

THERMAL REACTIONS OF (2,4,6-TRI-tert-BUTYLPHENYL)PHOSPHONOUS DICHLORIDE
AND ITS DERIVATIVES; FORMATION OF 2,3-DIHYDRO-1H-PHOSPHINDOLES

Masaaki Yoshifuji*, Ichiro Shima, Kaori Ando, and Naoki Inamoto*

Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo 113, Japan

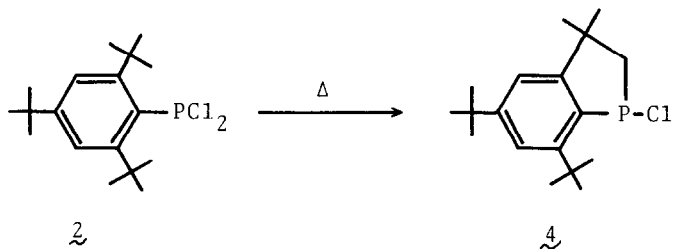
2,3-Dihydro-1H-phosphindole derivatives were obtained from thermal reactions of (2,4,6-tri-tert-butylphenyl)phosphonous dichloride in refluxing toluene, probably through cyclization involving phosphorus radicals with an adjacent methyl of *o*-tert-butyl groups.

Recently we reported that the reaction of (2,4,6-tri-tert-butylphenyl)-lithium with phosphoryl trichloride gave a very crowded molecule, bis(2,4,6-tri-tert-butylphenyl)phosphinic chloride (1).¹⁻³

The reaction of (2,4,6-tri-tert-butylphenyl)lithium with phosphorus trichloride gave the corresponding phosphonous dichloride (2) almost quantitatively and the first stable phosphobenzene, E-bis(2,4,6-tri-tert-butylphenyl)diphosphene (3),⁴ was obtained after dechlorination with magnesium metal.

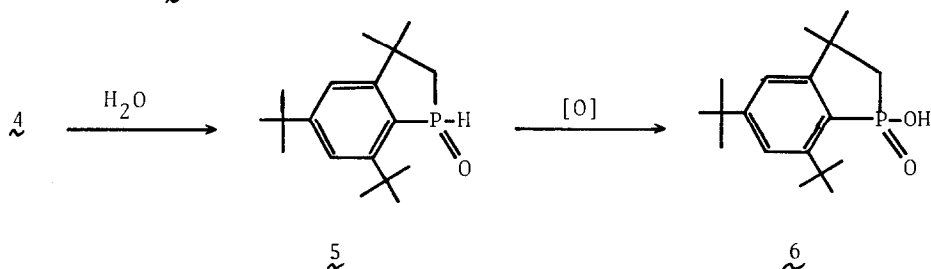
Very recently Majoral et al.⁵ have reported a thermal reaction of bis(2,4,6-tri-tert-butylphenyl)phosphinic chloride (1)¹ to a phosphindole 1-oxide derivative.

Now we wish to report our results on thermal reactions of 2 and its derivatives.⁶ The reactions involve interesting cyclizations of the phosphorus atom with one of the non-functionalized but sterically suitably located methyls of ortho tert-butyl groups to give 2,3-dihydro-1H-phosphindole derivatives in good yields.



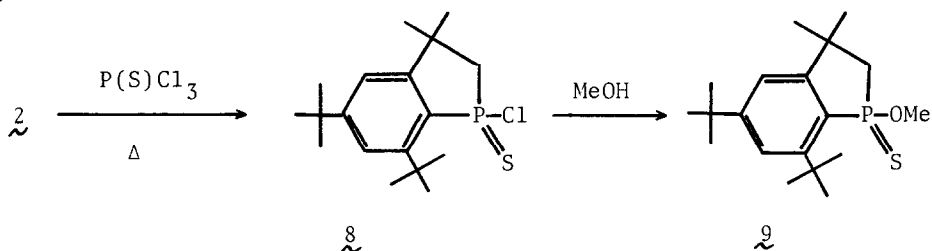
Compound 2 (prepared from 2.00 mmol of the corresponding bromobenzene) was refluxed in toluene (20 ml) in the presence of pyridine (0.2 ml)⁷ overnight to give 5,7-di-tert-butyl-1-chloro-3,3-dimethyl-2,3-dihydro-1H-phosphindole (4) (400 mg, 64 % yield).⁸ ¹H NMR (CDCl₃) δ 1.30 (s, 9H, p-Bu^t), 1.45 (br.s, 6H, 3-CH₃), 1.53 (s, 9H, o-Bu^t), 2.43 (m, 2H, 2-CH₂), and 7.07 - 7.40 (m, 2H, aromatic). ³¹P NMR (CDCl₃) δ 111.5 ppm (from external 85% H₃PO₄).

Compound **4** was easily hydrolyzed with atmospheric moisture to give the corresponding phosphinous acid (**5**), which was easily oxidized to give the corresponding phosphinic acid (**6**).



5: 1H NMR ($CDCl_3$) 1.34 (s, 9H, p-Bu^t), 1.52 (s, 6H, 3-CH₃), 1.58 (s, 9H, o-Bu^t), 2.34 - 2.40 (m, 2H, 2-CH₂), 7.28 - 7.54 (m, 2H, aromatic), and 8.3 (dt, 1H, P-H, $^1J_{PH} = 480$ Hz, $^3J_{HCPH} = 3$ Hz). ^{31}P NMR ($CDCl_3$) 36.6 ppm ($J = 483.4$ Hz).

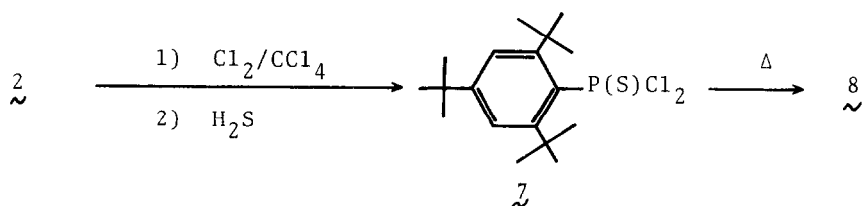
6: colorless powder from methanol, mp > 300 °C. 1H NMR ($CDCl_3$) 1.34 (s, 9H, p-Bu^t), 1.47 (s, 6H, 3-CH₃), 1.58 (s, 9H, o-Bu^t), 2.13 (d, 2H, 2-CH₂, $^2J_{HCP} = 14.4$ Hz), 6.95 (variable, s, 1H, OH), and 7.23 - 7.51 (m, 2H, aromatic). ^{31}P NMR ($CDCl_3$) 65.6 ppm.



In an attempt to prepare (2,4,6-tri-tert-butylphenyl)phosphonothioic dichloride (**7**) through sulfur transfer reaction was refluxed **2** (prepared from 2.00 mmol of the corresponding bromide) for 3 days in toluene (15 ml) in the presence of thiophosphoryl trichloride (4.93 mmol) and pyridine (0.2 ml). However, the product was 5,7-di-tert-butyl-chloro-3,3-dimethyl-2,3-dihydro-1H-phosphindole 1-sulfide (**8**, 1.35 mmol, 67 % yield), mp 165 - 168 °C (decomp). 1H NMR ($CDCl_3$) 1.35 (s, 9H, p-Bu^t), 1.48 (br.s, 6H, 3-CH₃), 1.73 (s, 9H, o-Bu^t), 2.74 (dd, 1H, 2-CH₂, $^2J_{PH} = 8.4$ Hz, $^2J_{HH} = 15.6$ Hz), 3.08 (dd, 1H, 2-CH₂, $^2J_{PH} = 12.9$ Hz, $^2J_{HH} = 15.6$ Hz), and 7.30 - 7.65 (m, 2H, aromatic). ^{31}P NMR ($CDCl_3$) 93.5 ppm. Mass spectrum m/e 342.1328 (M^+). Calcd for $C_{18}H_{28}ClPS$: 342.1320.

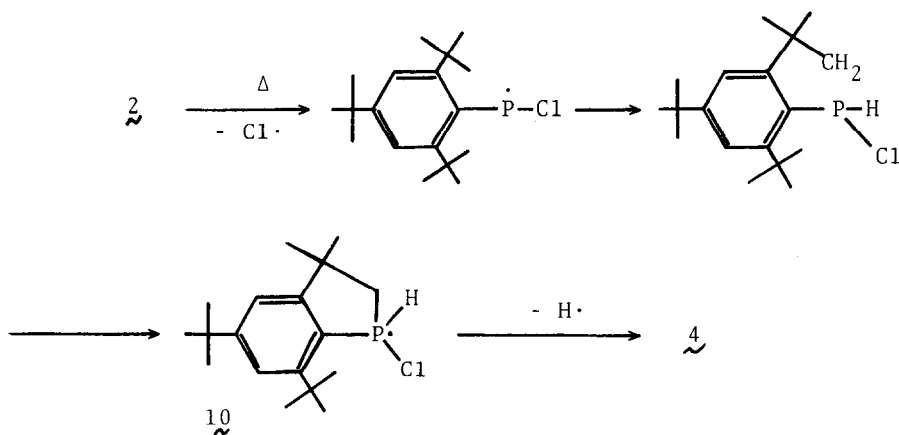
A solution of **8** (0.267 mmol) in methanol (10 ml) was refluxed for 1 h to give methyl ester (**9**) (0.243 mmol, 91 %), mp 128 - 129 °C (from methanol), 1H NMR 1.30 (s, 9H, p-Bu^t), 1.36 (s, 3H, 3-CH₃), 1.50 (s, 3H, 3-CH₃), 1.62 (s, 9H, o-Bu^t), 2.27 - 2.46 (m, 2H, 2-CH₂), 3.73 (d, 3H, OCH₃, $^3J_{PH} = 15.0$ Hz), and 7.18 - 7.55 (m, 2H, aromatic). ^{31}P NMR (CH_3OH) 107.3 ppm, mass spectrum m/e 338.1850 (M^+). Calcd for $C_{19}H_{31}OPS$: 338.1867.

Attempts to prepare **7** by the reaction of the corresponding phosphoryl compound with 2,4-bis(4-methoxyphenyl)-1,3-dithia-2,4-diphosphetane 2,4-disulfide⁹ (Lawesson's reagent) failed. The compound **7** was alternatively prepared from **2** with chlorine followed by hydrogen sulfide in 96 % yield, mp 148.5 - 149 °C. ¹H NMR (CDCl₃) 1.29 (s, 9H, p-Bu^t), 1.57 (s, 18H, o-Bu^t), and 7.25 (d, 2H, ⁴J_{PH} = 7.74 Hz, aromatic). ³¹P NMR (CDCl₃) 81.1 ppm. ¹³C NMR (CDCl₃) 134.7 ppm (d, ¹J_{PC} = 117.2 Hz, ipso).



However the yield of **8** by the direct thermal reaction of **2** under the same conditions for **2** was low (less than 5 %) indicating that **8** might be formed via **4** followed by sulfurization in the reaction of **2** with P(S)Cl₃, and actually **4** reacted with P(S)Cl₃ to give **8** in good yield (74 %).

The reaction mechanism of the thermal cyclization to the phosphindole **4** has not been clear so far, however, a mechanism involving phosphino radicals might be the most plausible although attempts to detect CIDNP signals in ³¹P NMR during the reaction of **2** have been unsuccessful: generation of phosphino radicals, intramolecular hydrogen abstraction from methyls of o-tert-butyl groups, and cyclization to form phosphoranyl radicals (**10**). Very recently Cetinkaya et al. have reported the formation of radical species by ESR spectrum in the reaction of 2,4,6-tri-tert-butylphenylbis(trimethylsilyl)methylphosphinous chloride with butyllithium to give the corresponding phosphindole.¹⁰ Although a cyclization reaction of 2,4,6-tri-tert-butyl nitrosobenzene with tertiary phosphines was reported to give 5,7-di-tert-butyl-1,3,3-dimethyl-2,3-dihydro-1H-indole and a nitrene



mechanism has been postulated as an intermediate,^{11,12} a phosphinidene intermediate, a phosphorus analogue of nitrene, might not be involved in the present cyclization reactions, since the phosphinidenes should have given either diphosphene (3) or cyclic secondary phosphine, neither of which was detected by means of ³¹P NMR spectroscopy during the reaction. Further mechanistic studies are in progress.

This type of cyclization seems to be general, because it has been found in our laboratory that 2,4,6-tri-tert-butylthiobenzaldehyde thermally or homolytically cyclized to 6,8-di-tert-butyl-4,4-dimethylbenzo[c]thiane.¹³

This work was supported in part by the Scientific Research Grant-in-Aid of the Ministry of Education, Science and Culture of Japan (Nos. 464163, 543008, and 57540276).

REFERENCES AND FOOTNOTES

1. M. Yoshifuji, I. Shima, and N. Inamoto, Tetrahedron Lett., 1979, 3963.
2. M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu, and T. Higuchi, Angew. Chem., 92, 405 (1980); Angew. Chem., Int. Ed. Engl., 19, 399 (1980).
3. M. Yoshifuji, I. Shima, N. Inamoto, and T. Aoyama, Tetrahedron Lett., 1981, 3057.
4. M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu, and T. Higuchi, J. Am. Chem. Soc., 103, 4587 (1981).
5. A. Baceiredo, G. Bertrand, P. Mazerolles, and J.-P. Majoral, J. Chem. Soc., Chem. Commun., 1981, 1197.
6. M. Yoshifuji, I. Shima, and N. Inamoto, presented in part at the 41st Annual Meetings of Chem. Soc. Jpn. (April 1 - 5, 1980, Osaka, Japan) and at the International Conference on Phosphorus Chemistry (June 1 - 5, 1981, Duke Univ. N. C., U. S. A.)
7. The cyclization occurred in the absence of pyridine, however, the yield of the cyclization product was low (ca. 30 %).
8. All new compounds gave satisfactory values in their elemental analyses.
9. L. Horner and H. Lindel, Phosphorus and Sulfur, 12, 259 (1982).
10. B. Çetinkaya, P. B. Hitchcock, M. F. Lappert, A. J. Thorne, and H. Goldwhite, J. Chem. Soc., Chem. Commun., 1982, 691.
11. L. R. C. Barclay, P. G. Khazanie, K. A. H. Adams, and E. Reid, Can. J. Chem., 55, 3273 (1977).
12. Y. Inagaki, T. Hosogai, R. Okazaki, and N. Inamoto, Bull. Chem. Soc. Jpn., 53, 205 (1980).
13. R. Okazaki, N. Fukuda, H. Oyama, and N. Inamoto, presented at the 10th International Symposium on the Organic Chemistry of Sulphur (Sept. 6 - 10, 1982, Univ. College of North Wales, Bangor, U. K.).

(Received in Japan 1 December 1982)