Tetraphenylphosphonium Hydrogendifluoride: a New Source of Fluoride Ion

Stephen J. Brown and James H. Clark*
Department of Chemistry, University of York, Heslington, York YO1 5DD, U.K.

Tetraphenylphosphonium hydrogendifluoride, a soluble and thermally stable reagent, acts as a source of fluoride ion in a variety of organic reactions.

Ionic fluorides are among the most important and versatile reagents in organic chemistry, being widely used as sources of fluorine for the preparation of organofluorine compounds[1,2] and as reagents for a variety of base-assisted reactions.[3,4] The two most common classes of fluorides in general use today are the alkali metal fluorides and the quaternary ammonium fluorides. While many fluoride reagents based on these compounds have been developed, their applications are inevitably hampered by the familiar problems associated with fluorides such as poor solubility, hygroscopicity, or low thermal stability.[3] As part of our programme of research into the development and applications of fluorophosphoranes[5] we have discovered a new and surprisingly powerful fluoride ion source, tetraphenylphosphonium hydrogendifluoride, Ph_4PHF_2.

We recently reported the preparation of at least three different forms of tetraphenylfluorophosphorane from tetraphenylphosphonium bromide *via* the hydrogendifluoride hydrate, $Ph_4P^+HF_2^-\cdot H_2O$.[5] In its original form, the hydrogendifluoride salt gave an i.r. spectrum consistent with the presence of a simple, undistorted HF_2^- anion.[5] Exhaustive drying of this salt at moderate temperatures (typically 50 °C at 0.1 mmHg) however, results in significant changes in the i.r. spectrum, most notably the splitting and weakening of the characteristic HF_2^- band at 1208 cm^{-1}. The dried material analyses as Ph_4PHF_2. Prolonged exposure to the atmosphere results in the formation of the monohydrate, $Ph_4PHF_2\cdot H_2O$ which gives an i.r. spectrum identical to that of the original, undried material.[5] The observed changes in the i.r. spectrum are reminiscent of those observed for other distorted HF_2^- systems[6] and lead us to believe that we have obtained a form of hydrogendifluoride containing a $P^+ \cdots F^-$ interaction similar to that observed in Ph_4PF.[5]

The possible distortion of the normally unreactive HF_2^- ion in Ph_4PHF_2 together with the desirable properties of the reagent (ease of preparation and drying, and high solubility) leads to its use as an *in situ* F^- source. Normal hydrogendifluorides such as those of the alkali metals will only behave as F^--like reagents towards highly activated electrophiles such as 2,4,6-trinitrochlorobenzene.[7] Typical F^- reactions with the dried hydrogendifluoride proved to be very successful (Table 1) although reaction stoicheiometry proved to be less than straightforward. In a typical reaction, equimolar amounts of dried Ph_4PHF_2 and $PhCH_2Br$ reacted together in MeCN at 52 °C. The amount of halogen exchange levelled off at 50% (by g.l.c.) after *ca.* 2.5 h. Only by using a twofold excess of the hydrogendifluoride could quantitative fluorination be achieved. Analysis of the product mixture revealed the presence of $Ph_4PH_2F_3$ as well as Ph_4PBr and $PhCH_2F$, showing that one molecule of HF is scavenged from an HF_2^- anion by another HF_2^- anion. The importance of reagent drying is illustrated in Figure 1 where it can be seen that the presence of 1 mol equiv. water, while not stopping the reaction, significantly reduces the rate of reaction. In at least one reaction system investigated so far, that of the oligomerisation of hexafluoropropene,[8] as little as 0.6 mol equiv. water was sufficient to stop the reaction completely.

The reactions given in Table 1 were chosen to demonstrate the F^--like behaviour of Ph_4PHF_2. Thus we have successfully employed the reagent in reactions employing F^- as a nucleophile (halogen exchange reaction and a fluoride-catalysed fluorocarbon oligomerisation) and as a base or hydrogen bond electron donor[3] (in alkylation and fluoride-catalysed Michael reactions). In all the examples reported, the reactivity of our reagent is comparable to more conventional F^- reagents. The rate of reaction of Ph_4PHF_2 with $PhCH_2Br$ ($t_{\frac{1}{2}}$ = 25 min at 52 °C) for example, can be compared to that achieved with KF–18-crown-6 ($t_{\frac{1}{2}}$ = 11.5 h at 82 °C)[9] using an F^- concentration of 0.12 M in acetonitrile in both cases.

In summary, anhydrous Ph_4PHF_2 is an extremely promising F^- source that is potentially useful in many areas of organic chemistry. The reagent is very soluble in polar aprotic solvents

Table 1. Reactions using Ph_4PHF_2.[a]

Reaction type	Substrate	Solvent	T/°C	Time/h	Product[b]	Yield/%[c]
Halogen exchange	$PhCH_2Br$	MeCN	52	2.5	$PhCH_2F$	100
	$Me[CH_2]_6I$	MeCN	80	2	$Me[CH_2]_6F$	46
	$2,4\text{-}(NO_2)_2C_6H_3Cl$	MeCN	80	2	$2,4\text{-}(NO_2)_2C_6H_3F$	100
Fluorocarbon oligomerisation	C_3F_6	MeCN	25	[d]	C_6F_{12}[e]	
	C_3F_6	DMF[f]	25	[d]	$C_6F_{12} + C_9F_{18}$[e,g]	
Alkylation	$PhCH_2Br$	MeOH	52	4	$PhCH_2OMe$	100
Michael addition	$PhCH{=}CHCOPh$ + $EtNO_2$[h]	MeCN	25	1	$MeCH(NO_2)\text{-}CH(Ph)CH_2COPh$	100
	$Me_2C{=}CHCOMe$ + $EtNO_2$[h]	MeCN	25	1	$MeCH(NO_2)\text{-}CMe_2CH_2COMe$	44

[a] Reactions were carried out using 2 mol equiv. of reagent (typically 0.12 M solutions) unless stated otherwise. [b] Products were identified by comparison with authentic materials and/or by g.l.c.–mass spectra. [c] G.l.c. yields. [d] The production of a separate layer of oligomer was evident within minutes of bubbling in the fluorocarbon. [e] A mixture of isomers. [f] DMF = *N,N*-dimethylformamide. [g] The ratio of dimers to trimers produced was 1 : 1.6. [h] Reactions were carried out using 10 mol equiv. of nitroethane and 0.1 mol equiv. of reagent with respect to the Michael acceptor.

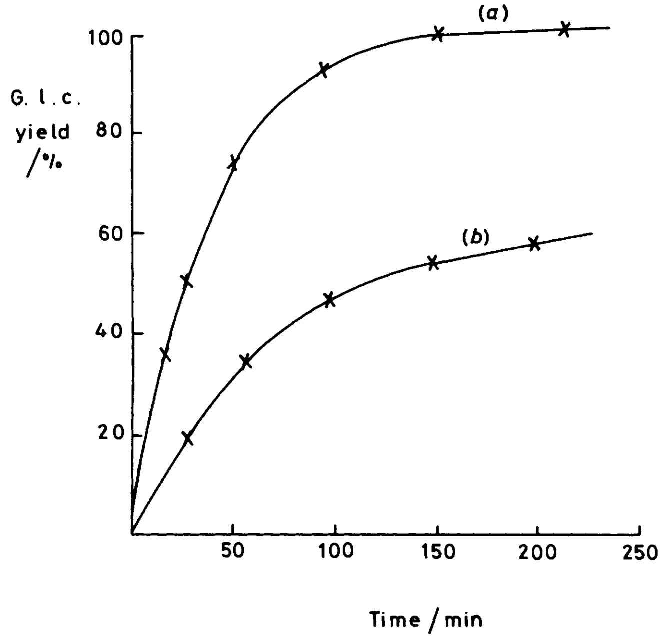

Figure 1. Rate of production of $PhCH_2F$ from $PhCH_2Br$ in MeCN at 52 °C using two mol equiv. of (a) Ph_4PHF_2 and (b) $Ph_4PHF_2{\cdot}H_2O$.

such as acetonitrile and dimethyl sulphoxide and is also soluble in halogenated aliphatic solvents such as chloroform. It is easily prepared[5] and dried, only picks up limited quantities of water from the atmosphere over long periods of time, and enjoys good thermal stability.†

We gratefully acknowledge the S.E.R.C. (for a studentship to S. J. B.), I.C.I. Mond Division, and several individuals for helpful suggestions including Dr. R. D. Powell and members of the York Fluorine group.

Received, 10th January 1985; Com. 053

References

1 M. Gerstenberger and A. Haas, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 647.
2 W. Prescott, *Chem. Ind. (London)*, 1978, 56.
3 J. H. Clark, *Chem. Rev.*, 1980, **80**, 429.
4 G. G. Jakobson and N. E. Akmentova, *Synthesis*, 1983, 169.
5 S. J. Brown and J. H. Clark, *J. Chem. Soc., Chem. Commun.*, 1983, 1257.
6 I. Gennick, K. M. Harman, and M. M. Potvin, *Inorg. Chem.*, 1977, **16**, 2033.
7 V. A. Sokolenko, *Reakts. Sposobnast Org. Soedin*, 1968, **5**, 429; *Chem. Abs.*, 1969, **70**, 19310.
8 W. Brunskill, W. T. Flavers, R. Gregory, and R. N. Haszeldine, *J. Chem. Soc., Chem. Commun.*, 1979, 1444.
9 C. L. Liotta and H. P. Harris, *J. Am. Chem. Soc.*, 1974, **96**, 2250.

---

† HF loss does not occur at temperatures below *ca.* 130 °C.