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Preparation of Sterically Protected 3,4-Bis(phosphinidene)cyclobutenes and Their Isomerism[1)]

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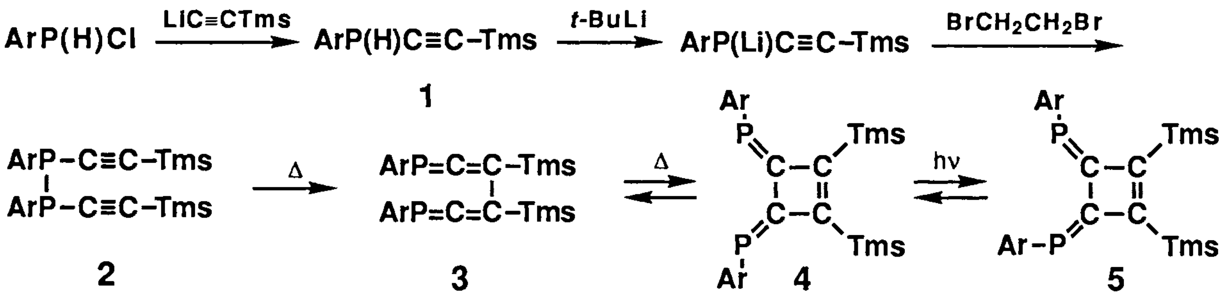
Sterically protected bis(phosphinidene)cyclobutenes were prepared starting from the diphosphane and their isomerism involving a 1,6-diphosphahexa-1,2,4,5-tetraene intermediate, which is both cumulative and conjugated, was studied. X-Ray crystallographic study of the (*E,Z*)-phosphinidenecyclobutene shows that the molecule suffers from large steric congestion between intra- and inter-substituents.

Sterically protected and multiple-bonded organophosphorus compounds are currently of interest. Utilizing the 2,4,6-tri-*t*-butylphenyl group (abbreviated to Ar) as a protecting group, we have been successful in isolation and characterization of diphosphenes[2)] and phosphaethylenes[3)] containing low-coordinated phosphorus atom(s) (coordination number 2) as stable molecules. Organophosphorus compounds involving conjugated systems[4)] such as phosphabutadienes[5)] have been isolated as well as cumulative double bonding systems such as phosphaallene[6)] and diphosphaallenes.[7)] As a more extended conjugated system, bis(phosphinidene)-cyclobutenes[8)] have been studied by Appel *et al.* Very recently, Märkl *et al.* have reported the synthesis of 1,6-dipospha-1,2,4,5-hexatetraene.[9)] We now report here our own results[10)] on the phosphorus containing Cope rearrangement which takes place under mild conditions involving 1,6-diphospha-1,2,4,5-hexatetraene as an intermediate of both conjugated and cumulative system.

Chloro(2,4,6-tri-*t*-butylphenyl)phosphine[11-13)] was allowed to react with (trimethylsilylethynyl)lithium to give 2,4,6-tri-*t*-butylphenyl(trimethylsilylethynyl)phosphine (**1**)[14)] in 53% yield. ^{31}P NMR (36.3 MHz, pentane, 25 °C, ext. 85% H_3PO_4): $\delta_P = -100.9$, d, $^1J_{PH} = 249.2$ Hz.



Ar = 2,4,6-$Bu^t_3C_6H_2$; Tms = Me_3Si.

When the phosphine **1** was lithiated with two equiv. of *t*-butyllithium in THF at –78 °C, followed by addition of 0.5 equiv. of 1,2-dibromoethane at that temperature, 1,2-bis(2,4,6-tri-*t*-butylphenyl)-1,2-

bis(trimethylsilyl-ethynyl)diphosphane (**2**) was obtained in 48% yield. δ_P ($CDCl_3$, 25 °C) = −38.5. UV/VIS (hexane): λ_{max} = 250 nm (ε 27300). ^{13}C NMR (50 MHz, THF-d_8, −40 °C, TMS): δ_C = 105.91 (t, $^1J_{CP}$ = 25.7 Hz; $P\underline{C}{\equiv}C$), 121.66 (s; $PC{\equiv}\underline{C}$). The diphosphane **2** was unstable toward heat and gradually isomerized even at room temperature to a phosphaallenyl compound, 3,4-bis(trimethylsilyl)-1,6-bis(2,4,6-tri-*t*-butylphenyl)-1,6-diphospha-1,2,4,5-hexatetraene (**3**). δ_P ($CDCl_3$, 25 °C) = 42.9. δ_C (THF-d_8, −40 °C) = 115.49 (dd, J_{CP} = 13.2 Hz and 13.3 Hz; $P{=}C{=}\underline{C}$), 233.63 (d, $^1J_{CP}$ = 36.9 Hz; $P{=}\underline{C}{=}C$). λ_{max} = 263 nm (ε 31000). The configuration of **3**, however, has not been determined so far. This phosphaallenyl compound **3** was further converted but very slowly at room temperature to the (*E,E*)-3,4-bis(phosphinidene)cyclobutene **4**. Mp 160 - 162 °C. ^1H NMR (200 MHz, $CDCl_3$, 25 °C, TMS) δ = −0.33 ($Si\underline{Me_3}$). δ_P ($CDCl_3$, 25 °C) = 162.5. δ_C ($CDCl_3$, 25 °C) = 176.16 (t, $^2J_{CP}$ = 4.6 Hz; $\underline{C}Tms$), 183.92 (dd, J_{CP} = 18.3 and 14.1 Hz; $P{=}\underline{C}$). λ_{max} = 314 nm (ε 25600). The yield of **4** based on **1** was 44% along with **3** (35% yield), after 30-min refluxing in toluene without the isolation process of **2**. The reaction of **3** to **4** in boiling toluene seemed to be reversible , because the pure **4** afforded **3** on heating. Furthermore, on irradiation of the cyclobutene **4** in hexane at 0 °C with a Xe lamp with a Toshiba UV-29 filter, a medium pressure mercury lamp with a Pyrex filter, or sunlight, **4** isomerized to the corresponding *E,Z*-derivative **5** as yellow crystals. Mp 218 - 220 °C. δ = −0.42 and 0.38 ($Si\underline{Me_3}$). δ_P = 197.4 and 176.6, ABq, $^3J_{PP}$ = 14.6 Hz. λ_{max} = 299 nm (ε 35300). The photo-isomerization of (*E,E*)-**4** to (*E,Z*)-**5** was completed in 1.5 h leading to the photo-equilibrium state (**4** : **5** = 1 : 5). Taking the Dreiding model into account, it seems likely that Z,Z-isomer is too crowded to be formed even by photo-isomerization.

Optimized structure and total energy of each parent compound of $C_4H_4P_2$ were calculated by ab initio method using GAUSSIAN 88 Program[15)] at the HF/6-31G* level. The relative energies (MP2/6-31G*//HF/6-31G*) were calculated as follows: (Z,Z)-bisphosphinidenecyclobutene, 0.0; (*E,Z*)-bisphosphinidenecyclobutene, 0.4; (*E,E*)-bisphosphinidenecyclobutene, 1.0; 1,6-diphosphahexa-1,2,4,5-tetraene, 14.7; and 3,4-diphospha-1,5-diyne, 23.2 kcal/mol. It should be noted that the (Z,Z)-cyclobutene is the most stable among those isomers in contrast to the actual Ar series.

The structure of (*E,Z*)-**5** was unambiguously determined by X-ray crystallographic analysis. Figure 1 is an ORTEP drawing[16)] of the molecular structure for **5**.[17)] The cyclobutene ring is planar within 0.00(1) Å. P1, P2, Si1, Si2, C5, C8, C23, and C26 lie approximately on this plane, although their deviations from this plane are −0.03(1), 0.05(1), −0.02(1), 0.07(1), 0.02(2), 0.10(3), 0.02(2), and −0.03(2) Å, respectively, and are significant. It can be seen from Fig. 1 that this molecule has a pseudo mirror plane which goes through the cyclobutene ring, except for the *p*-*t*-butyl groups on C8 and C26 atoms. Short contacts in **5** are divided into those in the substituents and those between the substituents. Most of the intra-substituent short contacts are found between *o*-*t*-butyl groups and P=C π-systems, indicating that each P=C π-system is covered by four methyl groups from above and below. Both bulky aryl groups are perpendicular to the P=C π-systems (the pseudo mirror plane of the molecule) to release these steric congestion as in (Z)-2-phenyl-1-(2,4,6-tri-*t*-butylphenyl)phosphaethylene.[18)] P1-C1 and P2-C2 bond lengths are in good agreement with 1.660(6) Å in (*E*)-2-phenyl-1-(2,4,6-tri-*t*-butylphenyl)phosphaethylene,[18)] but slightly shorter than 1.672(2) Å in the (*Z*)-derivative,[18)] 1.690(8) and 1.679(6) Å in (*E,E*)-3,4-diphenyl derivative,[8)] and 1.692(3) Å in 1-mesityl-2,2-diphenylphosphaethylene.[19)]

The present phosphorus-containing phospha-Cope rearrangements seem to be more facile than those of the all-carbon systems[20,21)] which normally require much more vigorous conditions or need catalyst such as Ni(0) or Ni(2) complexes to proceed.

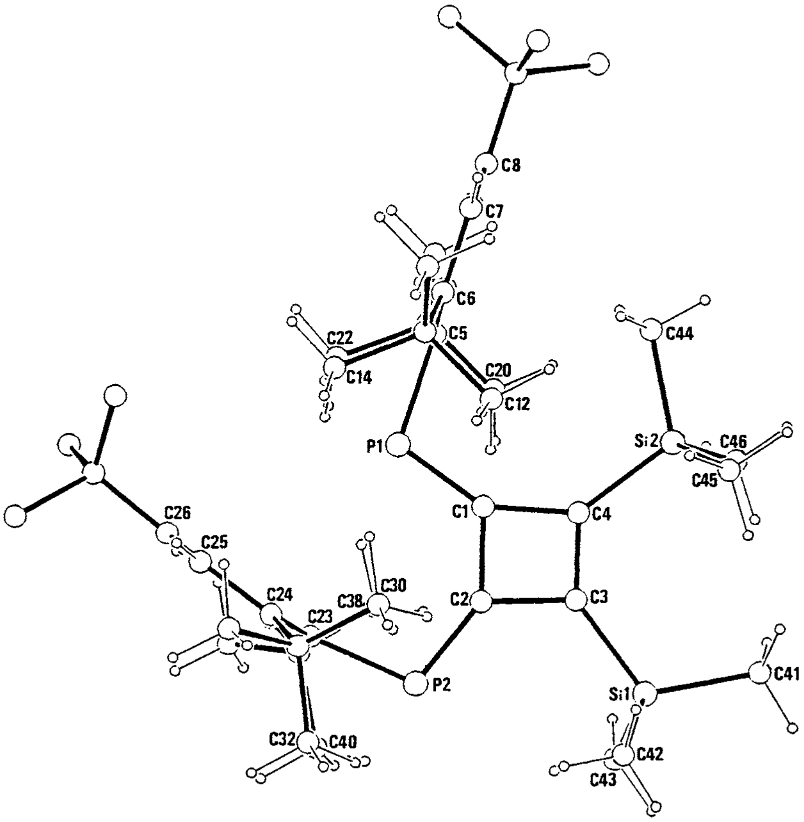


Fig. 1. View of **5** perpendicular to the cyclobutene ring. *o*-*t*-Butyl groups on C8 and C26 atoms are disordered and only those with the higher occupancy factors are shown for clarity. Selected bond distances (Å) and angles (°): P1-C1, 1.665(7); P1-C5, 1.861(6); P2-C2, 1.662(7); P2-C23, 1.840(7); Si1-C3, 1.866(7); Si2-C4, 1.863(7); C1-C2, 1.523(9); C1-C4, 1.508(9); C2-C3, 1.500(9); C3-C4, 1.397(9); P1-C1-C2, 125.1(5); P1-C1-C4, 147.4(5); P2-C2-C1, 143.2(5); P2-C2-C3, 129.0(5); Si1-C3-C2, 125.3(5); Si1-C3-C4, 142.1(5); Si2-C4-C1, 139.4(5); Si2-C4-C3, 128.4(5); C1-C2-C3, 87.7(5); C1-C4-C3, 92.2(5); C2-C1-C4, 87.5(5); C2-C3-C4, 92.6(5).

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1) Dedicated to Prof. Rolf Appel on the occasion of his 70th birthday.

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17) *Crystal data*: $C_{46}H_{76}P_2Si_2$, M = 747.23, monoclinic, space group $P2_1/n$, a = 16.332(5), b = 20.063(6), c = 15.222(4) Å, β = 99.57(2)°, U = 4918(2) Å^3, Z = 4, D_c = 1.009 g cm^{-3}, μ = 1.59 cm^{-1}. 5687 Reflections with $2\theta \leq 45$ ° were recorded on a four circle diffractometer using graphite-monochromated Mo-Kα radiation. Of these 3269 with $[I > 3\sigma(I)]$ were judged as observed. The structure was solved using MULTAN 80.[22] Both *o-t*-butyl groups are disordered. Each of these was resolved into two positions of *t*-butyl groups from difference Fourier maps. Their occupancy factors were refined to be 0.70 and 0.30 for C8 *t*-butyl group, and 0.51 and 0.49 for C26 *t*-butyl group, respectively. H-atoms and disordered C-atoms were refined isotropically. Full-matrix least-squares refinement with anisotropic temperature factors for nonhydrogen atoms converged to R= 0.067 and R_w = 0.080.[23] Further details of the crystal structure investigation are available from the Cambridge Crystallographic Data Centre.

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