0	-252.8	-245.9	-256.4	-251.1
Diff.	-0.1	-0.1	-0.2	-0.4	-0.6	+0.4
Chemical shifts (ppm) of bridgehead phosphorus atoms						
δ_A (XY) - δ_A (X_2)	+0.4	-0.5	-0.4	+0.3	-0.6	-0.3
δ_C (XY) - δ_A (Y_2)	+0.3	+0.5	+0.3	-0.2	+1.5	+1.4
Av. δ_A δ_C (XY)	130.7	132.9	131.2	107.8	111.3	109.0
Av. δ_A (X_2,Y_2)	130.4	132.9	131.3	107.8	110.9	108.5
Diff.	+0.3	0.0	-0.1	0.0	+0.4	+0.5
Chemical shifts (ppm) of phosphorus atoms carrying halogens						
δ_B (XY) - δ_B (X_2)	+0.0	+0.9	+0.3	+1.7	+1.1	+2.6
δ_D (XY) - δ_B (Y_2)	-0.3	0.0	-1.0	-2.6	-1.0	-3.7
Av. δ_B δ_D (XY)	138.0	157.0	143.3	141.1	163.7	147.7
Av. δ_B (X_2,Y_2)	138.1	156.6	143.6	141.5	163.7	148.2
Diff.	-0.1	+0.4	-0.3	-0.4	0.0	-0.5

TABLE 6 Relationship between n.m.r. parameters for β-P_4B_3XY compounds and those for β-$P_4B_3X_2$ and β-$P_4B_3Y_2$

B	S	S	S	Se	Se	Se
X	I	Br	I	I	Br	I
Y	Br	Cl	Cl	Br	Cl	Cl
Couplings (Hz) influenced similarly by X and Y						
$^2J_{AC}$ (XY)	78.4	72.1	76.5	86.6	80.1	83.6
Av. $^2J_{AC}$ (X_2,Y_2)	78.4	72.1	75.9	86.3	79.8	83.5
Diff.	0.0	0.0	+0.6	+0.3	+0.3	+0.1
Couplings (Hz) influenced dissimilarly by X and Y						
$^2J_{BC}$ (XY)	56.4	58.4	56.5	53.9	55.9	53.4
$^2J_{CD}$ (XY)	57.4	58.8	58.2	55.5	57.5	56.9
$^2J_{BC}$ (X_2)	56.1	58.3	56.1	53.8	56.1	53.8
$^2J_{CD}$ (Y_2)	58.3	58.8	58.8	56.1	57.2	57.2
Av. $^2J_{BC}$ $^2J_{CD}$ (XY)	56.9	58.6	57.4	54.7	56.7	55.2
Av. $^2J_{BC}$ (X_2,Y_2)	57.2	58.6	57.5	55.0	56.7	55.5
Diff.	-0.3	0.0	-0.1	-0.3	0.0	-0.3
$^1J_{AB}$(XY)-$^1J_{AB}$(X_2)	-7.9	-6.6	-14.4	-9.3	-7.0	-16.6
$^1J_{AD}$(XY)-$^1J_{AB}$(Y_2)	+8.6	+6.1	+15.6	+10.7	+7.2	+17.8
Av. $^1J_{AB}$ $^1J_{AD}$ (XY)	-263.6	-283.5	-270.7	-269.1	-291.2	-277.2
Av. $^1J_{AB}$ (X_2,Y_2)	-263.9	-283.2	-271.3	-269.8	-291.3	-277.8
Diff.	+0.3	-0.3	+0.6	+0.7	+0.1	+0.6
Chemical shifts (ppm) of the bridgehead phosphorus atoms						
δ_A (XY) - δ_A (X_2)	+8.4	+3.3	+12.1	+8.4	+3.4	+12.0
δ_A (XY) - δ_A (Y_2)	-7.7	-3.1	-10.3	-7.6	-3.2	-10.6
δ_A (XY)	159.8	170.7	163.4	158.1	169.1	161.7
Av. δ_A (X_2,Y_2)	159.4	170.6	162.5	157.7	169.0	161.0
Diff.	+0.4	+0.1	+0.9	+0.4	+0.1	+0.7
Chemical shifts (ppm) of the apical phosphorus atoms						
δ_C (XY) - δ_C (X_2)	+1.3	-0.7	+0.4	+1.6	-0.6	+0.6
δ_C (XY) - δ_C (Y_2)	-1.7	+0.7	-1.2	-1.8	+0.7	-1.5
δ_C (XY)	197.3	198.3	196.4	173.1	174.3	172.2
Av. δ_C (X_2,Y_2)	197.5	198.3	196.8	173.2	174.3	172.6
Diff.	-0.2	0.0	-0.4	-0.1	0.0	-0.4
Chemical shifts (ppm) of phosphorus atoms carrying halogens						
δ_B (XY) - δ_B (X_2)	+1.2	+1.0	+1.1	+0.8	+0.9	+0.5
δ_D (XY) - δ_B (Y_2)	-3.3	-1.3	-5.2	-2.9	-1.3	-4.9
Av. δ_B δ_D (XY)	112.1	140.0	118.7	112.3	142.8	119.5
Av. δ_B (X_2,Y_2)	113.2	140.2	120.8	113.4	143.0	121.7
Diff.	-1.1	-0.2	-2.1	-1.1	-0.2	-2.2

approach. Electrons flow along the chain to the more electronegative halogen. This flow deshields the phosphorus nuclei. The effect decreases gradually along the chain in the direction of the less electronegative ligand at P_B. However, all chemical shifts and coupling constants can be calculated from the corresponding means of the pure β-$P_4B_3X_2$ compounds (Table 6). The coupling constants $^2J_{BD}$ can not be calculated because of the equivalence of δ_B and δ_D in the β-$P_4S_3X_2$ molecules. It increases as the size of the halogen atoms increase, possibly indicating that the substituents change their position relative to the phosphorus-sulphur frame. This change in geometry may contribute to changes in $^1J_{AB}$ and $^1J_{AD}$, too, because the bonds between these atoms are affected directly by the bond angle in the basal P_3-unit.

A comparison of the β-P_4S_3XY and the β-P_4Se_3XY molecules reveals that the chemical shifts of P_A, P_B and P_D are moved about 2 ppm to higher frequencies. In contrast the phosphorus atom P_C has a significant shift to lower frequencies (about 15 ppm).

EXPERIMENTAL

The ^{31}P-n.m.r. spectra were measured using a BRUKER AC 250 spectrometer operating at 101.256 MHz. A C_6D_6 capillary was used as the lock and external reference, chemical shifts are reported relative to 85 % H_3PO_4-H_2O. The n.m.r. data were calculated by iterative fitting using PANIC [11].

α-$P_4S_3I_2$ [2], β-$P_4S_3I_2$ [5,6], α-$P_4Se_3I_2$ [1], β-$P_4Se_3I_2$ [3,4] were made according to literature methods.

The α-P_4B_3XY molecules were prepared by reacting a solution of 0.5g α-$P_4B_3I_2$ in 20 ml CS_2 with an amount of metal halide (bismuth or mercury) equivalent to half of the iodine atoms present. The solution was stirred at 297 K for 15 hours. For the preparation of α-P_4B_3BrCl we used α-$P_4B_3Br_2$. The β-forms were obtained in the same way. In this case the reaction temperature was lowered to 253 K to prevent isomerization to the α-molecules. The reaction time was 5 hours.

ACKNOWLEDGEMENTS

We wish to express our gratitude to the DFG and the Fonds der chemischen Industrie.

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