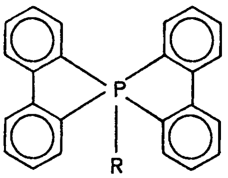
Alkyl Spirophosphoranes. Instability of an Alkyl Hexaco-ordinate Phosphate and an Alkyl Phosphorus(v) Hydride

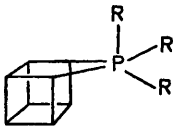
By E. Wayne Turnblom*
(*Department of Chemistry, Columbia University, New York* 10027)
and Dieter Hellwinkel†
(*Belfer Graduate School of Science, Yeshiva University, New York* 10033)

Summary While the spirophosphonium salt (**11**) forms the stable, isolable hexaco-ordinate species (**3a**) with 2,2′-dilithiobiphenyl, analogous reaction of the salt (**9a**) does not give an isolable alkyl hexaco-ordinate species; the homocubyl phosphorane (**12c**) is unstable with respect to the phosphine (**13**).

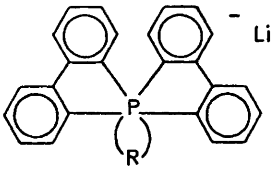
The occurrence of stable alkylphosphoranes in which phosphorus atom is incorporated into a small carbocyclic system has been observed in only two types of compounds, the bisbiphenylylenephosphoranes (**1a**)[1] and the homocubyl phosphoranes (**2**).[2] Unlike their acyclic analogues,[3] these substances are isolable, and it has been suggested that their stability is due to incorporation of phosphorus atom into a small ring system, which should stabilize its pentaco-ordinate derivatives in general.[2a] Hexaco-ordinate phosphorus compounds with phosphorus–carbon bonds are also rare, the only examples being hexa-aryl compounds derived from (**3a**),[1a,4] and no hexaco-ordinate phosphorus species with alkyl substituents has yet been prepared. The phosphahomocubane system might give such species, since a small ring system is necessary to generate (**3a**) as well as stable hexa-aryloxy[5] and hexa-alkoxy[6] phosphate species. Similarly, the same alkyl ring system might be expected to stabilize an alkyl phosphorus(v) hydride, since the analogous compound (**1b**) has been isolated and is of moderate stability.[7] We report that this alkyl ring destabilizes (**3b**) and (**12c**) to such an extent that they cannot be isolated.



(1) a; Me or Bu^n
b; R = H

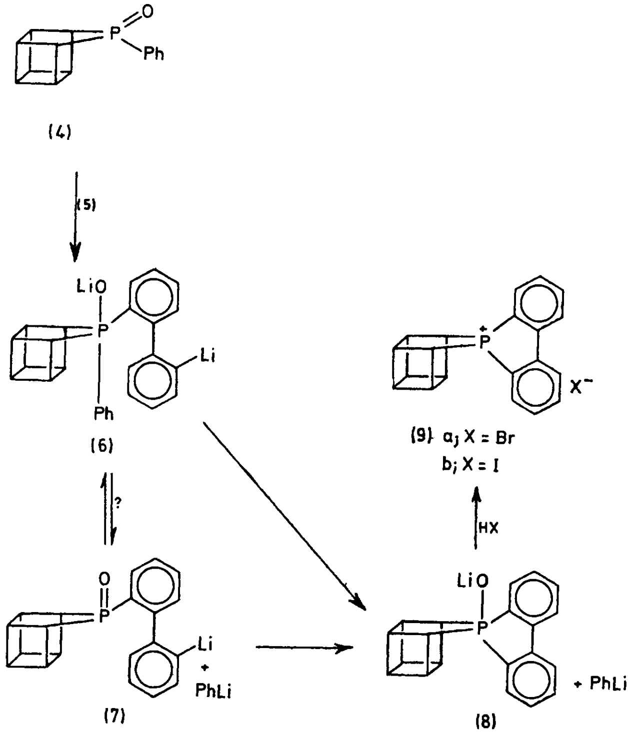


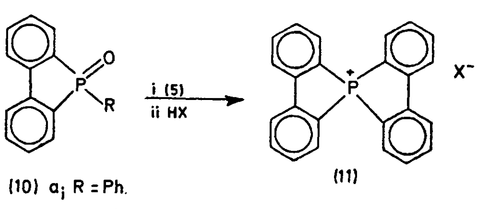
(2) R = Ph or Me



(3) a; R = biphenyl 2,2′-diyl
b; R = homocubyl

Addition of an ether–benzene solution of (**4**)[8] to an ether solution of 2,2′-dilithiobiphenyl (**5**)‡ gave, after hydrolysis with aqueous HBr, the spirophosphonium salt (**9a**) (90%).§ This reaction is expected to take place readily, since reaction of (**4**) with organolithium compounds proceeds with attack at phosphorus,[2] and ring closure of either (**6**) or (**7**)





(10) a; R = Ph
b; R = biphenyl-2-yl

(11)

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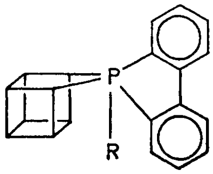
† On leave from Universität Heidelberg, Summer 1971.

‡ Prepared from 2,2′-di-iodobiphenyl in ether with Bu^{n}Li in hexane.

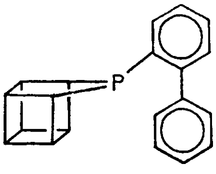
§ ^{1}H n.m.r. spectrum ($CDCl_3$–CD_3OD, Me_4Si): τ 2·14 (m, 8H, Ar-H), 5·52 (m, 6H), and 6·02 (m, 2H, cage protons). Elemental analysis (low carbon values) suggested the presence of iodide, and treatment of an aqueous solution of the salt with dilute H_2O_2 gave a yellow colour characteristic of iodine. Hydrolysis of (**8**) with aqueous HI gave pure (**9b**), m.p. 272° (decomp.) which gave satisfactory analyses.

to give (**8**) should occur readily. A similar sequence occurs on treatment of (**10a**)[9] and (**10b**)[7] with (**5**), giving (**11**) after acid hydrolysis,[10] and a related sequence is involved in the synthesis of (**11**) from triphenyl phosphate and (**5**).[1a]

While (**11**) reacts with (**5**) to give the stable hexacoordinate species (**3a**),[1a,4] all attempts to obtain the similar species (**3b**) by reaction of (**9a**) with (**5**) in ether or tetrahydrofuran failed. Aqueous work-up of the reaction mixture always gave (**12a**); in contrast, (**3a**) is stable in water. Work-up with D_2O gave (**12a**) containing one atom of deuterium in the aromatic portion.¶ Thus (**9a**) reacts with (**5**) to give (**12b**), but further closure to (**3b**) probably does not occur. Direct spectroscopic detection of (**3b**) or (**12b**) was not possible owing to solubility problems. Since penta-arylphosphoranes are rather poor Lewis acids,[11] the electron-releasing and bulky homocubane system either destabilizes (**3b**) and prevents its isolation, or prevents its formation completely, the reaction stopping at (**12b**). (**12a**) was identified by independent synthesis from (**9a**) and 2-lithiobiphenyl (62%; m.p. 171—172·5°),¶ and was identical to the material obtained above.



(**12**) **a**; R = biphenyl-2-yl
b; R = 2′-lithiobiphenyl-2-yl
c; R = H
d; R = Me



(**13**)

The salt (**11**) also forms the stable, isolable hydride (**1b**) with $LiAlH_4$;[7] (**9a**) reacts readily with $LiAlH_4$ in ether at room temperature to give after isolation not (**12c**), but instead a white insoluble substance formulated as a complex of (**13**) and AlH_3. This assignment is based on the presence of an i.r. band at 1785 cm^{-1}, characteristic of the Al–H bond in co-ordinated AlH_3,[7] and a band at 695 cm^{-1}, characteristic of a monosubstituted benzene. Reaction of this substance with 6N-HCl gives the free phosphine (**13**) (50% overall, m.p. 67—68°).¶,†† Thus (**12c**), once it is formed, rearranges readily to the phosphine (**13**), which forms an adduct with AlH_3. The analogous rearrangement of (**1b**) occurs only to a small extent.[7]

That there is no inherent destabilization of other pentavalent derivatives of (**9**) is also shown by the synthesis of (**12d**) from (**9a**) and MeLi (71%; m.p. 93—94°).¶

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¶ ^{1}H n.m.r. and mass spectrum are in accord with the assigned structure.

†† Analyses for C, H, and P were satisfactory.

[1] (a) D. Hellwinkel, *Chem. Ber.*, 1965, **98**, 576; (b) M. Schlosser, T. Kadibelban, and G. Steinhoff, *Annalen.*, 1971, **743**, 25.

[2] (a) T. J. Katz and E. W. Turnblom, *J. Amer. Chem. Soc.*, 1970, **92**, 6701; (b) E. W. Turnblom and T. J. Katz, *ibid.*, 1971, **93**, 4065.

[3] *Cf.* methyltetraphenylphosphorane: D. Seyferth, W. B. Hughes, and J. K. Heeren, *J. Amer. Chem. Soc.*, 1965, **87**, 2847, 3467.

[4] D. Hellwinkel, *Chem. Ber.*, 1966, **99**, 3628, 3642, 3660, 3668; D. Hellwinkel and S. F. Mason, *J. Chem. Soc.* (*B*), 1970, 640.

[5] D. Hellwinkel and H. Wilfinger, *Chem. Ber.*, 1970, **103**, 1056.

[6] B. C. Chang, D. B. Denney, R. L. Powell, and D. W. White, *Chem. Comm.*, 1971, 1070.

[7] D. Hellwinkel, *Chem. Ber.*, 1969, **102**, 528.

[8] T. J. Katz, Jo C. Carnahan, jun., G. M. Clarke, and N. Acton, *J. Amer. Chem. Soc.*, 1970, **92**, 734.

[9] G. Wittig and E. Kochendoerfer, *Chem. Ber.*, 1964, **97**, 741; G. Wittig and A. Maercker, *ibid.*, p. 747.

[10] Acyclic arylphosphine oxides do not give phosphonium salts with aryl-lithium compounds. See G. Wittig and H. J. Cristau, *Bull. Soc. chim. France*, 1969, 1293.

[11] D. Hellwinkel and H. J. Wilfinger, *Tetrahedron Letters*, 1969, 3423.