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SYNTHESIS AND STRUCTURES OF E- AND Z-PHOSPHAETHYLENES

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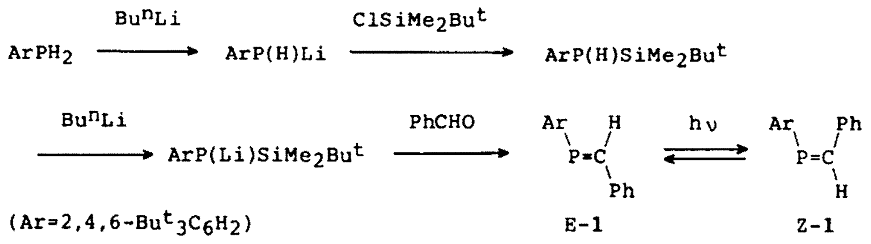
Abstract---The X-ray analyses of sterically protected E- and Z-2-phenyl-1-(2,4,6-tri-t-butylphenyl)phosphaethylenes (E-**1** and Z-**1**) were carried out and the structures in the crystal are discussed.

We have been interested in unusual compounds containing phosphorus atoms in lower co-ordination states. By introducing an extremely bulky group into a molecule, we were successful in preparation and characterization of such compounds as diphosphenes,1,2) 1,3-diphospha-allenes,3) and phosphaethylenes.4) In this paper, we wish to report the preparation and structures of some phosphaethylenes.

RESULTS AND DISCUSSION

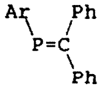
The sterically protected phosphaethylenes, E- and Z-2-phenyl-1-(2,4,6-tri-t-butylphenyl)phosphaethylenes (E-**1** and Z-**1**), were prepared by the method described before using lithium t-butyldimethylsilyl(2,4,6-tri-t-butylphenyl)phosphide as a starting material.4) 2,2-Diphenyl-1-(2,4,6-tri-t-butylphenyl)phosphaethylene (**2**)5) was not available under similar conditions by using benzophenone instead of benzaldehyde probably because nucleophilic attack at carbonyl was retarded due to the steric hindrance of the bulky phosphide. However, when chlorotrimethylsilane was adopted instead of using chloro-t-butyldimethylsilane, we were successful in obtaining **2** although the yield was low.

We were interested in the structures of E- and Z-phosphaethylenes (E- and Z-**1**) and carried out the X-ray analyses.



E-**1** Z-**1**

We have reported the X-ray structure of Z-**1** disclosing some striking features around the P=C bond.6) (1) P-C1 bond length is shorter than a typical bond length for the P-C single bond (1.85 - 1.90 Å). (2) The P=C system is almost coplanar. (3) The bulky aryl moiety is almost perpendicular to the above P=C system, while the phenyl group is almost parallel to this system.



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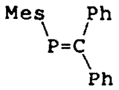

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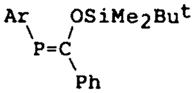

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$(Mes=2,4,6\text{-}Me_3C_6H_2)$

Table 1. Some Important Bond Lengths and Angles for **1** and **3**

Compound	E-1	Z-1$^{a)}$	3$^{b)}$
bond length /Å			
P-C^1	1.660(6)	1.674(2)	1.692(3)
P-C^8	1.854(5)	1.851(2)	1.828(3)
C^1-C^2	1.464(8)	1.465(3)	1.487, 1.490
bond (dihedral) angle /°			
P-C^1-C^2	125.4(4)	139.1(2)	127.2, 116.2
C^8-P-C^1	100.5(3)	105.8(1)	107.5
C^8-P-C^1-C^2	178.7(4)	1.0(3)	1.2, -179.4
tilt angle$^{c)}$ /°			
∠Ph	14.2(6)	7.2(3)	42.9, 36.6
∠Ar	85.2(2)	88.3(1)	71.0
∠PhAr	71.9(5)	83.7(1)	55.4, 71.9

a) Data taken from Ref. 6. b) Data taken from Ref. 8. c) Definitions ∠Ph, ∠Ar, and ∠PhAr are given in the text.

Table 2. Distortion Angles and Distance of Aromatic Ring in **1**

Parameter$^{a)}$	E-1	Z-1
a_1 /°	7.6(8)	10.6(3)
a_2 /°	2.7(7)	5.4(2)
a_3 /°	3.0(7)	5.8(2)
d_P /Å	0.42(1)	0.640(4)

a) Definition of parameters is shown in Fig. 3.

The P=C system in all the phosphaethylenes listed in Table 1 is essentially coplanar (see dihedral angle ∠C^8-P-C^1-C^2), as in Z-2-t-butyldimethylsilyloxy-2-phenyl-1-(2,4,6-tri-t-butylphenyl)phosphaethylene (**4**).$^{7)}$ The figures in Table 1 indicate that Z-1 is more sterically crowded than E-1, i.e. P-C^1, ∠P-C^1-C^2, and ∠C^8-P-C^1. The sp^2 carbon in the P=C system of Z-1 is very much deformed (see angle ∠P-C^1-C^2). The steric congestion also appeared to be released by inclining bulky aryl groups by 70 - 90° for **1** and **3**. In **1**, the tilting angles are almost 90°, whereas in **3**, the angle is not so large, but the two phenyls at 2-position rotate to a propeller shape to release its steric repulsion and to lengthen the bond length of P-C^1.

In contrast to the structure of trans-stilbene,$^{9)}$ it is interesting to note that the phenyl ring at 2-position in Z-1 is almost coplanar to the P=C system whereas the trans phenyl at 2-position in E-1 slightly tilts from the coplanarity although the deviation is not large compared to that observed for **4** (54.8°).$^{7)}$

Figures 1 and 2 show the stereoscopic views of the molecular structures of E-1 and Z-1 in the crystal, respectively. E-1 and Z-1 have similar structures except for the phenyl groups at C^1's. The P-C^1 bond length for E-1 is shorter than that for Z-1. Both of the P-C^1 bond lengths are close to the value calculated for $HP{=}CH_2$ by ab initio method at the 6-31G* level (1.652 Å)[7] and rather shorter than that observed for 1-mesityl-2,2-diphenylphosphaethylene (**3**: 1.692(3) Å) by Bickelhaupt et al.[8]

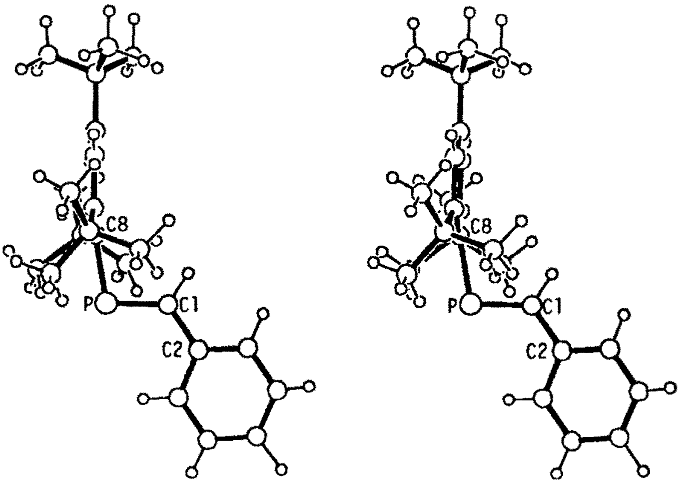

Figure 1. Stereoscopic view of E-1 in the crystal determined by X-ray analysis.

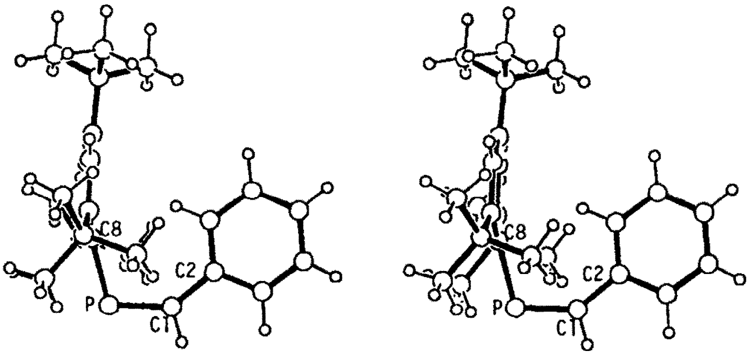

Figure 2. Stereoscopic view of Z-1 in the crystal determined by X-ray analysis.

Table 1 shows some important bond lengths and angles and dihedral angles observed for the both phosphaethylenes, E-1 and Z-1, together with the reported data for 3.[8] Here in Table 1, C^1 means the carbon atom of the P=C system, whereas C^2 and C^8 indicate the ipso carbons of the phenyl(s) at 2-position and that of the bulky aryl at 1-position (phosphorus), respectively. Therefore, in **3**, there are two kinds of C^2's (i.e., cis and trans). Table 1 also shows the tilt angles of the aromatic rings in **1** and **3**. The angles /Ph and /Ar mean tilting angles of phenyl(s) at 2-position and Ar (here in **2**, Ar means mesityl) at 1-position from the P=C plane, respectively, whereas /PhAr does the interplanar angle made by Ph and Ar.

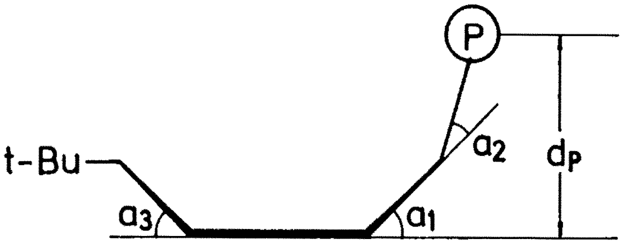

Figure 3. Side profile of the Ar moiety on the phosphorus atom. Hydrogen atoms and ortho-t-butyl groups are omitted for clarity: a_1-a_3 and d_P are parameters which indicate deformation from flat benzene to boat form.

We have been interested in deformation to boat form of the Ar attached to the phosphorus atom.[10] The magnitude of deformation from a flat aromatic plane is indicated by the definition of angles a_1-a_3 and distance d_P as shown in Figure 3. The parameters are listed in Table 2 and every number indicates that Z-**1** is more distorted than E-**1**, as expected. The 2,4,6-tri-t-butylphenyl moieties in the compounds **1** are deformed to boat form in a similar manner as bulky phosphorus compounds we previously prepared and reported. These are rare examples of boat form benzene rings without any bridge in the molecule.[11]

CONCLUSION

The X-ray analyses of sterically protected phosphaethylenes (E- and Z-**1**) were carried out and the structures in crystal were discussed. The P=C system is almost coplanar and steric congestion is released mostly by changing of the bond angles and by tilting of aromatic rings.

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EXPERIMENTAL

Meterial. Starting from lithium t-butyldimethylsilyl-2,4,6-tri-t-butylphenylphosphide and benzaldehyde, E-2-phenyl-1-(2,4,6-tri-t-butylphenyl)phosphaethylene (E-**1**) was obtained as described previously.[4] The Z isomer (Z-**1**) was obtained by photoreaction of E-**1**.[4] Each isomer thus obtained was not isomerized in refluxing toluene for 8 h. 2,2-Diphenyl-1-(2,4,6-tri-t-butylphenyl)phosphaethylene (**2**) was obtained as follows. 2,4,6-Tri-t-butylphenylphosphine (101.2 mg, 0.363 mmol) was lithiated[12] in 8 ml of ether at 0 °C for 2 h with 1.1 equiv. of butyllithium (in hexane) with stirring for 2 h and 0.632 mmol of trimethylsilyl chloride was added at 0 °C for 1 h and was again lithiated with 3.3 equiv. of t-butyllithium (in pentane) at -78 °C for 30 min. Into the resulting solution was added benzophenone (83.2 mg, 0.457 mmol) in ether (5 ml) and was stirred for 2 h. The solvent was evaporated and the residue was chromatographed over silica gel (hexane) to give 32.2 mg (0.0728 mmol) of **2** (yield 20%) as an oil. **2**: ^{1}H NMR ($CDCl_3$) δ 7.6-7.2 (m, 5H, trans-Ph), 7.39 (d, 2H, $^4J_{PH}$= 3.4 Hz, arom.-Ar), 7.1-6.7 (m, 3H, m+p-cis-Ph), 6.6-6.3 (m, 2H, o-cis-Ph), 1.47 (s, 18H, o-Bu^t), 1.34 (s, 9H, p-Bu^t); ^{31}P NMR ($CDCl_3$) δ 242.4 ppm from external 85% H_3PO_4; ^{13}C NMR ($CDCl_3$) δ 180.2 (d, $^1J_{PC}$= 45.4 Hz), 145.9 (d, $^2J_{PC}$= 28.6 Hz, C^2) and 142.6 (d, $^2J_{PC}$= 16.9

Hz, $C^{2'}$), 135.8 (d, $^{1}J_{PC}$= 63.0 Hz, C^{8}); UV (hexane) λ_{max} (ε) / nm: 213 (3.66 x 10^{4}), 253sh (2.19 x 10^{4}), 326 (1.47 x 10^{4}); HRMS m/z observed: 442.2777, calcd for $C_{31}H_{39}P$ 442.2788.

X-Ray crystallographic and refinement data for E-1 (recrystallized from pentane). $C_{25}H_{35}P$, M= 366.53, monoclinic, space group C_2/c, a= 41.62(1), b= 5.951(2), c= 18.661(5) Å, β= 98.57(2)°, ρ_c= 1.065 g·cm^{-3}, Mo Kα radiation. 4048 Reflection with 2θ ≤ 50.0° were recorded. The structure was solved by MULTAN.[13] Full-matrix least-squares refinement of positional and anisotropic thermal parameters for non-hydrogen atoms and of positional parameters only for hydrogen atoms, to which isotropic temperature factors 1.0 Å^2 greater than those of atoms bonded to them were assigned, led to convergence at R= 0.063 using 1838 observed reflections (I ≥ 3σ(I)).[14] Fractional coordinates and temperature factors with standard deviations and bond distances and angles for E-1 are to be deposited at the Cambridge Crystallographic Data Centre.[15]

X-Ray crystallographic and refinement data for Z-1. These data are available at CCDC by quoting the Reference 6.

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