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Sulfurization Reaction of 1,3-Diphosphaallene. X-Ray Structure of *cis*-2,4-Bis(2,4,6-tri-t-butylphenyl)-1,2,4-thiadiphosphetane 2,4-Disulfide

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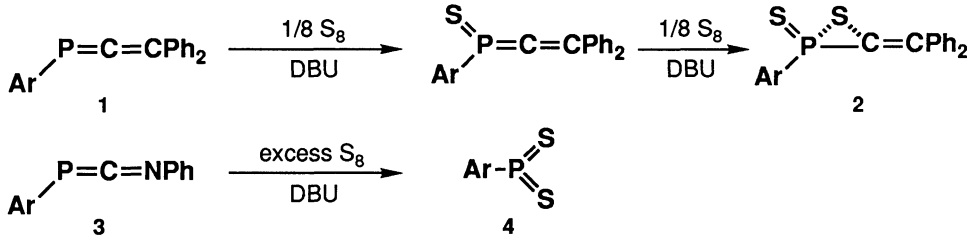
1,3-Bis(2,4,6-tri-t-butylphenyl)-1,3-diphosphaallene was reacted with elemental sulfur to give *cis*-2,4-bis(2,4,6-tri-t-butylphenyl)-1,2,4-thiadiphosphetane 2,4-disulfide and the structure was determined by X-ray crystallography.

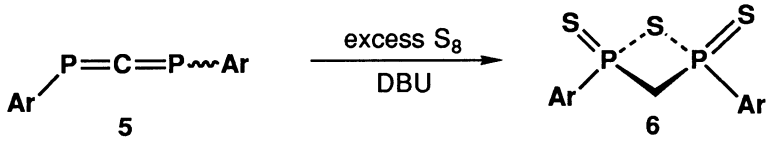
Phosphorus compounds in low coordination states are of current interest and multiple bonded P^{III}-compounds such as phosphaalkenes, phosphaalkynes, and diphosphenes have been extensively investigated. Kinetic stabilization by bulky substituents have turned out to be effective to the studies on such compounds and this strategy has also been used to prepare phosphorus compounds with cummulative double bonds, such as phosphaallenes ArP=C=X (X = CR_1R_2, NR, O, and PR), by using extremely bulky 2,4,6-$Bu^t_3C_6H_2$ (= Ar) as a protecting group.[1-3] We report here the sulfurization reaction of 1,3-diphosphaallene and the crystal structure of one of the products, as yet unknown 1,2,4-thiadiphosphetane.

We have reported that 3,3-diphenyl-1-(2,4,6-tri-t-butylphenyl)-1-phosphaallene (**1**) reacted with elemental sulfur in the presence of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) to give 3-diphenylmethylene-2-(2,4,6-tri-t-butylphenyl)thiaphosphirane 2-sulfide (**2**)[4] as in the case of phosphaalkenes.[5] In contrast, under similar conditions, formation of 2,4,6-tri-t-butylphenyldithioxophosphorane (**4**)[6] was observed during the reaction of 3-phenyl-1-(2,4,6-tri-t-butylphenyl)-3-aza-1-phosphaallene (**3**) with sulfur.[7]



Ar = 2,4,6-$Bu^t_3C_6H_2$; DBU = 1,8-diazabicyclo[5.4.0]undec-7-ene

The reaction of 1,3-bis(2,4,6-tri-t-butylphenyl)-1,3-dipohosphaallene (**5**) with elemental sulfur in benzene at room temperature did not proceed either in the absence of a base or in the presence of a weak base such as lutidine or triethylamine. However, sulfurization of the compound **5** occurred by adding a small amount of DBU into a benzene solution of **5** and elemental sulfur.[8] Chromatographic separation of the resulting mixture afforded *cis*-2,4-bis(2,4,6-tri-t-butylphenyl)-1,2,4-thiadiphosphetane 2,4-disulfide (**6**).



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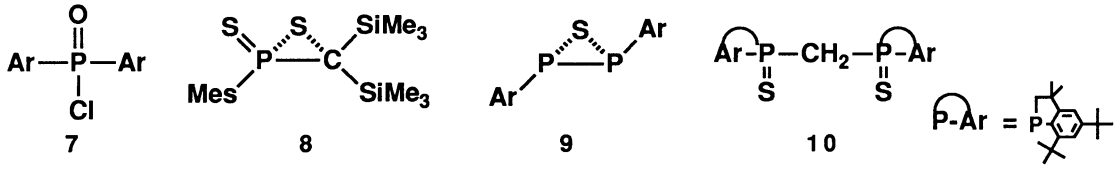
6: yield 28%; mp 234 - 236 °C; ^{1}H NMR ($CDCl_3$) δ 7.10 (4H, m, arom.), 4.52 (1H, dt, $^2J_{HH}$ = 13.6 Hz, $^2J_{PH}$ = 11.4 Hz, CH), 4.19 (1H, pseudo q, $^2J_{HH}$ = 13.6 Hz, $^2J_{PH}$ = 12.6 Hz, CH), 1.46 (36H, s, o-Bu^t), and 1.21 (18H, s, p-Bu^t); ^{31}P NMR ($CDCl_3$) δ 47.4 (s); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 151.9 (d, $^2J_{PC}$ = 4.6 Hz, o-arom.), 151.8 (s, p-arom.), 135.0 (dd, $^1J_{PC}$ = 79.2 Hz, $^3J_{PC}$ = 6.0 Hz, ipso-arom.), 124.0 (bs, m-arom.), 71.8 (t, $^1J_{PC}$ = 47.2 Hz, PCP), 40.8 (pseudo t, J = 6.4 Hz, o-$\underline{C}Me_3$), 34.5 (s, p-$\underline{C}Me_3$), 34.5 (s, o-$C\underline{Me}_3$), and 30.9 (s, p-$C\underline{Me}_3$); IR (KBr) 782 and 762 cm^{-1}; FDMS m/z 662.

Compound **6** posesses hitherto unknown thiadiphosphetane skeleton, and its ring structure was confirmed by X-ray crystallography.[9] Figure 1 is an ORTEP drawing[10] of **6** where the disordered o-t-butyl group on C21 is shown by open (occupancy of 0.45) and full bonds. Selected bond lengths and angles, dihedral angles, and intramolecular short contacts are listed in Table 1. The four-membered ring (P1, S1, P2, and C1) has a puckered form rather than planar as is seen from the dihedral angles listed in Table 1. The puckering angle between the plane (P1, S1, and C1) and the plane (P2, S1, and C1) is 19.2°. Two aryl groups are on the same side of the four-membered ring, and this central ring is surrounded by four o-t-butyl groups (Fig. 1). Two phenyl groups are nearly parallel (8.0°) and perpendicular (av. 87°) to the basic four-membered ring, and the distance between the centroids of the two aromatic rings is 5.2 Å. There is no short contact less than 4.0 Å between the two aryl groups, but the bulky o-t-butyl groups have unusually short contacts with the central part of the molecule as shown in Table 1. These short contacts induce the deformation of the bulky phenyl groups to the boat form, which is commonly observed for the Ar-P containing compound.[11] The deformations of the Ar groups in **6**, 15.5 and 15.0°, defined by the angles between the planes (C2, C3, C7) and (C3, C4, C6, C7) and the planes (C20, C21, C25) and (C21, C22, C24, C25), respectively, are comparable to an average value (18.5°) for bis(2,4,6-tri-t-butylphenyl)phosphinic chloride (**7**),[12] where a large deformation is found for non-bridged benzene derivatives. P1, P2, S2, S3, C2, and C20 atoms are approximately coplanar within 0.10 Å. This plane makes angles of 88°, 83°, and 78°, respectively, with the four-membered ring and the phenyl groups (C2 - C7) and (C20 - C25). The P=S bond lengths (1.923(3) and 1.926(3) Å) are slightly shorter than that for 2-mesityl-3,3-bis(trimethylsilyl)thiaphosphirane 2-sulfide (**8**) (1.932(3) Å).[13] The P-S bond lengths within the ring (2.120(3) and 2.127(3) Å) are slightly longer than 2.049(3) Å for **8** and 2.103(3) Å for *E*-2,3-bis(2,4,6-tri-t-butylphenyl)-1,2,3-thiadiphosphirane (**9**).[14] The endocyclic P-C bonds (1.872(8) and 1.867(7) Å) are compatible with the average distance of 1.889 Å for 1,3-diphosphetane derivatives.[15]

Recently, Karsch et al. reported the sulfurization reaction of diphosphaallene **5** in toluene at 60 °C for 24 h, which afforded **10**.[16] Under our sulfurization reaction conditions, the activation of sulfur by DBU may take an



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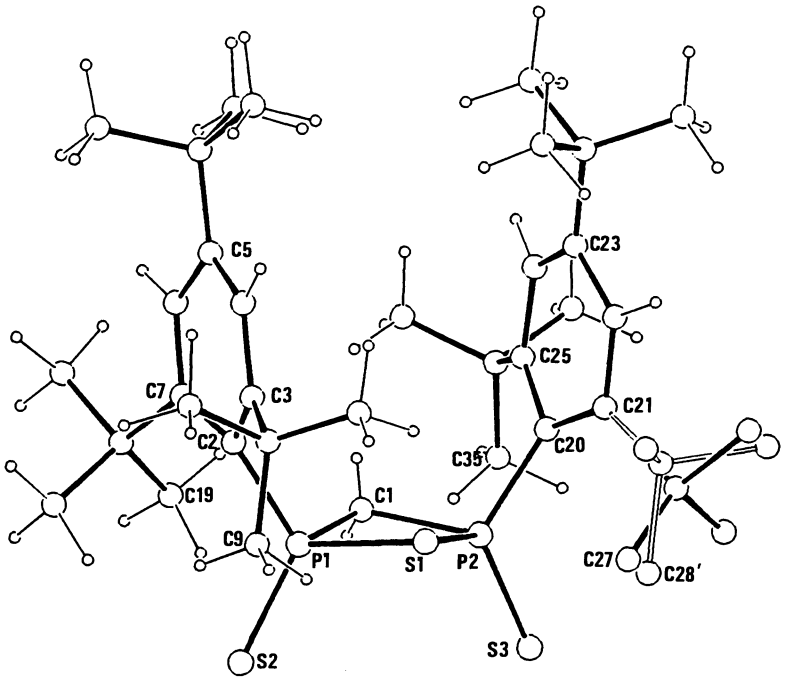

Fig. 1. X-Ray structure of **6** showing the atom labelling scheme.

Table 1. Selected Bond Distances and Angles, Dihedral Angles and Intramolecular Short Contacts

Bond distance / Å		Bond angle / °		Dihedral angle / °		Intramol. short contact / Å	
P1-S1	2.120(3)	S1-P1-C1	88.1(2)	C1-P1-S1-P2	-12.8(2)	P1--C9	3.18(1)
P2-S1	2.127(3)	S1-P2-C1	88.0(3)	S1-P2-C1-P1	-14.6(3)	P1--C19	3.38(1)
P1-C1	1.872(8)	P1-S1-P2	83.0(1)	P2-P1-C2-C3	-76.0(6)	P2--C27	3.32(2)
P2-C1	1.867(7)	P1-C1-P2	97.6(4)	P2-P1-C2-C7	88.1(6)	P2--C35	3.16(1)
P1-S2	1.923(3)	S2-P1-C2	121.1(2)	P1-S1-P2-C1	12.9(2)	P2--C28'	3.15(2)
P2-S3	1.926(3)	S3-P2-C20	122.4(3)	P2-C1-P1-S1	14.7(3)	S1--C9	3.24(1)
P1-C2	1.842(7)			P1-P2-C20-C21	92.3(6)	S1--C27	3.00(2)
P2-C20	1.839(7)			P1-P2-C20-C25	-70.6(7)		

important role and the mechanism resulting in the formation of the diphosphetane **6** is under investigation.

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8) To a solution of the diphosphaallene **5** (116 mg, 0.21 mmol) and elemental sulfur (29.3 mg, 0.92 mg-atom) in benzene (7 ml) was added one drop of DBU via syringe. The color changed to red gradually and the solution was stirred for 12 h. Removal of the solvent followed by chromatographic separation afforded 38.0 mg of **6** and 15.2 mg of 2,4-bis(2,4,6-tri-t-butylphenyl)-1,2,4-oxadiphosphetane 2,4-disulfide (**11**). **11**: yield 11%; mp 268 - 270 °C; ^{1}H NMR ($CDCl_3$) δ 7.12 (4H, dd, $^{4}J_{PH}$ = 3.1 Hz, $^{6}J_{PH}$ = 2.4 Hz, arom.), 4.21 (1H, dt, $^{2}J_{PH}$ = 12.9 Hz, $^{2}J_{HH}$ = 0.5 Hz, CH), 4.16 (1H, dt, $^{2}J_{PH}$ = 10.5 Hz, $^{2}J_{HH}$ = 0.7 Hz, CH), 1.46 (36H, d, $^{5}J_{PH}$ = 5.9 Hz, o-Bu^{t}), and 1.24 (18H, s, p-Bu^{t}); ^{31}P NMR ($CDCl_3$) δ 89.1 (s); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 70.3 (t, $^{1}J_{PC}$ = 48.5 Hz, PCP); IR (KBr) 820, 734 cm^{-1}; FDMS m/z 646.

9) *Crystal data*: $C_{37}H_{60}P_2S_3$, M = 663.03, monoclinic, space group $P2_1/n$, a =21.113(5), b = 11.741(5), c = 16.835(4)Å, β = 105.88(2)°, U = 4014(2) Å^3, Z = 4, Dc = 1.097 g cm^{-3}. 5272 Reflections with 2θ ≤ 45° were recorded on a four circle diffractometer using graphite-monochromated Mo-Kα radiation. Of these 2977[with $I > 3\sigma(I)$] were judged observed. The structure was solved using MULTAN80. H-atoms and disordered C-atoms of o-t-butyl group on C21 (occupancy factors: 0.55 and 0.45) were refined isotropically. Full-matrix least-squares refinement with anisotropic temperature factors for nonhydrogen atoms converged to R = 0.060. Atomic co-ordinates and thermal parameters, and bond lengths and angles are available from authors on request.

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