Topochemical [2+2] Dimerization of Kinetically Stabilized 1-Phosphaallenes in the Solid State

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The thermolysis of two bulky 1-phosphaallenes in the solid state afforded diphosphanylidenecyclobutane or 2,4-dimethylene-1,3-diphosphacyclobutane. The regioselectivity of the [2+2] dimerization depends largely on the crystal structure of the 1-phosphaallenes, and the reaction path seems to be affected by the presence of bulky 2,4,6-tri-*tert*-butylphenyl (Mes*) group. This topochemical reaction was also controlled by the substituents at the 3-position of the 1-phosphaallene skeleton.

Introduction

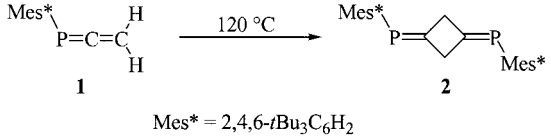
Chemical reactions in the solid state generally display high regio- and stereoselectivity due to the topochemically controlled conditions; each molecule is regularly disposed and has low locomotive energy.[1] The [2+2] cycloaddition of alkenes in the solid state has been a well established[2] reaction since the dimerization of (*E*)-cinnamic acid was reported by Liebermann and Bergami.[3] The crystalline arrangement of molecules is controlled by various non-covalent interactions; however, it is difficult to design a molecule that crystallizes at will.[2,4] Intermolecular interactions of organic molecules through van der Waals forces are generally weak, and most nonpolar molecules tend to give effective crystal packing to minimize the intermolecular repulsions.[1] Most reactions performed in the solid state proceed on irradiation, but some are known to occur on heating or rubbing.[1,2]

We studied the synthesis and isolation of low-coordinated phosphorus compounds[5] containing the 2,4,6-tri-*tert*-butylphenyl (= Mes*) group as a sterically bulky protecting group.[6] The inherent lability of the multiple bonds of phosphorus is suppressed by the presence of the bulky substituent to permit their isolation at ambient temperature (ca. 25°C) and even in air.[5] Recently, we reported the preparation of several 1-phosphaallenes containing the P=C=C skeletons[7] by using a lithium phosphanylidene carbenoid [Mes*P=C(Br)Li].[8] This synthetic protocol enabled us to obtain 1-phosphaallenes in excellent yields and without any tedious experimental procedures.

On the other hand, in the course of our research on kinetically stabilized 1-phosphaallene derivatives, we found that several 1-phosphaallenes afforded [2+2] dimers in a head-to-tail mode on heating in the solid state. The regioselectivity of the dimerization depended on the substituents at the 3-position, which was supported by X-ray crystallographic analysis. Phosphorus−carbon multiple bonds are nearly apolar, and contact between them is apparently difficult if they are sterically protected by bulky substituents. Nevertheless, the crystal packing of 1-phosphaallene bearing the bulky Mes* group was suitable for the regio- and stereoselective [2+2] dimerization of the P=C=C moiety.

Results and Discussion

1-(2,4,6-Tri-*tert*-butylphenyl)-1-phosphaallene (**1**) was synthesized as described in the literature[7a] and recrystallized from ethanol (Scheme 1). A single crystal of **1** was studied by X-ray crystallography, and Figure 1 displays the structure obtained. The bond lengths and angles in the −P=C=C moiety are nearly identical to those of 1-(2,4,6-tri-*tert*-butylphenyl)-3,3-diphenyl-1-phosphaallene.[9] Two molecules of **1** are paired in the crystalline state and the hydrogen atom bonded to the C2 atom is in close proximity to the aromatic ring of the other molecule. Indeed, the CH−π interaction is assumed to be a noncovalent interaction operating in the crystal structure.[10] As a consequence, the C2···C1 intermolecular distance was found to be 3.83(1) Å, as depicted in Figure 1, together with a C2···C2 distance of 3.66(2) Å. Such an intermolecular distance is close to the



Scheme 1

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sum of the van der Waals radii (3.70 Å) and lies in the range of length within which two molecules can interact with each other in the solid state.[1,2] Additionally, the minimal CH···aryl distance was observed to be 3.36 Å.

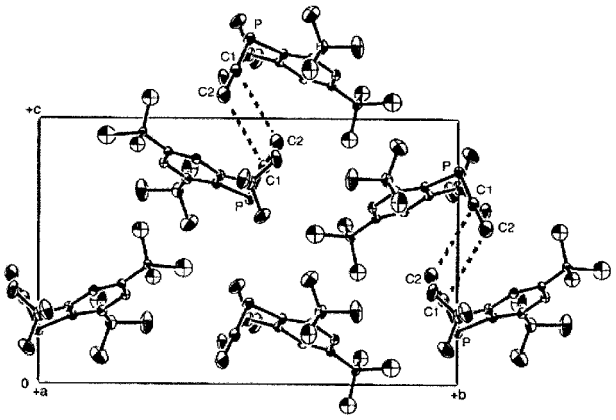


Figure 1. The structure of **1** including a packing diagram. Hydrogen atoms are omitted for clarity. The *tert*-butyl group in the *para*-position is disordered and the atoms with the predominant occupancy factor (0.56) are shown. Bond lengths (Å) and angles: P−C1 1.637(7), P−C_{Mes*} 1.894(5), C1−C2 1.34(1), C1−P−C_{Mes*} 101.5(3), P−C1−C2 174.3(6)

The single crystals of **1** were heated at 120 °C for 1 day during which time the color changed from colorless to yellow. The ^{31}P NMR spectrum of the reaction mixture (in solution) suggested that a new compound **2** was formed (Scheme 1). The ^{31}P chemical shift observed for **2** is within the region of phosphaethenes (−P=C<), indicating that the 1-phosphaallene cyclizes through the C=C bonds. A yellow crystal obtained after heating was analyzed by X-ray crystallography, and we observed some contraction in the crystal lattice of **2** compared with **1**. As displayed in Figure 2, **2** includes a planar 1,3-(diphosphanylidene)cyclobutane skeleton formed by a head-to-tail [2+2] dimerization of the C=C bonds. This regioselectivity can be explained by looking at the crystal structure of **1**, as shown in Figure 1: The crystal structures of both **1** and **2** are similar in shape. The phosphorus atom of **2** deviates from the aromatic Mes* plane as indicated by the two dihedral angles P−C_{ipso}−C_{ortho}−$C_{t\mathrm{Bu}}$ of 28(1)° and 29(1)°, not only due to the release of steric congestion but also due to the approach of the P=C=C groups to each other. In comparison, the P−C_{ipso}−C_{ortho}−$C_{t\mathrm{Bu}}$ dihedral angles of **1**, both 12(1)°, are smaller than those of **2**. It should be noted that this [2+2] dimerization of **1** upon heating did not occur in solution and thus can only occurs in the crystalline state. In order to obtain **2**, the temperature of the reaction must be kept just below the melting point. A probable cause of the incompleteness of the dimerization (see Exp. Sect.) is that the supply of heat is not sufficient for the dimerization to proceed to completion. Moreover, an amorphous solid of **1** did not undergo the topochemical [2+2] dimerization.

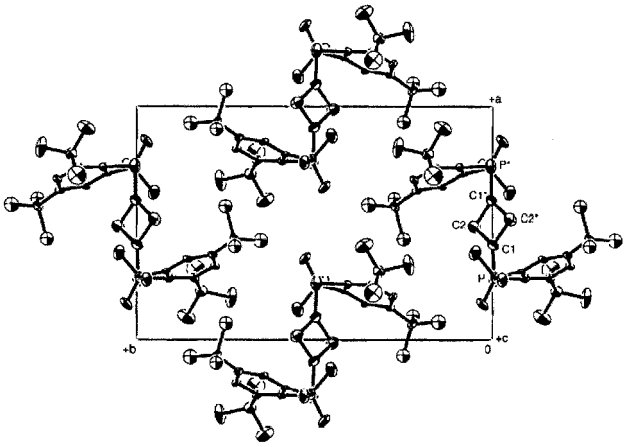
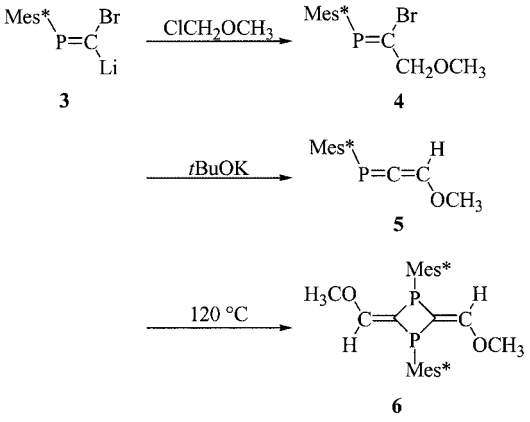


Figure 2. The structure of **2** including a packing diagram. Hydrogen atoms are omitted for clarity. The *tert*-butyl group in the *para*-position is disordered and the atoms with the predominant occupancy factor (0.58) are shown. Bond lengths (Å) and angles: P−C1 1.68(1), P−C_{Mes*} 1.80(1), C1−C2 1.48(2), C1−C2* 1.53(2), C1−P−C_{Mes*} 94.8(6), P−C1−C2 132(1), P−C1−C2* 135(1), C2−C1−C2* 91.5(10), C1−C2−C1* 88.5(10)

We then studied functionalized 1-phosphaallenes bearing heteroatoms to form the 3-methoxy-1-phosphaallene **5**. As displayed in Scheme 2, the 1-bromo-2-phosphaethenyllithium **3** was allowed to react with chloromethyl methyl ether to afford the corresponding 2-bromo-3-methoxy-1-phosphapropene **4**. Compound **4** was then treated with potassium *tert*-butoxide to afford the 3-methoxy-1-phosphaallene **5** in moderate yield. In the ^{31}P NMR spectrum, the signal for the phosphorus atom in **5** showed a lower-field δ_p shift than that in **1**. In the ^{13}C NMR spectrum of **5**, the signal corresponding to the sp carbon is observed at a higher field than that in **1**, whereas the signal for the terminal sp^2 carbon is present at a lower chemical shift. These NMR spectral properties were similar to those found for the 1-phenylallene derivatives.[11] Compound **5** was purified by column chromatography, because the attempted recrystallizations failed. On the other hand, heating **5** without solvent at 120 °C for 2 h in the solid phase afforded a dimerized product **6**. Figure 3 displays the X-ray structure of **6** revealing a planar 2,4-dimethylene-1,3-diphosphacyclobutane skeleton with a *trans* conformation. Compound **6** was obtained as a single geometrical isomer. In contrast to **1**, the P=C bond of **5** dimerized in a head-to-tail manner. It is of interest to note that no [2+2] dimerization of **5** occurred in solution.

[2+2] Dimerization of 1,3,3-triphenyl-1-phosphaallene proceeded in a head-to-tail fashion with respect to the P=C bonds affording a 2,4-dimethylene-1,3-diphosphacyclobutane derivative.[12] Theoretical investigations indicated that both the HOMO and the LUMO of 1-phosphaallene [HP=C=CH_2] are dominated by the P=C bond which have larger orbital coefficients.[13] The resonance structure [HP^+C^-=CH_2] was also suggested although its contribution was found to be negligible.[9,13] These results hence



Scheme 2

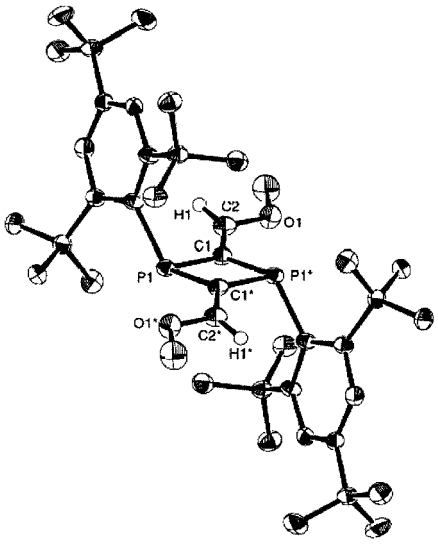


Figure 3. The molecular structure of **6**. Hydrogen atoms except H1 are omitted for clarity. Bond lengths (Å) and angles (°): P−C1 1.839(2), P−C1* 1.832(2), P−C_{Mes*} 1.883(2), C1−C2 1.338(3), C2−O 1.335(3), O−C_{Me} 1.435(3), C1−P−C1* 82.18(10), P−C1−P* 97.82(10), C1−P−C_{Mes*} 101.37(10), C1*−P−C_{Mes*} 123.9(1), P−C1−C2 129.1(2), P−C1*−C2* 129.4(2), C1−C2−O 121.7(2)

correspond to the reactivity of **5**. In contrast, **1** cyclized at positions corresponding to the terminal C=C bond. As indicated in Figure 1 and 2, the [2+2] dimerization of **1** is strongly affected by the arrangement of molecules in the crystalline state. In the case of **5**, the methoxy group may function to arrange the molecules under the topochemical conditions.[14]

The mechanism of these topochemical dimerizations of the 1-phosphaallenes has not yet been elucidated so far. It is known that allenes dimerize through biradical intermediates, mostly to give a head-to-head dimer on irradiation.[15] As for the low-coordinated phosphorus compounds, 1-phosphacumulenes have displayed head-to-head dimerization at the terminal C=C bonds or head-to-tail dimerization with respect to the P=C moieties at ambient temperature (ca. 25°C). These dimerizations of phosphacumulenes were performed in solution and biradical intermediates have been predicted,[16] suggesting that the dimerizations of **1** and **5** may include the generation of a radical species.

This work provides the first example of a topochemically controlled reaction of low-coordinated phosphorus compounds. Indeed, the Mes* group protects the unsaturated P=C bond and enables its handling under ordinary conditions, but it is also apparent that the Mes* group controls the arrangement of the molecules in the crystalline state to effect the regioselective [2+2] cycloaddition of the 1-phosphaallenes. We are continuing our investigation of topochemical reactions of **1**, **5**, and other low-coordinated phosphorus compounds on heating, irradiation, or rubbing.

Experimental Section

Thermolysis of 1-(2,4,6-Tri-*tert*-butylphenyl)-1-phosphaallene (1): Single crystals of **1** (50 mg, 1.7 mmol; crystallized from EtOH) were heated at 120 °C in a 5-mm capillary tube for 24 h. The residual yellow crystals were dissolved in [D]chloroform, and the peaks in the ^{31}P NMR spectrum corresponding to **1** and **2** were observed in a 1:3 ratio. A yellow crystal was picked out for X-ray crystallography. When single crystals of **1** were heated at 120 °C for 1 h, the signals in the ^{31}P NMR spectrum for **1** and **2** were observed in a 5:1 ratio. An amorphous solid of **1** did not undergo dimerization. Moreover, after melting, the reaction did not proceed. **2:** ^{31}P NMR (162 MHz, $CDCl_3$): δ = 214 (quin., $^3J_{P,H}$ = 15 Hz) ppm. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.38 (br. S, 4 H, *m*-Mes*), 2.81 (t, $^3J_{P,H}$ = 15 Hz, 4 H, CH_2), 1.47 (s, 36 H, *o*-*t*Bu), 1.34 (s, 18 H, *p*-*t*Bu) ppm. Elemental analysis of the crystals after heating. $C_{20}H_{31}P{\cdot}0.3H_2O$ (307.8): calcd. C 78.09, H 10.35; found C 78.01, H 10.16.

Preparation of the 2-Bromo-3-methoxy-1-phosphapropene 4: To a solution of 2,2-dibromo-1-(2,4,6-tri-*tert*-butylphenyl)-1-phosphaethene[17] (300 mg, 0.67 mmol) in THF (15 mL) was added butyllithium (0.67 mmol, 1.6 M solution in hexane) at −78 °C and stirred for 15 min. Chloromethyl methyl ether (0.67 mmol) was added to the solution at −78 °C and stirred for 1 h. The reaction mixture was warmed to room temperature (ca. 25°C) and the solvent was removed in vacuo. Extraction with hexane and purification of the resulting solution by silica gel column chromatography (hexane/EtOAc, 20:1) gave **4** (212 mg, 77 % yield). **4:** Pale yellow amorphous solid. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 261 ppm. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.45 (d, $^4J_{P,H}$ = 1 Hz, 2 H, *m*-Mes*), 4.43 (d, $^3J_{P,H}$ = 19 Hz, 2 H, CH_2), 3.47 (s, 3 H, OMe), 1.52 (s, 18 H, *o*-*t*Bu), 1.37 (s, 9 H, *p*-*t*Bu) ppm. $C_{21}H_{34}BrOP$ (413.4): calcd. C 61.01, H 8.29; found C 61.17, H 8.25.

Preparation of the 3-Methoxy-1-phosphaallene 5 and 6: To a solution of **4** (220 mg, 0.53 mmol) in THF (15 mL) was added a solution of potassium *tert*-butoxide (0.53 mmol) in 5 ml of THF at 0 °C during 30 min. The reaction was then warmed to room temperature (ca. 25°C). The solvent was removed in vacuo, followed by extraction with hexane. The hexane solution was purified by neutral Al_2O_3 column chromatography (hexane) to afford **5** (114 mg, 64 % yield). **5:** Pale yellow amorphous solid. ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = 142 ppm. ^{1}H NMR (400 MHz, $CDCl_3$): δ = 7.40 (br. s, 2 H, *m*-Mes*), 7.06 (d, $^3J_{P,H}$ = 19 Hz, 1 H, CH), 3.48 (s, 3 H, OMe), 1.61 (s, 18 H, *o*-*t*Bu), 1.33 (s, 9 H, *p*-*t*Bu) ppm. ^{13}C{^{1}H} NMR (101 MHz, $CDCl_3$): δ = 230.9 (d, $^1J_{P,C}$ = 22 Hz, P=C), 153.7 (d, $^2J_{P,C}$ = 3 Hz, *o*-Mes*), 150.1 (s,

p-Mes*), 139.4 (d, $^2J_{P,C}$ = 7 Hz, C=C), 136.7 (d, $^1J_{P,C}$ = 70 Hz, *ipso*-Mes*), 122.5 (s, *m*-Mes*), 57.9 (s, OMe), 38.7 (s, *o*-*C*Me$_3$), 35.4 (s, *p*-*C*Me$_3$), 34.1 (d, $^4J_{P,C}$ = 8 Hz, *o*-C*Me*$_3$), 31.8 (s, *p*-C*Me*$_3$) ppm. HRMS (FAB) calcd. for $C_{21}H_{33}O$ 332.2264; found *m*/*z* = 332.2263. Compound **5** (100 mg, 0.30 mmol) was heated at 120 °C for 2 h to afford a pale yellow solid, which was then cooled to room temperature. The residue was washed with hexane and 41 mg of **6** was obtained. **6:** Pale yellow crystals (hexane), m.p. 213−215 °C. $^{31}P\{^1H\}$ NMR (162 MHz, $CDCl_3$): δ = 25 ppm. ^1H NMR (400 MHz, $CDCl_3$): δ = 7.54 (4 H, brs, *m*-Mes*), 5.44 (dd, $^3J_{P,H}$ = 10, $^3J_{P,H}$ = 4 Hz, 2 H, CH), 3.31 (s, 6 H, OMe), 1.61 (s, 36 H, *o*-*t*Bu), 1.32 (s, 18 H, *p*-*t*Bu ppm. $C_{42}H_{66}P_2$ (632.9): calcd. C 75.87, H 10.01; found C 75.58, H 9.91.

X-ray Crystallography for 1, 2, and 6: A Rigaku RAXIS-IV imaging plate detector with graphite-monochromated Mo-K_α radiation (λ = 0.71070 Å) was used. The structure was solved by direct methods (SIR92),[18] expanded using Fourier techniques (DIRDIF94).[19] Structure solution, refinement, and graphical representation were carried out using the teXsan package.[20] The disordered *tert*-butyl groups were treated by use of restraints and constraints for the displacement parameters.

Crystal Data for 1: $C_{20}H_{31}P$, M = 302.44, monoclinic $P2_1/c$ (No. 14), a = 9.9210(7), b = 18.0799(8), c = 11.5631(5) Å, β = 94.776(5)°, V = 2066.9(2) Å^3, Z = 4, $\rho_{calcd.}$ = 0.972 g cm^{-3}, μ = 0.127 mm^{-1}, $F(000)$ = 664, T = 296 K, 14211 reflections measured ($2\theta_{max.}$ = 55.0°), 4477 observed (R_{int} = 0.078), $R1$ = 0.104 [$I > 3.0\sigma(I)$], R_W = 0.150 (all data).

Crystal Data for 2: $C_{40}H_{62}P_2$, M = 604.88, monoclinic $P2_1/a$ (No. 14), a = 11.253(1), b = 17.031(2), c = 9.618(2) Å, β = 97.779(3)°, V = 1826.4(5) Å^3, Z = 2, $\rho_{calcd.}$ = 1.100 g cm^{-3}, μ = 0.144 mm^{-1}, $F(000)$ = 664, T = 233 K, 11495 reflections measured ($2\theta_{max.}$ = 55.0°), 4140 observed (R_{int} = 0.078), $R1$ = 0.122 ($I > 3.0\sigma(I)$], R_W = 0.177 (all data).

Crystal Data for 6: 1/2 $C_{42}H_{66}P_2$, M = 332.46, triclinic $P\bar{1}$ (#2), a = 9.5661(5), b = 13.830(2), c = 9.1541(6) Å, α = 107.02(2), β = 116.620(5), γ = 93.20(2)° V = 1010.2(2) Å^3, Z = 2, $\rho_{calcd.}$ = 1.093 g cm^{-3}, μ = 0.139 mm^{-1}, $F(000)$ = 364, T = 120 K, 5514 reflections measured ($2\theta_{max}$ = 55.0°), 3707 observed (R_{int} = 0.040), $R1$ = 0.064 [$I > 1.0\sigma(I)$], R_W = 0.096 (all data).

Crystallographic data (excluding structure factors) for the structures reported in this paper (**1**, **2**, and **6**) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-214761 for **1**, -214762 for **2**, and -214763 for **6**.

Acknowledgments

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