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A NEW DIRECT METHOD FOR INTRODUCING 2-(2,4,6-TRI-t-BUTYLPHENYL)-2-PHOSPHAVINYLIDENE GROUP. FORMATION OF 1-PHOSPHA- AND 1,3-DIPHOSPHA-ALLENES

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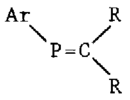
Abstract: 2-Phosphavinylidene group was introduced by the corresponding trimethylsilyllithio compound toward carbonyl compounds to give 1-phosphaallenes, whereas 1,3-diphosphaallene was prepared by the reaction of 1-chloro-2-phosphavinyllithium toward a phosphinous chloride followed by dehydrochlorination.

Compounds carrying the 2-(2,4,6-tri-t-butylphenyl)-2-phosphavinylidene skeleton have been of current interest bacause they have phosphorus atoms in low coordination states but very stable due to steric protection by the bulky phenyl group. Phosphaethylenes **1**,[1,2] 1-phosphaallenes **2**,[3,4] 1,3-diphosphaallenes **3**,[5,6] and 1-phospha-1,2,3-butatriene **4**[7] are among those examples.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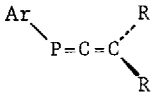
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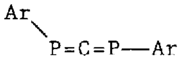
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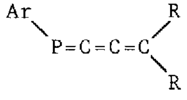
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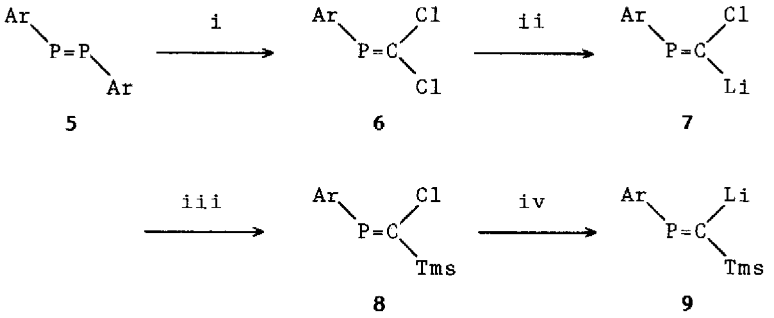
(Ar = 2,4,6-$Bu^t{}_3C_6H_2$)

We have found that 1-silyl-2-phosphavinyl-lithium **9** is a convenient and direct reagent for introducing "ArP=C" unit in the formation of such compounds as **2**.

2,2-Dichloro-1-(2,4,6-tri-t-butylphenyl)-1-phosphaethylene **6**[8] was prepared from the diphosphene **5** and dichlorocarbene in a slightly modified manner reported by Koenig et al.[9] in 60 - 65% yield. A solution of **5** (54.5 mg, 0.099 mmol) in THF (8 ml) was cooled at -78°C and was added carbon tetrachloride (0.050 ml, 0.52 mmol). Butyllithium (0.52 mmol) in hexane was added slowly and a cooling bath was removed immediately after the addition of butyllithium to allow the mixture to warm up to room temperature. The solvent was removed in vacuo and the residue was chromatographed over silica gel (pentane as an eluent) to give pure **6** as a stable compound. **6**: ^{31}P NMR δ_P (THF) 233.4. By-products under these conditions were 2,2,3,3-tetrachloro-1-(2,4,6-tri-t-butylphenyl)phosphirane (δ_P -63.8 in THF)[10] in less than 34% yield and 3,3-dichloro-1,2-bis(2,4,6-tri-t-butylphenyl)-1,2-diphosphirane (δ_P -69.0 in THF)[9] in 8 - 10% yield.

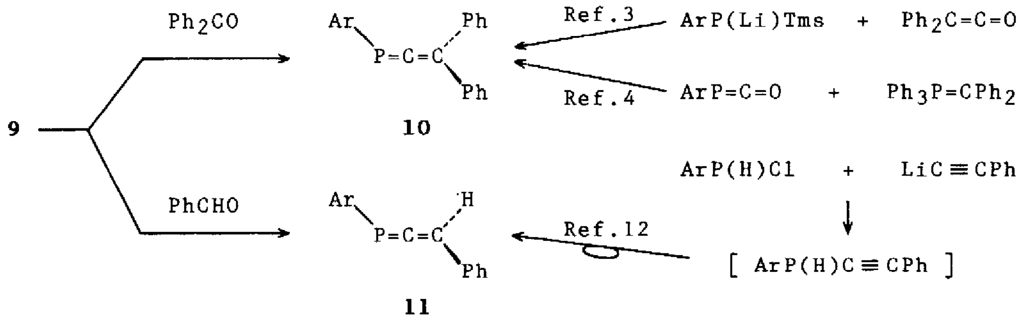


(Tms = Me_3Si)

Reagents: i, CCl_4 + Bu^nLi; ii, Bu^nLi; iii, TmsCl; iv, Bu^tLi.

The dichlorophosphaethylene **6** (63.2 mg, 0.176 mmol) in THF (4 ml) was lithiated at the E position with butyllithium (0.211 mmol) at -78 °C for 6 min followed by addition of chlorotrimethylsilane (76.3 mg, 0.703 mmol) at -78 °C with stirring for 5 min and was warmed up to room temperature. The volatiles were removed by rotary evaporation and the residue was chromatographed over silica gel (pentane as an eluent) to give Z-2-chloro-1-(2,4,6-tri-t-butylphenyl)-2-trimethylsilyl-1-phosphaethylene **8** in 90 - 98% yield.[11] **8**: mp 102.8 - 106.2 °C. ^1H NMR ($CDCl_3$): δ 7.40 (2H, d, J = 1.32 Hz, arom.), 1.46 (18H, o-Bu^t), 1.33 (9H, p-Bu^t), 0.26 (9H, d, J = 1.10 Hz, Tms). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 176.0 (d, J = 81.79 Hz, P=$\underline{C}$), 150.3 (p-arom.), 121.7 (m-arom.), 153.1 (d, J = 2.44 Hz, o-arom.), 136.1 (d, J = 62.86 Hz, i-arom.), 37.8 (o-$\underline{C}Me_3$), 35.0 (p-$\underline{C}Me_3$), 31.4 (p-Me), 32.7 (d, J = 7.33 Hz, o-Me), -1.27 (d, J = 9.16 Hz, Tms). ^{31}P NMR ($CDCl_3$): δ_P 285.7. MS m/z 398 (M+2, 11%), 396 (M, 25), 381 (M-Me, 93), 57 (t-Bu, 100).

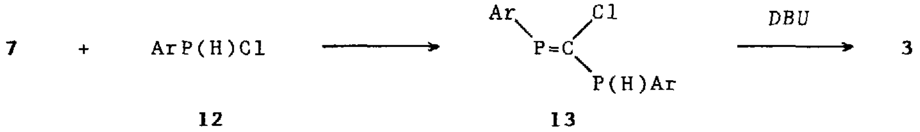
The chloride **8** (63.1 mg, 0.159 mmol) in THF (2.5 ml) was lithiated with t-butyllithium (0.556 mmol) at -78 °C for 13 min and was allowed to react with benzophenone (107.8 mg, 0.592 mmol) in THF (1 ml) at that temperature. The mixture was stirred for 5 min at -78 °C and then warmed up to room temperature. After usual work-ups including column chromatography (silica gel, pentane), 3,3-diphenyl-1-(2,4,6-tri-t-butylphenyl)-1-phosphaallene **10** was obtained in 45% yield. Very similarly, when benzaldehyde was employed, the corresponding phosphaallene **11** was obtained in 16% yield.



The present method, which involves the Peterson-type reaction of **9** with benzophenone and benzaldehyde, seems convenient and straightforward, compared with some other reported methods.[4,12] **10**:[3] Mp 157 - 160 °C. ^{1}H NMR ($CDCl_3$): δ 7.39 (2H, d, J = 1.54 Hz, arom.), 7.26 (10H, s, Ph), 1.50 (18H, s, o-Bu^t), 1.32 (9H, s, p-Bu^t). ^{31}P NMR ($CDCl_3$) δ_P 71.7 (s). **11**: Colorless crystals (originally reported as orange crystals).[12] Mp 109.0 - 114.2 °C. ^{1}H NMR ($CDCl_3$): δ 7.29 (2H, d, J = 2.4 Hz, Ar-arom.), 7.17 (5H, s, Ph), 6.57 (1H, d, J = 27.0 Hz, =C$\underline{H}$), 1.63 (18H, s, o-Bu^t), 1.28 (9H, s, p-Bu^t). ^{31}P NMR ($CDCl_3$) δ_P 75.2 (d, J = 24.4 Hz).

It should be noted that the present feature differs from that in carbon chemistry[13,14] in the following way. 1) Halogen-metal exchange reaction does not proceed in the case of vinyl chloride. 2) α-Silylvinyl-lithium reacts with ketones, however, the reaction stops in the way to allenes resulting in the formation of the corresponding alcohols. Therefore, in order to accomplish the Peterson type reaction, the alcohols should be converted to halides with thionyl chloride followed by elimination of the resulting silyl halides with fluoride eventually to give allenes.[13]

On the other hand, **7** as a nucleophile reacted with phosphinous chloride **12**[12,15,16] in place of chlorotrimethylsilane to give **13** and the following dehydrochlorination with 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) proceeded almost quantitatively to give diphosphaallene **3**.[5] **13**: ^{31}P NMR ($CDCl_3$) δ_P 262.5 (dd, J_{PP} = 109.9 Hz, J_{PH} = 21.4 Hz, $\underline{P}$=C), -33.7 (dd, J_{PP} = 109.9 Hz, J_{PH} = 231.9 Hz, $\underline{P}$H).[17] The total yield of **3** based on **7** was 33% after purification through silica gel column chromatography (pentane as an eluent). **3**: ^{31}P NMR ($CDCl_3$) δ_P 141.7.



Further studies on utilization of the reagents **7** and **9** as nucleophiles are in progress.

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References and Notes

1) M. Yoshifuji, K. Toyota, and N. Inamoto, Tetrahedron Lett., **26**, 1727 (1985); M. Yoshifuji, K. Toyota, I. Matsuda, T. Niitsu, N. Inamoto, K. Hirotsu, and T. Higuchi, Tetrahedron, **44**, 1363 (1988).

2) K. Issleib, H. Schmidt, and Chr. Wirkner, *Z. Anorg. Allg. Chem.*, **488**, 75 (1982).

3) M. Yoshifuji, K. Toyota, K. Shibayama, and N. Inamoto, *Tetrahedron Lett.*, **25**, 1809 (1984).

4) R. Appel, P. Fölling, B. Josten, M. Siray, V. Winkhaus, and F. Knoch, *Angew. Chem., Int. Ed. Engl.*, **23**, 619 (1984).

5) M. Yoshifuji, K. Toyota, and N. Inamoto, *J. Chem. Soc., Chem. Commun.*, **1984**, 689.

6) H. H. Karsch, H.-U. Reisacher, and G. Müller, *Angew. Chem., Int. Ed. Engl.*, **23**, 618 (1984).

7) G. Märkl and H. Sejpka, *Angew. Chem., Int. Ed. Engl.*, **25**, 1003 (1986).

8) R. Appel, C. Casser, M. Immenkeppel, and F. Knoch, *Angew. Chem., Int. Ed. Engl.*, **23**, 895 (1984).

9) G. E.-Moghadam, J. Bellan, C. Tachon, and M. Koenig, *Tetrahedron*, **43**, 1793 (1987).

10) 2,2,3,3-Tetrachloro-1-(2,4,6-tri-t-butylphenyl)phosphirane: MS (relative intensity): m/z 444 (M+4, 57%), 442 (M+2, 121%), and 440 (100%). The MS pattern was consistent with a compound bearing 4 chlorine atoms. ^{1}H NMR ($CDCl_3$): δ 7.27 and 7.32 (2H, arom.), 1.53 (18H, o-Bu^t), 1.27 (9H, p-Bu^t).

11) Regio selectivity for **8** was high, i.e., Z : E = 95 : 5, and each isomer could be separated by column chromatography: δ_P (THF) 310.3 (E isomer). Photo-isomerization was observed by ^{31}P NMR analysis indicating that an equilibrium reaches after 1.5-h irradiation of of **8** in THF in an NMR sample tube with a medium pressure mercury lamp at 0 °C, Z : E = 85 : 15 (δ_P 287.1 : δ_P 310.3).

12) G. Märkl and S. Reitinger, *Tetrahedron Lett.*, **29**, 463 (1988).

13) T. H. Chan and W. Mychajlowskij, *Tetrahedron Lett.*, **15**, 171 (1974).

14) B.-Th. Gröbel and D. Seebach, *Chem. Ber.*, **110**, 867 (1977).

15) The phosphinous chloride **12**, δ_P (THF) 21.5 (d, $^1J_{PH}$ = 213.6 Hz), was alternatively prepared in high yield from the corresponding phosphine, $ArPH_2$, by mono-lithiation with butyllithium (1.1 equiv.) in THF at -78 °C, trimethylsilylation with chlorotrimethylsilane (1.2 equiv.) at room temperature, and chlorination with phosgene in toluene (1.4 equiv.) at 0 °C, successively.

16) A. H. Cowley, J. E. Kilduff, N. C. Norman, M. Pakulski, J. L. Atwood, and W. E. Hunter, *J. Am. Chem. Soc.*, **105**, 4845 (1983).

17) According to the large coupling constant $^2J_{PP}$, the configuration of **13** appeared to be Z. See footnote 15 in M. Yoshifuji, T. Niitsu, K. Toyota, N. Inamoto, H. H. Karsch, and H.-U. Reisacher, *Tetrahedron Lett.*, **29**, 333 (1988).

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