

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

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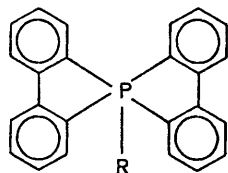
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Summary While the spirophosphonium salt (**11**) forms the stable, isolable hexaco-ordinate species (**3a**) with 2,2'-dilithiobiphenyl, analogous reaction of the salt (**9a**) does not give an isolable alkyl hexaco-ordinate species; the homocubyl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

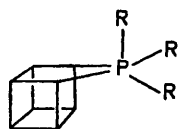
stability.⁷ We report that this alkyl ring destabilizes (**3b**) and (**12c**) to such an extent that they cannot be isolated.

Addition of an ether-benzene solution of (**4**)⁸ to an ether solution of 2,2'-dilithiobiphenyl (**5**)[‡] gave, after hydrolysis

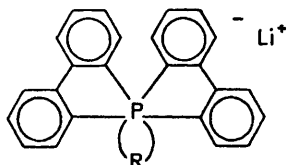
THE occurrence of stable alkylphosphoranes in which phosphorus atom is incorporated into a small carbocyclic system has been observed in only two types of compounds, the bisbiphenylenephosphoranes (**1a**)¹ and the homocubyl phosphoranes (**2**).² Unlike their acyclic analogues,³ these substances are 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



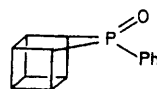
(1) a; R = Me or Buⁿ
b; R = H



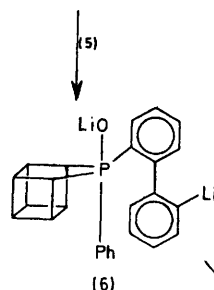
(2) R = Ph or Me



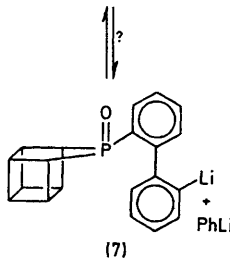
(3) a; R = biphenyl 2,2'-diyl
b; R = homocubyl



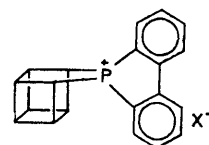
(4)



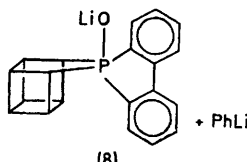
(6)



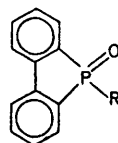
(7)



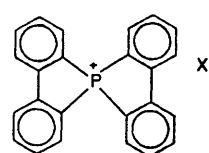
(9) a; X = Br
b; X = I



(8)



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



(11)

stable hexa-aryloxy⁵ and hexa-alkoxy⁶ 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

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**)

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† Prepared from 2,2'-di-iodobiphenyl in ether with BuⁿLi in hexane.

§ ¹H n.m.r. spectrum (CDCl₃-CD₃OD, Me₄Si): 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 H₂O₂ 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 D₂O 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)

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.

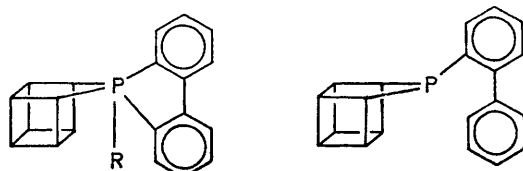
The salt (11) also forms the stable, isolable hydride (1b) with LiAlH₄;⁷ (9a) reacts readily with LiAlH₄ in ether at room temperature to give after isolation not (12c), but instead a white insoluble substance formulated as a complex of (13) and AlH₃. This assignment is based on the presence of an i.r. band at 1785 cm⁻¹, characteristic of the Al-H bond in co-ordinated AlH₃,⁷ 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 AlH₃. The analogous rearrangement of (1b) occurs only to a small extent.⁷

That there is no inherent destabilization of other penta-valent derivatives of (9) is also shown by the synthesis of (12d) from (9a) and MeLi (71%; m.p. 93–94°).[¶]

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

(13)

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

[¶] ¹H 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.