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Wavelength- and Temperature-dependent Photolysis of a Diphosphene. Generation of 2,4,6-Tri-t-butylphenylphosphinidene and E/Z Isomerization

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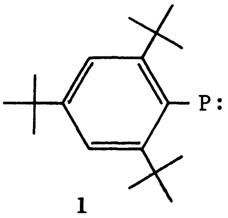
A phospha-indane derivative was obtained via intramolecular C-H insertion of the phosphinidene generated as an intermediate by the photolysis of E-1,2-bis(2,4,6-tri-t-butylphenyl)diphosphene whereas the photolysis through a Pyrex filter at -40 °C gave an equilibrium mixture of E and Z.

Phosphinidenes (RP:)$^{1)}$ as well as phosphinidene oxides (RP=O)$^{2)}$ and sulfides (RP=S)$^{2a,3)}$ have long been postulated as reactive intermediates as phosphorus analogues of nitrene or carbene. Since we reported the first isolation of a "true" diphosphene, E-1,2-bis(2,4,6-tri-t-butylphenyl)diphosphene (**2**),$^{4)}$ as a very stable compound by a steric protection method, the chemistry of multiple bonding containing heavier main-group elements has very much been developed.$^{5)}$ Although diphosphene is a formally dimeric product of phosphinidene, phosphinidene has not been detected so far. We now wish to report an intramolecular trapping experiment of a phosphinidene **1** as well as E/Z isomerization by the photolysis of **2** which was wavelength- and temperature-dependent.



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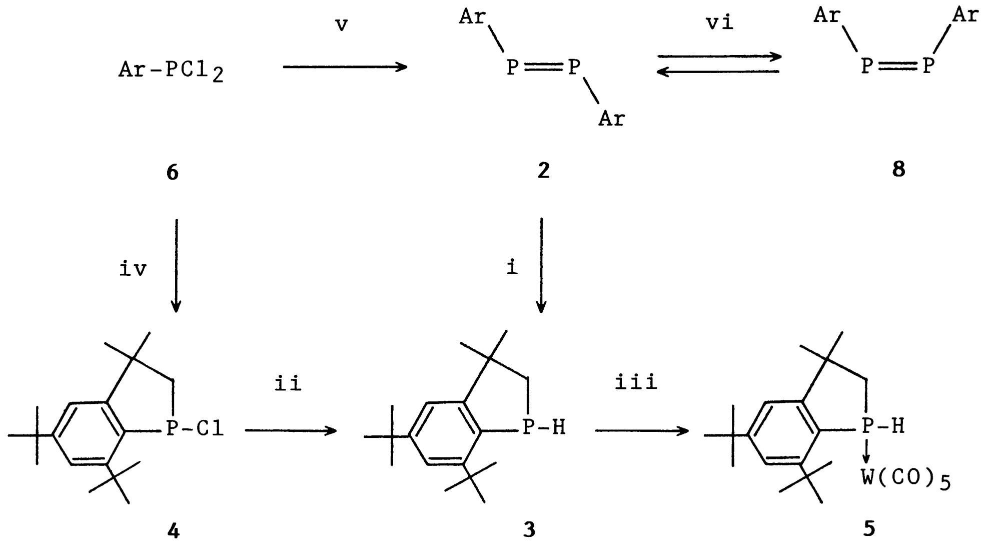
A solution of the diphosphene **2** (0.054 mmol) in tetrahydrofuran (THF, 1 ml) was irradiated with a medium pressure mercury lamp (100 W) in an NMR sample tube at −78 °C for 2 h under argon to give a phospha-indane **3** as an air sensitive phosphine almost quantitatively,[6)] whose NMR data were identical with those of an authentic sample prepared by the reduction of the corresponding chlorophospha-indane **4**[7)] with lithium aluminum hydride. The phospha-indane **3** was fully characterized as the penta(carbonyl)tungsten complex **5** as an air-stable compound.[8)] **3**: ^{31}P NMR ($CDCl_3$) δ_P −79.6 ppm (d, $^1J_{PH}$= 173.3 Hz). **5**: mp 109-110 °C, ^{31}P NMR ($CDCl_3$) δ_P −49.8 ppm (d, $^1J_{PH}$= 336.9 Hz; satellite of ^{183}W: $^1J_{PW}$= 229.5 Hz). Found: 598.1187. Calcd for $C_{23}H_{29}O_5P^{182}W$: M, 598.1212. Similar results were obtained when the photolysis of **2** was carried out at 0 °C to afford **3**. This photo-reaction seemed not to be temperature dependent. The same photolysis reaction of **2** in THF-d_8 gave **3** and no deuterium was incorporated into **3**, which indicated that the reaction occurred intramolecularly. It seems likely that **1** is too bulky to accomplish an intermolecular reaction since the photolysis in THF in the presence of methanol gave similar results to those in the absence of the trapping reagent. These results strongly suggested the intermediacy of phosphinidene **1** during the photolysis, in contrast to the results on the argon-laser



(Ar=2,4,6-$Bu^t{}_3C_6H_2$)

Reagents and Conditions: i, Hg lamp without Pyrex filter; ii, $LiAlH_4$; iii, $(THF)W(CO)_5$; iv, heat at 110 °C; v, Mg; vi, Hg lamp through Pyrex filter at −40 °C.

irradiation of **2** at 514.5 nm reported by Koenig et al.[9)]

On the other hand, however, when the irradiation was performed with the mercury lamp through a 2-mm thick Pyrex filter at -40 °C, the E/Z equilibrium was observed by monitoring the ^{31}P NMR at that temperature (E-**2**(δ_P 488.5) : Z-**8**(δ_P 367.8) = 4 : 3) in contrast to the intramolecular photocyclization reaction without filter. However, no change was observed in the ^{31}P NMR during the photolysis of **2** through a Pyrex filter above 0 °C. The isomer Z-**8** should be unstable to heat resulting in reversion to E-**2**. The photolysis of the diphosphene seems to be wavelength- and temperature-dependent.

Therefore, the diphosphene **2** is not a dimerization product of the phosphinidene **1**,[4a)] because if free **1** is generated as an intermediate during the reaction of the corresponding dichloride **6** with magnesium metal, **1** should give phospha-indane derivative **3** almost exclusively. Probably the formation of diphosphene might be explained by a dimerization of "phosphinidenoid" or chlorophosphide,[10)] since we were not able to detect any traces of phospha-indane derivatives in the crude reaction mixture during the preparation process of **2** from **6** with magnesium metal in THF as a solvent.

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6) A trace amount of $ArPH_2$ (**7**) was obtained together with **3**.

7) M. Yoshifuji, I. Shima, K. Ando, and N. Inamoto, Tetrahedron Lett., 24, 933 (1983).

8) The complex **5** (0.817 mmol) was obtained by stirring the phosphine **3** with 1.3 equiv. of $(THF)W(CO)_5$ in THF (30 ml) at room temperature overnight. The yield of **5** after purification by silica-gel chromatography was 38% based on ArBr used for the preparation of **6**. Both ^1H and ^{13}C NMR were reasonable for **5**.

9) A.-M. Caminade, M. Verrier, C. Ades, N. Paillous, and M. Koenig, J. Chem. Soc., Chem. Commun., 1984, 875.

10) For example, ArP(Cl)MgCl might operate as a reactive species during the reaction of **6** with magnesium metal to give **2**.

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