Preparation and *X*-Ray Crystal Structure of Diphenylbenzoyldifluorophosphorane

By SUSANNE NEUMANN, DIETMAR SCHOMBURG,* GERHARD RICHTARSKY, and REINHARD SCHMUTZLER*
(*Lehrstuhl B für Anorganische Chemie der Technischen Universität, Pockelsstr.* 4, 3300 *Braunschweig, Germany*)

Summary The first acylfluorophosphorane, $Ph_2PF_2[C(:O)Ph]$, has been isolated from the reaction of Ph_2POEt with benzoyl fluoride; the *X*-ray structure determination proved that the acyl group occupies an equatorial position at trigonal-bipyramidal phosphorus.

IT has been observed that one of the main products of the reaction of benzoyl fluoride with dimethylphenylphosphine (in the presence of CCl_3F)[1] is the known difluorophosphorane, $PhMe_2PF_2$.[2] We have subsequently studied the reactions of other phosphorus(III) compounds with benzoyl fluoride with a view to obtaining the corresponding phosphorus(V) difluorides. In the case of ester derivatives of the type Ph_2POR [$R = CMe_2CN$ (**1**); $R = Et$ (**2**)] the reaction took an unexpected course in that the n.m.r. spectra of the reaction mixture indicated formation of the same compound $Ph_2PF_2[C(:O)Ph]$ (**3**) in both cases,† *i.e.*, the group RO is displaced. A closer study of the reaction of (**2**) with benzoyl fluoride (allowed to react in a 1 : 1 molar ratio at room temperature) revealed transient formation of Ph_2PF. Eventually, white crystals (m.p. 96—98 °C) were precipitated which analysed for $Ph_2PF_2[C(:O)Ph]$ (**3**), yield 45%. The mass spectrum of (**3**) did not exhibit the molecular ion at *m/e* 328; the base peak (*m/e* 225) corresponds to $M - [PhC(:O)]$. An i.r. absorption at 1,660 cm^{-1} is believed to be due to the C=O vibration of the benzoyl group.

The observed formation of (**3**) may be rationalized as occurring in two steps [equations (1) and (2)].‡

$$\underset{(\mathbf{2})}{Ph_2POEt} + PhC(:O)F \rightarrow Ph_2PF + PhC(:O)OEt \qquad (1)$$

$$Ph_2PF + PhC(:O)F \rightarrow \underset{(\mathbf{3})}{Ph_2PF_2[C(:O)Ph]} \qquad (2)$$

Formation of (**3**) had previously been suggested in the reaction of benzoyl fluoride with the P^{III} amide, Ph_2PNHPr^n,[3]§ but the compound had not been isolated. In the present work we have isolated and fully characterized

---

† N.m.r. data for (**3**): ^{19}F, δ_F (CCl_3F) 58·8 p.p.m. (d, J_{PF} 705 Hz); ^{31}P, δ_P (H_3PO_4, 85%) 61·0 p.p.m. (1 : 2 : 1 t).

‡ Formation of ethyl benzoate, $PhC(:O)OEt$, has been established by g.l.c.

§ The presence of (**3**) was suggested, based on n.m.r. data of a reaction mixture.

what we believe to be the first acyl-substituted fluorophosphorane and, probably, the first acylphosphorane.

The characterization of (**3**) included a single crystal *X*-ray structure determination.¶ The structure of (**3**) (Figure) may be described as a distorted trigonal bipyramid with the fluorine atoms in axial and the benzoyl and phenyl groups in equatorial positions. The plane of the carbonyl function is twisted only 3·1° out of the phosphorus equatorial plane; for the benzoylic phenyl ring the angle is 13·9°. In contrast, the two phosphorus-bonded benzene rings are twisted by 71·4 and 84·6° away from the phosphorus equatorial plane which leads to extremely short non-bonding distances between the fluorine atoms and the *ortho*-hydrogens of the two rings (2·012—2·263 Å, compared to the sum of the van der Waals radii, 2·55 Å[4]). By these interactions the fluorine atoms are bent away from the two benzene rings attached to phosphorus in the direction of the benzoyl group (C_{phenyl}–P–F angles of 92·2—93·4°, compared to $C_{benzoyl}$–P–F angles of 84·7 and 85·6°). The phosphorus–fluorine bond lengths [1·661(2) and 1·669(2) Å] are intermediate between those in Me_3PF_2 (gas phase electron diffraction)[5] and $(C_6F_5)_3PF_2$ (*X*-ray),[6] reflecting the electronegativity of the three carbon substituents at phosphorus. The phosphorus–benzoyl bond [1·868(4) Å] is considerably longer than the two phosphorus–phenyl bonds [1·806(3) and 1·812(3) Å] which are comparable to those found in $(C_6F_5)_3PF_2$ [1·819(4) Å].

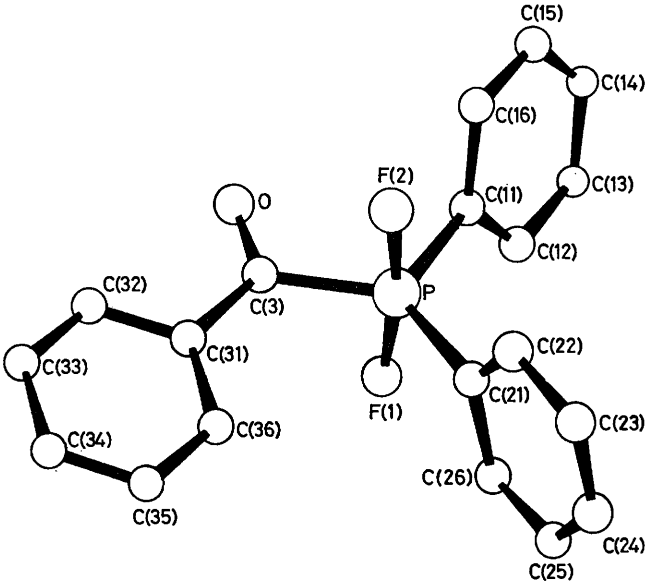

FIGURE. The structure of $Ph_2PF_2[C(:O)Ph]$ (**3**).

(*Received*, 6*th July* 1978; *Com.* 717.)

¶ *Crystal data:* (**3**), monoclinic, space group $P2_1/c$, $a = 10·368(4)$, $b = 11·098(5)$, $c = 14·926(14)$ Å, $\beta = 107·45(5)°$, $Z = 4$, D_c 1·33 g cm^{-3}.

The intensity data were collected on a Stoe diffractometer using Mo-$K\alpha$ radiation by the θ–2θ scan technique at a scan rate of 3° min.$^{-1}$ 2840 unique reflections were measured in the range of $2\theta \leqslant 50°$. The structure was determined by Patterson and Fourier techniques (SHELX-76, G. M. Sheldrick). Least-square refinement using 1957 reflections with $I \geqslant 2\sigma(I)$ led to $R = 0·050$ and $R_G = \Sigma w(F_o - F_c)^2/\Sigma wF_o{}^2]^{0·5}$ 0·061.

The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

[1] G. Richtarsky, unpublished observations.
[2] G. S. Reddy and R. Schmutzler, *Z. Naturforsch.*, 1970, **25b**, 1199.
[3] C. Brown, M. Murray, and R. Schmutzler, *J. Chem. Soc.* (*C*), 1970, 878.
[4] L. Pauling, 'Die Natur der chemischen Bindung,' Verlag Chemie, Weinheim/Bergstrasse, 1968, p. 249.
[5] H. Yow and L. S. Bartell, *J. Mol. Struct.*, 1973, **15**, 209.
[6] W. S. Sheldrick, *Acta Cryst.*, 1975, **B31**, 1776.