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Reaction of Dichlorocarbene with Phosphaethylenes.
Preparation of Phosphaallene from Phosphaethylene via Dichlorophosphirane

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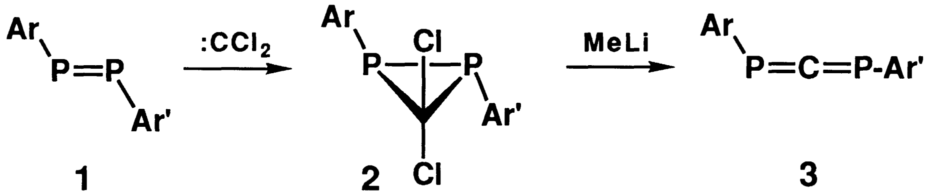
The reaction of dichlorocarbene with (*E*)- and (*Z*)-2-phenyl-(2,4,6-tri-*t*-butylphenyl)phosphaethylenes gave *trans*-dichlorophosphirane which was converted to phosphaallene with *t*-butyllithium, while 2,2-diphenylphosphaethylene gave a vinylphosphaindane derivative.

We have been interested in isolation and characterization of unusual phosphorus compounds in low coordination states. Using extremely bulky 2,4,6-tri-*t*-butylphenyl group as a protecting group, we have been successful in obtaining some double bonded organophosphorus compounds.[1,2]

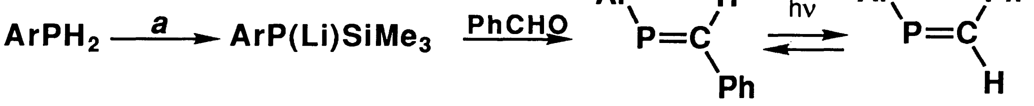
We[3,4] and others[5] have recently reported that sterically protected diphosphenes (**1**) reacted with dichlorocarbene to give dichlorodiphosphiranes (**2**) and that the reaction of the phosphiranes with methyllithium afforded 1,3-diphosphaallenes (**3**). This reaction in total is an insertion of carbon atom into the phosphorus-phosphorus double bond, leading to the corresponding diphosphaallenes.



1 **2** **3**

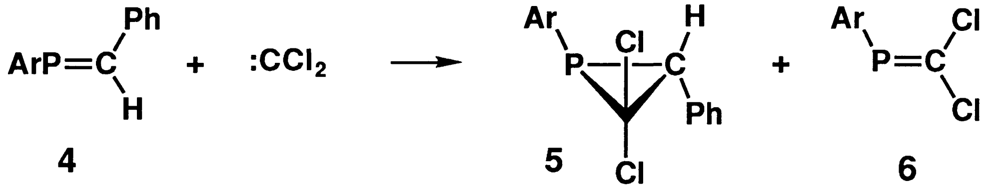
Ar = 2,4,6-$Bu^t_3C_6H_2$; Ar'= 2,4,6-$Pn^t_3C_6H_2$ or Ar

We now report the further application of this reaction to phosphaethylenes in order to obtain phosphiranes as an intermediate to the corresponding phosphaallene. The phosphaethylenes carrying 2,4,6-tri-*t*-butylphenyl group (abbreviated to Ar group), (*E*)-**4** and (*Z*)-**4**, were prepared from 2,4,6-tri-*t*-butylphenylphosphine by the method described previously,[6,7] except that chlorotrimethylsilane was used instead of *t*-butylchlorodimethylsilane, as shown below. Both of the isomers were separated by column chromatography.



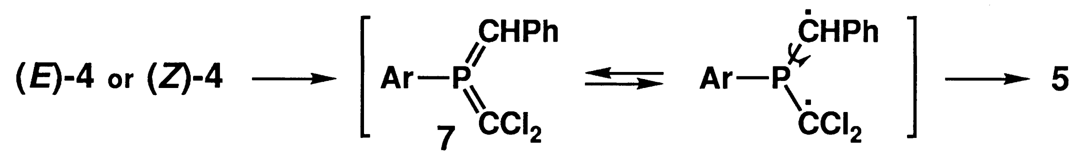
(*E*)-**4** (*Z*)-**4**

a: 1) *n*-BuLi, 2) Me_3SiCl, 3) *n*-BuLi



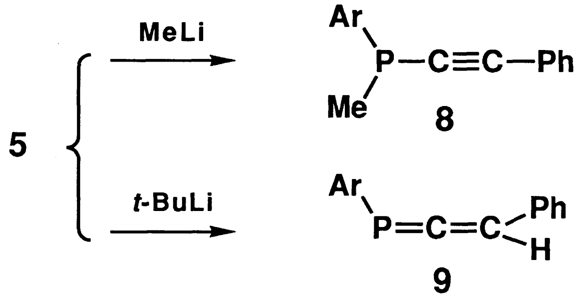
The phosphaethylene (*E*)-**4** (122 mg, 0.333 mmol) was dissolved in pentane at 0 °C and potassium *t*-butoxide (186 mg, 1.94 mmol) was suspended in the solution. Chloroform (197 mg, 1.65 mmol) was added to it while stirring and the stirring was continued for 10 min. The mixture was then warmed up to room temperature and the solvent was removed by rotary evaporation. The residue was chromatographed over silica gel using pentane as eluent to give 41.2 mg of **5** in 35% yield as a colorless oil together with 2,2-dichlorophosphaethylene **6**[8] in 22% yield [^{31}P NMR (hexane) δ_P 231.0; mp 155 - 158 °C] and (*E*)-**4** in 25% recovery. **5**: δ_P ($CDCl_3$) -111.6, ^{1}H NMR ($CDCl_3$) δ 7.36 (5H, s, Ph), 7.32, 7.28 (1H + 1H, ABq, J= 2.0 Hz, Ar), 3.30 (1H, s, C$\underline{H}$Ph), 1.70 (9H, s, o-Bu^t), 1.36 (9H, s, o-Bu^t), 1.29 (9H, s, p-Bu^t); $^{13}C\{^1H\}$ NMR ($CDCl_3$) δ 157.61 (d, J= 9.4 Hz, o-Ar), 156.08 (d, J=2.0 Hz, o'-Ar), 150.09 (s, p-Ar), 134.79 (d, J= 11.3 Hz, i-Ph), 130.56 (d, J= 59.4 Hz, i-Ar), 130.15 (d, J= 9.1 Hz, m-Ar), 128.30 (s, o-Ph), 127.42 (s, p-Ph), 123.67 (s, m-Ph), 121.78 (s, m'-Ar), 76.19 (d, J= 50.7 Hz, CCl_2), 50.50 (d, J= 29.8 Hz, $\underline{C}$HPh), 38.90 (s, o-$\underline{C}Me_3$), 38.53(s, o'-$\underline{C}Me_3$), 34.70 (s, p-$\underline{C}Me_3$), 34.22 (s, o-Me), 34.53 (d, J= 5.8 Hz, o'-Me), 31.22 (s, p-Me); UV (hexane) λ_{max} (ε) 265 (8910); Found: *m/z* 448.1838. Calcd for $C_{26}H_{35}Cl_2P$: M, 448.1853. The NOE experiments indicated that the configuration of **5** is trans because the methine proton at the position 3 at δ 3.30 was enhanced when a peak at δ 1.36 due to one of the methyls of o-*t*-butyl groups was irradiated.

On the other hand, if (Z)-**4** was allowed to react with dichlorocarbene under the same conditions, the phosphirane **5** was obtained in 47% yield together with **6** in 37% yield and the starting phosphaethylene (Z)-**4** in 7% recovery. The reaction of dichlorocarbene with phosphaethylenes might not proceed in one-step mechanism because both (*E*)- and (Z)-phosphaethylenes **4** gave the phosphirane **5** of trans configuration. The reaction might proceed via phosphorane **7** in two steps involving free rotation about the P-C(H)Ph bond as depicted in the following Scheme to give the same *trans*-phosphirane **5** of less steric hindrance. However, we have not yet observed any evidence for the existence of **7**.



Furthermore, the reaction from phosphaethylene to phosphirane could be carried out in aqueous media using the Makosza method[9] to give rather better results. (*Z*)-Phosphaethylene (Z-**4**) (110 mg, 0.30 mmol) was dissolved in 3 ml of a 50% NaOH aqueous solution and 537 mg (4.50 mmol) of chloroform was added at room temperature with stirring in the presence of benzyltriethylammonium chloride (68 mg, 0.3 mmol). The mixture was refluxed for 2 h, and the usual workup gave 72.5 mg of **5** in 54% yield together with 50.5 mg of the starting Z-phosphaethylene (Z)-**4** in 37% recovery. Very similarly, (*E*)-phosphaethylene (*E*)-**4** gave the same phosphirane **5** in 58% yield and the starting (*E*)-**4** in 26% recovery. It should be noted that no other by-products including **6** were observed under the latter aqueous reaction conditions.

Using the dichlorophosphirane **5** thus obtained, attempts were made to prepare phosphaallene, as has been successful in the preparation of 1,3-diphosphaallenes. However, when methyllithium was used as a base, methyllithium reacted as a nucleophile to result in the P-C bond cleavage leading to an alkylated product, as follows: the phosphirane **5** (204.5 mg, 0.455 mmol) was dissolved in ether (25 ml) at -78 °C and was added 0.688 mmol of methyllithium in ether. After the usual workup 78.4 mg of methyl(phenylethynyl)(2,4,6-tri-*t*-butylphenyl)phosphine (**8**) in 44% yield together with **5** in 26% recovery. **8**: δ_P (hexane) -63.8; ^{1}H NMR ($CDCl_3$) δ 7.48 - 7.40 (2H, m, o-Ph), 7.43 (2H, d, J= 2.5 Hz, Ar), 7.24 - 7.34 (3H, m, m,p-Ph), 1.67 (18H, s, o-Bu^t), 1.56 (3H, d, J= 8.5 Hz, Me), 1.31 (9H, s, p-Bu^t); ^{13}C{^{1}H} NMR ($CDCl_3$) δ 156.90 (d, J= 14.6 Hz, o-Ar), 150.37 (d, J= 2.3 Hz, p-Ar), 131.44 (d, J= 36.2 Hz, i-Ar), 131.15 (d, J= 3.0 Hz, o-Ph), 128.23 (s, m-Ph), 128.09 (s, p-Ph), 123.89 (d, J= 2.2 Hz, i-Ph), 123.06 (d, J= 7.7 Hz, m-Ar), 107.90 (d, J= 9.5 Hz, $\underline{C}$Ph), 92.08 (d, J= 9.5 Hz, P$\underline{C}$C), 39.32 (d, J= 4.4 Hz, o-$\underline{C}$Me$_3$), 34.88 (s, p-$\underline{C}$Me$_3$), 34.15 (d, J= 8.1 Hz, o-Me), 31.21 (s, p-Me), 16.65 (d, J= 24.4 Hz, PMe); IR (neat) $\nu_{C\equiv C}$ 2168 cm^{-1}; LRMS (70 eV) *m/z* 392 (M+, 100%); Found: *m/z* 392.2631. Calcd for $C_{27}H_{35}P$: M, 392.2633.

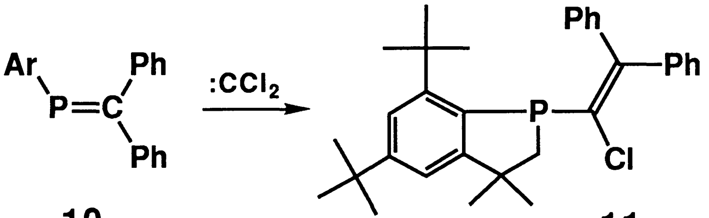


On the other hand, if *t*-butyllithium was employed as a base at -78 °C, the reaction gave 3-phenyl-1-(2,4,6-tri-*t*-butylphenyl)phosphaallene (**9**), as follows: the phosphirane **5** (140 mg, 0.383 mmol) was dissolved in ether (150 ml) and was added 0.388 mmol of *t*-butyllithium in pentane at -78 °C with stirring. The mixture was warmed up to room temperature immediately and the solvents were removed by rotary evaporation. After chromatography, the phosphaallene **9** was obtained in 62% yield. **9**:[10,11] δ_P ($CDCl_3$) 75.5 (d, J= 24.4 Hz); ^{1}H NMR ($CDCl_3$) δ 7.32 (2H, d, J= 2.5 Hz, Ar), 7.17 (5H, brs, Ph), 6.22 (1H, d, J= 27.0 Hz, C$\underline{H}$Ph), 1.63 (18H, s, o-Bu^t), 1.28 (9H, s, p-Bu^t) .

These results indicate that *t*-butyllithium is a suitable reagent compared to methyllithium which is often used for the synthesis of allenes. Recently there have been reported several preparative methods[10,11] of the phosphaallene **9**. We have now accomplished a formal insertion of a carbon atom into the P=C double bond resulting in the formation of the P=C=C bond. The present method provides an alternative and straightforward way to the preparation of phosphaallenes.

When diphenylphosphaethylene **10**[6,7] was allowed to react with dichlorocarbene generated by carbon tetrachloride and butyllithium, no corresponding diphosphirane was obtained, probably because of the steric reasons. Instead of 3-membered ring compound, (1-chloro-2,2-diphenylethenyl)-5,7-di-*t*-butyl-3,3-dimethyl-1-phosphaindane **11** was obtained in 50% yield after chromatographic purification together with **10** in 29% recovery. The mechanism of the formation of **11** might be explained by the **7**-type of intermediate and C-H insertion of phosphoranyl radicals followed by elimination of hydrogen chloride. **11**: mp 193 - 195 °C; ^{31}P{^{1}H} NMR ($CDCl_3$) δ_P 4.78; ^{1}H NMR ($CDCl_3$) δ 7.39 - 7.20 (1H + 10H, Ar, Ph), 7.04 (1H, d, J= 1.7

Hz, Ar), 2.23 (1H, dd, J_{PH}= 3.8 Hz, J= 13.7 Hz, CH), 2.17 (1H, dd, J_{PH}= 29.9 Hz, J= 13.7 Hz, CH), 1.46 (3H, s, Me), 1.34 (9H, s, o-Bu^t), 1.32 (9H, s, p-Bu^t), 1.20 (3H, s, Me); LRMS (70 eV) *m/z* 488 ($M^{+\cdot}$ 54%), 453 (M-Cl, 100%); Found: C, 78.19; H, 8.02; Cl, 7.33%. Calcd for $C_{32}H_{38}ClP$: C, 78.58; H, 7.83; Cl, 7.25%. The structure was further confirmed by the ^{13}C NMR spectrum of the labelled compound which was obtained by an experiment using ^{13}C-enriched carbon tetrachloride as a source of ^{13}C-dichlorocarbene[12)] as well as by various kinds of 2-D NMR measuring techniques.



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12) $^{13}C\{^1H\}$ NMR ($CDCl_3$) of **11** was tentatively assigned as follows: δ 158.64 (d, J= 6.8 Hz, C^{3a}), 152.55 (C^7), 152.23 (C^5), 150.55 (d, J= 22.1 Hz, $\underline{C}Ph_2$), 141.51 (i-Ph), 141.51 (d, J= 8.3 Hz, i-Ph), 138.68 (d, J= 70.2 Hz, Cl$\underline{C}$=), 131.64 (d, J= 16.6 Hz, C^{7a}), 130.03 (d, J= 4.4 Hz, o-Ph), 129.02 (o-Ph), 127.96 (p-Ph), 127.89 (p-Ph), 127.80 (m-Ph), 127.42 (m-Ph), 122.46 (d, J= 3.8 Hz, C^4), 118.17 (C^6), 45.59 (d, J= 3.9 Hz, C^3), 40.21 (d, J= 7.8 Hz, C^2), 37.23 (d, J= 2.2 Hz, C^7-$\underline{C}Me_3$), 34.93 (C^5-$\underline{C}Me_3$), 34.68 (d, J= 2.8 Hz, C^3-Me), 31.96 (d, J= 8.4 Hz, C^3-Me'), 31.44 (C^7-$C\underline{Me_3}$), 31.17 (C^5-$C\underline{Me_3}$).

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