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Formation of a Phospha-alkyne via Migration of the Phenyl Group from Phosphorus to Carbon

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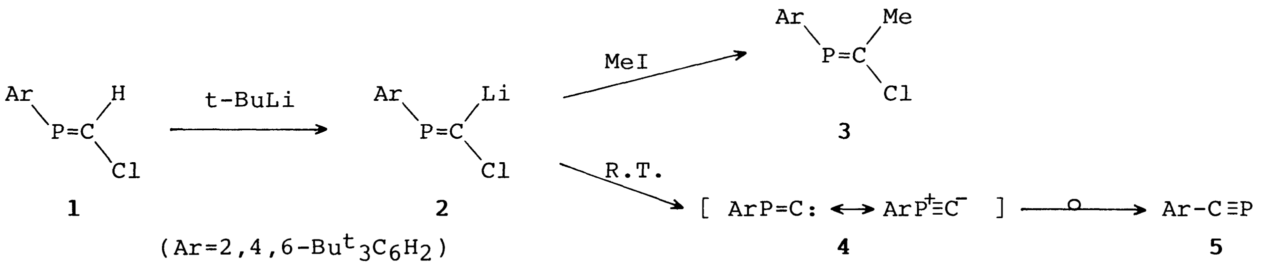
E-2-Chloro-1-(2,4,6-tri-t-butylphenyl)-1-phospha-ethylene was allowed to react with t-butyllithium as a base to give 2-(2,4,6-tri-t-butylphenyl)-1-phospha-acetylene, suggesting the generation of a phosphorus analogue of isonitrile followed by migration of the phenyl group from phosphorus to carbon.

Phosphorus compounds in low coordination states are of current interest.$^{1)}$ Phospha-alkynes are the species having triple bonded phosphorus atom in the lowest coordination state. Since Becker et al. reported the first isolation of a stable phospha-alkyne, 3,3-dimethyl-1-phospha-1-butyne,$^{2)}$ there have been many reports on the chemistry of sterically protected phospha-alkynes,$^{3,4)}$ involving 2,4,6-tri-t-butylphenyl$^{5)}$ as a protecting group.



A THF solution of E-2-chloro-1-(2,4,6-tri-t-butylphenyl)-1-phospha-ethylene (**1**)$^{6)}$ was reacted with 2.2 equiv. of t-butyllithium for 40 min at -78 °C under argon to give a greenish yellow solution. Then the reaction mixture was allowed to warm up to room temperature to give a purple solution. The phospha-alkyne (**5**) was obtained in 53% yield$^{7)}$ after column chromatography (silica gel, pentane). When methyl iodide was allowed to react as a quenching reagent before warming up, E-2-chloro-1-(2,4,6-tri-t-butylphenyl)-1-phospha-1-propene (**3**)$^{8)}$ was obtained as an alkylated product of **2** in 85% yield after chromatography (silica gel, pentane). **5**: Mp 125 -127 °C; ^{31}P NMR ($CDCl_3$) 33.8; ^{1}H NMR ($CDCl_3$), 7.30 (2H, d, J=1.0 Hz, arom.), 1.66 (18H, o-Bu^t), 1.30 (9H, p-Bu^t); ^{13}C {^{1}H} NMR ($CDCl_3$) 168.6 (d, J=53.5 Hz, $\underline{C}$≡P), 156.8 (d, 6.6 Hz, o-arom.), 151.4 (d, 5.9 Hz, p-arom.), 124.7 (d, 22.0 Hz, i-arom.), 121.1 (d, 1.5 Hz, m-arom.), 37.0 (o-$\underline{C}Me_3$), 35.4 (p-$\underline{C}Me_3$), 31.1 (p-$C\underline{Me}_3$), 30.9 (d, 2.2 Hz, o-$C\underline{Me}_3$). **3**: Mp 114 - 118 °C; ^{31}P NMR ($CDCl_3$) 224.8 (q, J=12.2 Hz); ^{1}H NMR ($CDCl_3$) 7.41 (2H, d, J=1.22 Hz, arom.), 1.52 (3H, d, 12.9 Hz, Me), 1.48 (18H, o-Bu^t), 1.33 (9H, p-Bu^t); ^{13}C{^{1}H} NMR ($CDCl_3$) 174.9 (d, J=46.4

Hz, $\underline{C}$=P), 154.0 (d, 2.4 Hz, o-arom.), 150.9 (p-arom.), 135.2 (d, 56.8 Hz, i-arom.), 121.9 (m-arom.), 38.0 (o-$\underline{C}$Me$_3$), 35.0 (p-$\underline{C}$Me$_3$), 32.6 (d, 7.3 Hz, o-C$\underline{Me}_3$), 31.4 (p-C$\underline{Me}_3$), 28.8 (d, 17.1 Hz, Me); Found m/z 338.1912; Calcd for $C_{20}H_{32}ClP$: M, 338.1930.

The results indicated that an intermediate of a phosphorus analogue of "isonitrile" (**4**) was first generated at low temperature and that on warming the aryl group migrated from the phosphorus atom to the carbon resulting in the formation of a phosphorus analogue of "nitrile" (**5**). According to the ab initio calculations for the HCP - HPC system,$^{9)}$ the linear HPC and HCP isomers correspond to the energy maximum and minimum, respectively, on the energy surface of the singlet ground state, and the relative energy between them is 83.9 kcal/mol at the MP4/6-31G** level. Our present results also indicated that **4** was not stable enough which permitted either observation or isolation, affording a rearranged product **5**. Moreover, when Z-2-chloro-1-(2,4,6-tri-t-butylphenyl)-1-phospha-ethylene was allowed to react with t-butyllithium under similar conditions, no formation of **5** was observed. Studies on the mechanisms of these reactions are in progress in these laboratories.

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7) When benzyl chloride was added before warming up, no benzylated product was obtained, but the yield of phospha-acetylene (**5**) was improved to 62%.

8) When ArP=CCl_2 was allowed to react with n-BuLi followed by quenching with MeI in THF, Z-ArP=C(Cl)Me was obtained in contrast to the results reported by Appel et al. done in ether and toluene. Mp 109 - 112 °C; ^{31}P NMR ($CDCl_3$) 225.3 (q, J=24.4 Hz); ^{1}H NMR ($CDCl_3$) 7.40 (2H, d, J=1.5 Hz, arom.), 2.41 (3H, d, 23.4 Hz, Me), 1.48 (18H, o-Bu^t), 1.33 (9H, p-Bu^t); ^{13}C{^{1}H} NMR ($CDCl_3$) 168.8 (d, J=58.6 Hz, $\underline{C}$=P), 153.4 (d, 1.5 Hz, o-arom.), 150.5 (p-arom.), 135.4 (d, 51.3 Hz, i-arom.), 121.8 (m-arom.), 37.9 (o-$\underline{C}$Me$_3$), 35.0 (p-$\underline{C}$Me$_3$), 32.6 (d, 7.3 Hz, o-C$\underline{Me}_3$), 31.4 (p-C$\underline{Me}_3$), 29.1 (d, 37.4 Hz, Me); Found m/z 338.1910; Calcd for $C_{20}H_{32}ClP$: M, 338.1930. See, R. Appel, C. Casser, and M. Immenkeppel, Tetrahedron Lett., 26, 3551 (1985).

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