

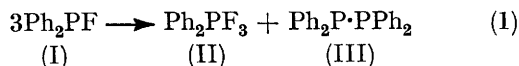
Fluorodiphenylphosphine

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Diphenylphosphinous and phenylphosphonous amides both react with benzoyl fluoride to give the corresponding carboxy amide and the mono- or di-fluorophosphine. The difluorophosphine is stable, whereas the monofluorophosphine, which can also be prepared by the action of sodium fluoride on chlorodiphenylphosphine in acetonitrile, disproportionates to give the trifluorophosphorane and tetraphenyldiphosphine. The title compound also reacts with benzoyl fluoride to give benzoyldifluorodiphenylphosphorane.

ONE of us has recently¹ described the preparation of fluorobis(pentafluorophenyl)phosphine by the reaction of the corresponding bromophosphine with sodium fluoride in boiling acetonitrile. We report here the preparation of fluorodiphenylphosphine both from chlorodiphenylphosphine by that method, and from phenyl-*N*-*n*-propylphosphinous amide by reaction with benzoyl fluoride.

A mixture of products was obtained when chlorodiphenylphosphine was treated with sodium fluoride in boiling acetonitrile for 4 hr. The ¹⁹F and ³¹P n.m.r. spectra of this mixture revealed signals which were readily assigned† to fluorodiphenylphosphine (I). The ¹⁹F spectrum exhibited a doublet, δ_F +202 p.p.m. (upfield of CCl₃), *J*_{FF} 905 Hz, and the ³¹P spectrum a low-field doublet, δ_P -168 p.p.m. (downfield of H₃PO₄), *J*_{PP} 905 Hz. Resonances due to the known trifluorodiphenylphosphorane (II)² and tetraphenyldiphosphine (III)^{3,4} were also detected. The ratio of (I) to (II) was increased from 1:3 to 1:2 when the reaction time was reduced to 1 hr. Compounds (II) and (III) are the products expected from disproportionation of (I), according to equation (1), a process which has been observed^{1,5} for other fluorophosphines.



A milder method of synthesising (I) was therefore

† The corresponding data¹ for (C₆F₅)₂PF are: δ_F +216.6 p.p.m., *J*_{FF} 1002 Hz; δ_P -136.0 p.p.m., *J*_{PP} 1000 Hz.

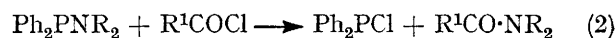
¹ M. Fild and R. Schmutzler, *J. Chem. Soc. (A)*, 1969, 840.

² E. L. Muettterties, W. Mahler, and R. Schmutzler, *Inorg. Chem.*, 1963, **2**, 613.

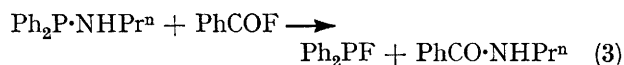
³ M. V. Crutchfield, C. H. Dungan, J. H. Letcher, V. Mark, and J. R. Van Wazer, *Topics in Phosphorus Chem.*, 1967, **5**, 227.

⁴ W. Kuchen and H. Buchwald, *Chem. Ber.*, 1958, **91**, 2871.

sought. Tervalent phosphorus-nitrogen compounds react with most derivatives of carboxylic acids to give amides,⁶ and in particular, acid chlorides give high yields of amides together with the corresponding chlorophosphines⁷ [equation (2)]. It was expected,



therefore, that the use of an acid fluoride would give fluorophosphines, and this expectation was realised. The weakly exothermic reaction of benzoyl fluoride with diphenyl-*N*-*n*-propylphosphinous amide [equation (3)] gave *N*-*n*-propylbenzamide and almost pure (I) (>90%).



The ¹⁹F n.m.r. spectrum of the reaction mixture, taken within 45 min. of the time of mixing, consisted mainly of a sharp doublet at high field, due to Ph₂PF. The ³¹P n.m.r. spectrum also corresponded to that of Ph₂PF prepared from Ph₂PCl.

Samples of diphenylfluorophosphine prepared from benzoyl fluoride slowly disproportionated to give (II) and (III), according to equation (1). Furthermore,

⁵ F. Seel, K. Rudolph, and W. Gombler, *Angew. Chem.*, 1967, **79**, 686; F. Seel and K. Rudolph, *Z. anorg. Chem.*, 1968, **363**, 233.

⁶ S. Goldschmidt and H. L. Krauss, 'Newer Methods of Preparative Organic Chemistry,' vol. 2, p. 31; R. Burgada, *Bull. Soc. chim. France*, 1963, 2335; V. P. Evdakov and E. I. Alipova, *Zhur. obshchei Khim.*, 1965, **35**, 1584; L. I. Mirzakh, V. P. Evdakov, and L. Y. Sandalova, *ibid.*, p. 1875; M. I. Kabachnik, T. A. Mastryukova, and A. E. Shipov, *ibid.*, 1963, **33**, 320; K. A. Bilevich, V. P. Evdakov, and E. K. Shlendova, *ibid.*, p. 3772; J. F. Brazier, R. Wolf, and R. Burgada, *Bull. Soc. chim. France*, 1966, 2109; M. P. Savage and S. Trippett, *J. Chem. Soc. (C)*, 1966, 1842.

⁷ R. F. Hudson, C. Brown, and R. J. G. Searle, unpublished work.

unstable and polymerised unless all traces of ammonium fluoride were removed before distillation. This was done by cooling the mixture in a refrigerator before filtration to remove inorganic material. The ^{19}F n.m.r. spectrum consisted of a sharp singlet, δ_{F} -18.5 p.p.m. (CFCl_3 , calc.).

Diphenyl-*N*-*n*-propylphosphinous amide was prepared from *n*-propylamine and chlorodiphenylphosphine, as described by Payne and his co-workers,¹³ as a colourless oil, b.p. $140^\circ/0.3$ mm., δ_{P} -40.5 p.p.m. *NNN'*-Tetramethylphenylphosphonous amide was similarly prepared from dichlorophenylphosphine and dimethylamine; b.p. $70^\circ/0.8$ mm., δ_{P} -101.5 p.p.m. (lit.,³ -100.3 p.p.m.).

Diphenylphosphinyl fluoride was made by dissolving diphenylphosphinyl chloride (2.0 g.) in dry benzene (10 ml.) and heating the solution under reflux with dry ammonium fluoride (1 g.) for 2.5 hr. The solid material was filtered off and the filtrate was distilled to give an oil (1.5 g.), b.p. $140^\circ/0.05$ mm., δ_{P} -39.2 (d, J_{PF} 1040 Hz; 70%) and -42.5 (s) p.p.m. [lit.^{14,3} values for $\text{Ph}_2\text{P}(\text{O})\text{F}$ and $\text{Ph}_2\text{P}(\text{O})\text{Cl}$ are -40 (1020 Hz) and -42.7 p.p.m., respectively], δ_{F} $+73$ p.p.m. (CFCl_3 , calc.) (J_{PF} 1025 Hz).

Reaction between Benzoyl Fluoride and NNN'-Tetramethylphenylphosphonous Amide.—Benzoyl fluoride (1.1 g.; freshly distilled) was treated at ca. 5° with the amide (0.9 g.) in an 8.5 mm. n.m.r. tube. The weakly exothermic reaction gave a slight precipitate which redissolved at room temperature. A sample of the mixture was placed in a second 4.6 mm. n.m.r. tube and the first tube was sealed under reduced pressure.

The ^{19}F n.m.r. spectrum recorded within 45 min. of mixing consisted solely of three groups of signals: δ_{F} (from CFCl_3 , calc.) -18.5 (s, PhCOF), $+93.5$ (d, J_{PF} 1169 Hz, PhPF_2^3), and $+129.5$ [d, J_{PF} 982 Hz, $\text{PhP}(\text{NMe}_2)\text{F}^9$] p.p.m. The doublets had an intensity ratio of ca. 2 : 1 respectively 1 hr. after mixing, but this ratio decreased with time, as did the intensity of the benzoyl fluoride signal. Within 3 hr. the benzoyl fluoride signal had disappeared completely, and the $\text{PhP}(\text{NMe}_2)\text{F}$ doublet had been reduced to ca. 8% of the total signal intensity, corresponding to the slight excess of $\text{PhP}(\text{NMe}_2)_2$ over a strict 1 : 2 molar ratio used in this experiment. The structural assignments were confirmed by the ^{31}P n.m.r. spectrum, which consisted of five low-field lines: a 1 : 2 : 1 triplet at δ_{P} -208 (J_{PF} 1170 Hz, $\text{PhPF}_2^{10,11}$) and a faint doublet at δ_{P} -158 p.p.m. [J_{PF} 994 Hz, to $\text{PhP}(\text{NMe}_2)\text{F}^9$]. The spectrum remained unchanged for 24 hr. A further equivalent of benzoyl fluoride was then added and the spectrum was examined at various time intervals. The only changes noted were due to conversion of the remaining $\text{PhP}(\text{NMe}_2)\text{F}$ into PhPF_2 ; no further reactions had taken place even after several weeks at 35° .

*Reaction between Benzoyl Fluoride and Diphenyl-*N*-*n*-propylphosphinous Amide.*—Benzoyl fluoride (1 g.) was treated at ca. 10° with the amide (2 g.) in a ^{31}P n.m.r. tube. The mildly exothermic reaction again gave a fine crystalline precipitate which redissolved on warming. The mixture was divided and dealt with as in the previous experiment.

The ^{19}F n.m.r. spectrum (0.75 hr. after mixing) consisted of a sharp doublet ($>90\%$) due to Ph_2PF and a doublet of doublets ascribed to $\text{Ph}_2\text{PF}_2\text{H}$, together with some very weak signals. No changes were noted during 4 hr.

The ^{31}P spectrum after ca. 10 hr. consisted of a low-field doublet (ca. 80%) and a complex pattern of signals between -40 and -80 p.p.m. Within 24 hr. the intensity of the doublet had dropped to 50% of the total, and a

pattern had begun to emerge in the region around $+16$ p.p.m. From the published¹⁴ chemical shift and coupling constant data for Ph_2PF , a theoretical spectrum of this material was constructed and found to correspond reasonably well with the more prominent lines in the ^{31}P spectrum of the reaction mixture. A prominent singlet at $+16$ p.p.m. was also clearly discernible (lit.³ value for Ph_2PFPh_2 , $+15.2$ p.p.m.).

After 4 days the ^{19}F n.m.r. spectrum indicated the presence of Ph_2PF (38%), $\text{Ph}_2\text{P}(\text{O})\text{F}$ (40%; spectrum identical with that of authentic sample), and the compound thought to be $\text{Ph}_2\text{PF}_2\text{H}$. The relative molar ratios of $\text{Ph}_2\text{P}(\text{O})\text{F}$ and $(\text{Ph}_2\text{PF} + \text{PhPF}_2\text{H})$ correspond reasonably with those for Ph_2PF_3 and Ph_2PF in the (sealed) ^{31}P n.m.r. tube.

In a further experiment benzoyl fluoride (1.2 g.) was added dropwise, under nitrogen, to $\text{Ph}_2\text{PNHPr}^n$ (2.4 g.). Colourless crystals, identified as *N*-*n*-propylbenzamide (i.r. spectrum identical with that of an authentic specimen), precipitated from the cooled mixture. The ^{19}F n.m.r. spectrum of this mixture consisted of a sharp, high-field doublet with only a trace of other signals. Distillation gave a mixture of P-F compounds in the early fractions and some amide in the last fraction (more amide was isolated from the pot residue). The early fractions, b.p. $90-95^\circ/0.04$ mm., solidified, and a solid, m.p. 118° , with a simple i.r. spectrum was isolated from this material. This was identified as tetraphenyldiphosphine by the yellow colour which it gave with pyridine and by its spectral properties⁴ (lit.,⁴ m.p. 120.5°). The ^{19}F n.m.r. spectrum of the early fractions of the distillate (CCl_4 solution) showed the presence of Ph_2PF , ' $\text{Ph}_2\text{PF}_2\text{H}$ ' and Ph_2PF_3 .² [δ_{F} (*ax*) (CFCl_3 , calc.) $+33.5$ p.p.m. (2F, dd, J_{PF} 847, J_{FF} 39 Hz) and δ_{F} (*eq*) $+79$ p.p.m. (1F, dt, J_{PF} 987, J_{FF} 39 Hz)]. Only a trace of $\text{Ph}_2\text{P}(\text{O})\text{F}$ was detected.

In some experiments the ^{19}F n.m.r. spectrum, in addition to the doublet due to Ph_2PF , contained a second doublet, δ_{F} (CFCl_3 , calc.) $+56$ p.p.m. (J_{PF} 733 Hz). In one case, when a $\text{PhCOF}:\text{Ph}_2\text{PNHPr}^n$ ratio of 2 : 1 was used, this signal increased in intensity during 2 days, and this increase was accompanied by a decrease in the intensity of the Ph_2PF and PhCOF signals. Reaction of Ph_2PF with PhCOF was confirmed as follows: benzoyl fluoride and $\text{Ph}_2\text{PNHPr}^n$ were mixed in a molar ratio of ca. 1.5 : 1 to give a mixture of products, the ^{19}F n.m.r. spectrum of which consisted largely of the doublets at $+202$ and $+56$ p.p.m. This spectrum remained essentially unchanged for several days at 0° , but on addition of an excess of PhCOF , the doublet at $+202$ p.p.m. disappeared within 12 hr. and the doublet at $+56$ p.p.m. increased in intensity by a corresponding amount. A decrease in the intensity of the PhCOF signal was also observed. The product is considered to be benzoyldifluorodiphenylphosphorane (VI). Assignment of the five-coordinate structure is supported by the ^{31}P spectrum, which has a 1 : 2 : 1 triplet, δ_{P} $+61$ p.p.m. (J_{PF} 730 Hz).

Reaction of Chlorodiphenylphosphine with Sodium Fluoride.—A mixture of chlorodiphenylphosphine (0.1 mole) and sodium fluoride (0.5 mole) was boiled with stirring in acetonitrile (100 ml.) for 4 hr., in the absence of air and moisture. The cooled solution was filtered and the solvent was removed to give a mixture of liquid and solid. The ^{19}F n.m.r. spectrum of the liquid revealed four groups of

¹³ G. Ewart, A. P. Lane, J. McKechnie, and D. S. Payne, *J. Chem. Soc.*, 1964, 1543.

¹⁴ R. Schmutzler, *J. Chem. Soc.*, 1964, 4551.

signals; a doublet, attributed to (I); a doublet of doublets and a doublet of triplets, attributed ² to (II); a doublet attributed to (IV); and a doublet of doublets, attributed to (V).

The ³¹P n.m.r. spectrum of the product showed a doublet due to (I), a doublet ¹⁴ due to (IV), a singlet due to (III), and a complex pattern of peaks in the region 0 to +100 p.p.m. ascribed to (II) and (V). The molar ratio of (II) to (I) was *ca.* 3 : 1, indicating that at least 90% of (I) had disproportionated according to equation (1).

The residue from the filtration was extracted with benzene; the ³¹P spectrum of the extract showed a single peak at +16.0 p.p.m. due to (III).

The experiment was repeated with only 1 hr. boiling in acetonitrile. After this time the ³¹P n.m.r. spectrum showed that almost all of the chlorodiphenylphosphine had been consumed, and the ratio of (I) to (II) was shown by ¹⁹F n.m.r. measurements to be *ca.* 1 : 2, corresponding to *ca.* 60% disproportionation.

Note Added in Proof: Fluorodiphenylphosphine was further characterised as the imine, Ph₂P(:NPh)F, by its reaction with phenyl azide. The product from this reaction was identified by comparison with an authentic sample, prepared from diphenyltrifluorophosphorane and *N*-phenylhexamethyldisilazane, [PhN(SiMe₃)₂].

EXPERIMENTAL

Preparation of N-Phenyldiphenylfluorophosphine Imine Imine.—Diphenyltrifluorophosphorane (12.1 g., 0.05 mole) and *N*-phenylhexamethyldisilazane (11.9 g., 0.05 mole) were heated with stirring under nitrogen to 120°, at which temperature a gas was evolved. This gas was collected in a dry ice-acetone trap, and identified as Me₃SF by its ¹H n.m.r. spectrum, yield, after 18 hrs. at 140°, 6.0 g. (33%). The liquid residue in the flask solidified on cooling, and was recrystallised from toluene to give Ph₂P(:NPh)F, m.p. 236–238° (Found: C, 73.1; H, 5.3; N, 4.5. C₁₈H₁₅FNP requires C, 73.2; H, 5.1; N, 4.7%). The ¹⁹F n.m.r. spectrum exhibited a doublet, δ_F + 72.7 p.p.m., *J*_{PF} 1109 Hz.

Reaction of Fluorodiphenylphosphine with Phenyl Azide.—Nitrogen was evolved when a filtered solution of the fluorophosphine in acetonitrile was run into a solution of phenyl azide in the same solvent. Removal of the solvent gave an oil whose ¹⁹F n.m.r. spectrum indicated the presence of Ph₂P(:NPh)F, (δ_F + 74.1 p.p.m., *J*_{PF} 1094 Hz) together with Ph₂PF₃ and Ph₂P(:O)F. The ³¹P n.m.r. spectrum was also consistent with the presence of Ph₂P(:NPh)F.

We thank Loughborough University of Technology and the S.R.C. for post-doctoral research fellowships (to M. M. and C. B., respectively).

[9/672 Received, April 25th, 1969]