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Preparation of 1,4-Diphosphabutatriene from 3-Dichloromethylene-1,2-diphosphirane

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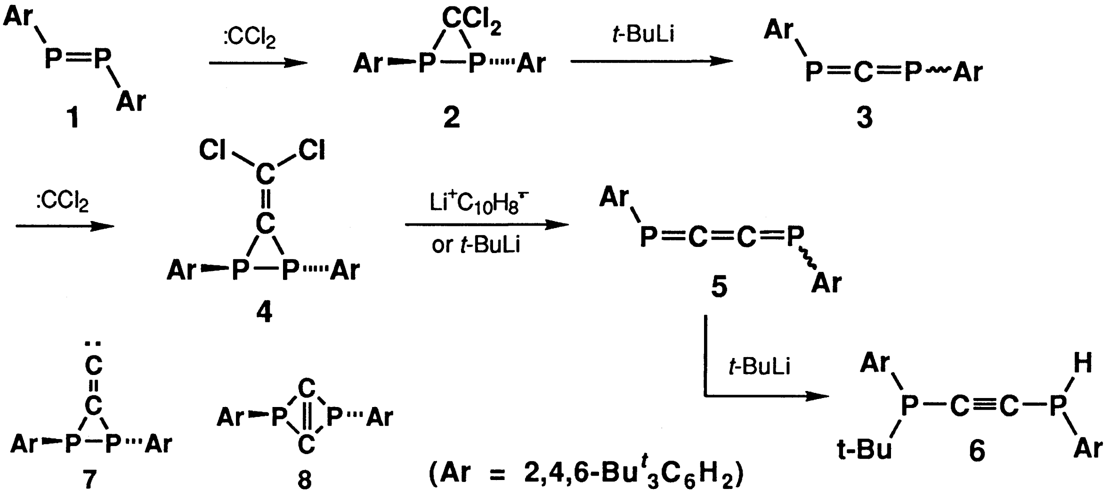
3-Dichloromethylene-1,2-bis(2,4,6-tri-*t*-butylphenyl)-1,2-diphosphirane reacted with lithium naphthalenide to give 1,4-bis(2,4,6-tri-*t*-butylphenyl)-1,4-diphosphabutatriene, whereas the reaction with *t*-butyllithium gave *t*-butyl-1,4-diphospha-2-butyne probably *via* the 1,4-diphosphabutatriene.

Since we[1] and others[2] first reported that dichlorocarbene reacted with diphosphene **1**[3] to give 3,3-dichloro-1,2-diphosphirane **2** and further converted to 1,3-diphosphaallene **3** by treatment with methyllithium or *t*-butyllithium, the following two new reactions have been discovered: dichlorocarbene reacts with 3,3-diphenyl-1-(2,4,6-tri-*t*-butylphenyl)-1-phosphaallene to give 2,2-dichloro-3-(diphenylmethylene)-1-(2,4,6-tri-*t*-butylphenyl)phosphirane which can be converted to 4,4-diphenyl-1-(2,4,6-tri-*t*-butylphenyl)-1-phosphabutatriene with butyllithium;[4] dichlorocarbene reacts with the 1,3-diphosphaallene **3** to give the 3-dichloromethylene-1,2-diphosphirane **4** whose structure was unambiguously determined by the X-ray crystallographic analysis.[4] We now report our preliminary results on the reaction of **4** with *t*-butyllithium[5] and lithium naphthalenide[6] to give 1,4-diphosphabutatriene **5**.[7]



In an attempt to utilize a vinylidene dichloride as a nucleophile in the Peterson reaction as exemplified in the preparation of phosphacumulenes,[8] the diphosphirane **4** (65 mg, 0.10 mmol) was dissolved in 3 ml of tetrahydrofuran (THF) at –78 °C and was added 0.22 mmol of *t*-butyllithium in pentane with stirring. The stirring was continued for 10 min and then the mixture was warmed up to room temperature. The solvent was removed *in vacuo* and the residue was chromatographed over silica gel to give 39.1 mg of 1-*t*-butyl-1,4-bis(2,4,6-tri-*t*-butylphenyl)-1,4-diphospha-2-butyne (**6**) as a pale yellow oil in 61% yield.[9] The compound **6** was a mixture of diastereoisomers according to the NMR studies.[10] **6**: ^{1}H NMR (600 MHz, $CDCl_3$) major:

δ = 0.66 (d, J = 14.4 Hz; $\underline{t\text{-Bu}}$P), 1.17 (s), 1.23 (s), 1.34 (s), 1.53 (s), 1.64 (s), 6.06 (br dd, J = 3.9 and 250.4 Hz; $\underline{\text{H}}$P), 7.22 (d, J = 3.2 Hz), 7.46 (s); minor: δ = 0.64 (d, J = 13.7 Hz; $\underline{t\text{-Bu}}$P), 1.24 (s), 1.31 (s), 1.33 (s),1.53 (s), 1.65 (s), 6.02 (br dd, J = 1.5 and 247.9 Hz; $\underline{\text{H}}$P), 7.15 (d, J = 1.5 Hz), 7.47 (s). ^{31}P NMR (81.0 MHz, $CDCl_3$) major: $\delta_P = -98.1$ ($^1J_{PH}$ = 250.6 Hz, $^3J_{PP}$ = 8.0 Hz; H$\underline{\text{P}}$), -23.5 ($^3J_{PP}$ = 8.0 Hz; t-Bu$\underline{\text{P}}$); minor: $\delta_P = -97.1$ ($^1J_{PH}$ = 248.2 Hz; H$\underline{\text{P}}$), -22.0 (t-Bu$\underline{\text{P}}$). IR (neat) 2401, 2241, 2087, 2069 cm^{-1}. MS (70 eV) m/z (rel intensity) 634 (M^+; 70), 577 ($M - C_4H_9$; 100). Found: m/z 634.4795. Calcd for $C_{42}H_{68}P_2$: M, 634.4796. The acetylenic compound **6** was probably formed *via* **5**, which was initially generated but reacted with t-butyllithium, as indicated by the results that the reaction of **5** with t-butyllithium gave **6**.$^{11)}$

On the other hand, when **4** (0.1 mmol) was allowed to react with 0.15 mmol of lithium naphthalenide in THF (5 ml) at −78 °C for 5 min with stirring, 24 mg of a 4:1 mixture of (E)- and (Z)-1,4-bis(2,4,6-tri-t-butylphenyl)-1,4-diphosphabutatrienes **5**$^{7)}$ was obtained in 40% yield after chromatographic purification along with 14 mg of the starting diphosphirane **4** (23% recovery). **5**: ^{31}P NMR δ_P = 180.0 (E) and 170.2 (Z). ^{1}H NMR δ = 1.34 (p-Bu^t), 1.57 (o-Bu^t), 7.43 (Ar) (E); and 1.29 (p-Bu^t), 1.48 (o-Bu^t), 7.30 (Ar) (Z).

Though the mechanism for the formation of butatriene **5** has not yet been confirmed, it is suitable to postulate the intermediary of a vinylidene carbene **7**$^{12)}$ through an electron transfer process to **4** from naphthalenide resulting in the rearrangement to **5** either directly or more likely indirectly *via* a highly strained intermediate,$^{13)}$ 2,4-diphosphabicyclo[1.1.0]-1(3)-butene **8**.

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9) The very similar results were obtained even after quenching of the reaction mixture with chlorotrimethylsilane at −78 °C before warming it up to room temperature.

10) Two sets of signals were observed both in ^{1}H NMR and in ^{31}P NMR spectra due to the two possible diastereoisomers in about 1.6 : 1 intensities.

11) The reaction of diphosphabutatriene **5** (0.75 mmol), prepared by the Märkl method,$^{7)}$ with 2.70 mmol of t-butyllithium in THF at −78 °C gave 1,4-diphospha-2-butyne **6** in 58% yield.

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