

Formation of a Carbon–Phosphorus Bond between a C–F Compound and Phosphorus(III) Fluorides: a Fluorine Analogue of the Kinnear–Perren Reaction Furnishing 1-Adamantylfluorophosphoranes

By JÖRN-VOLKER WEISS and REINHARD SCHMUTZLER*

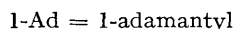
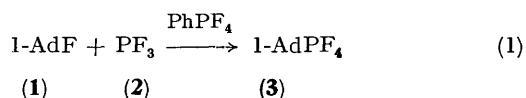
(Lehrstuhl B für Anorganische Chemie der Technischen Universität, 3300 Braunschweig, Pockelsstrasse 4, Germany)

Summary Insertion of phosphorus trifluoride into the C–F bond of 1-adamantyl fluoride in the presence of phenyltetrafluorophosphorane leads to formation of the otherwise inaccessible 1-adamantyltetrafluorophosphorane; the formation of a carbon–phosphorus bond is also observed

in the systems 1-adamantyl fluoride– Bu^tPF_2 – PhPF_4 and 1-adamantyl fluoride–1-adamantyl difluorophosphine– PhPF_4 from which the new compounds 1-adamantyl-*t*-butyltrifluorophosphorane and bis-(1-adamantyl)trifluorophosphorane, respectively, are obtained.

THE condensation of alkyl chlorides with phosphorus trichloride and aluminium chloride is a major preparative method for creating phosphorus-carbon bonds;¹ the adducts thus obtained serve as versatile intermediates in organophosphorus chemistry.² In contrast, no such reaction involving a carbon-fluorine compound and a P^{III} fluoride has yet been reported.

We have found that 1-adamantyltetrafluorophosphorane (3) is obtained in 80% yield when 1-adamantylfluoride (1) and PF₃ (2) in the presence of PhPF₄ are kept in a sealed tube for 5 days at room temperature. In a separate experiment, involving the same quantities of (1) and (2) under identical conditions, but in the absence of PhPF₄, only the formation of a trace of 1-adamantylphosphonic difluoride³ [19F n.m.r. spectroscopy; the phosphonic difluoride probably originates from partial hydrolysis of (3) formed under these conditions. It appears reasonable to formulate the reaction [equation (1)] as resembling a Kinnear-Perren reaction¹ [equation (2)].



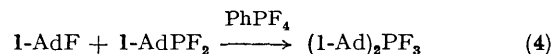
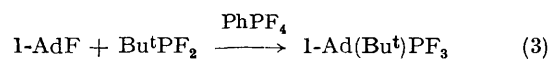
While in the Kinnear-Perren reaction, a stable complex of the chlorophosphorane with the aluminium halide is obtained, the fluorophosphorane (3) is recovered directly in the adamantyl fluoride-PF₃ reaction. PhPF₄ is believed to function as a Lewis acid sufficiently strong to activate the C-F bond in (1) but too weak to form an adduct with (3)

stable at room temperature. Compound (3) is a volatile solid (m.p. 43 °C; b.p. 77 °C at 2 Torr).

It is worth noting that fluorination of 1-adamantyl phosphonic difluoride³ with SF₄ has failed to give the tetrafluorophosphorane, although the fluorination of phosphoryl compounds with SF₄⁴ is an otherwise generally applicable route for the synthesis of fluorophosphoranes.⁵

Identification of (3) was straightforward from ³¹P and ¹⁹F n.m.r. data: δ_F +35.6 p.p.m. (ext. H₃PO₄); δ_F +59.9 p.p.m. (int. CCl₃F); J_{PF} 1040 Hz. The n.m.r. spectra are typical of a tetrafluorophosphorane undergoing pseudorotation;⁵ the appearance of the ¹⁹F n.m.r. spectrum was unchanged at temperatures down to -100 °C, and no effect of the bulky adamantyl substituent on the pseudorotation process was observed. The tetrafluorophosphorane (3) was characterized further by mass spectroscopy, the most intense fragment being the adamantyl cation (*m/e* 135). The PF₄ fragment (*m/e* 107) was also intense, while a molecular ion, as for other tetrafluorophosphoranes,⁶ was absent.

This preparative method has been extended to reactions of (1) with other P^{III} fluorides; the examples in equations (3) and (4) are typical.



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¹ A. M. Kinnear and E. A. Perren, *J. Chem. Soc.*, 1952, 3437.

² P. C. Crofts, *Quart. Rev.*, 1958, 12, 341; M. Fild and R. Schmutzler, in 'Organic Phosphorus Compounds,' eds., G. M. Kosolapoff and L. Maier, vol. 4, pp. 75 ff., Wiley-Interscience, New York, 1972; M. Fild, R. Schmutzler, and S. C. Peake, *ibid.*, pp. 155 ff.

³ J. V. Weiss and R. Schmutzler, unpublished work.

⁴ W. C. Smith, *J. Amer. Chem. Soc.*, 1960, 82, 6176.

⁵ Cf., for example, R. Schmutzler in 'Halogen Chemistry,' ed., V. Gutmann, vol. 2, p. 31, Academic Press, London and New York, 1967.

⁶ T. A. Blazer, I. K. Gregor, and R. Schmutzler, *Z. Naturforsch.*, 1969, 24b, 1081.