ELSEVIER

Journal of Fluorine Chemistry 92 (1998) 173–176

JOURNAL OF FLUORINE CHEMISTRY

Triphenylmethyl fluoride as a fluorinating agent in phosphorus–halogen chemistry

Volker Plack, Jens R. Goerlich, Reinhard Schmutzler*

Institut für Anorganische und Analytische Chemie der Technischen Universität, Postfach 3329, D-38023 Braunschweig, Germany

Received 26 June 1998; accepted 24 August 1998

Abstract

Triphenylmethyl fluoride **1** will effect chlorine–fluorine exchange in certain phosphorus chlorides. Exchange of chlorine for fluorine was observed only in $\sigma^3\lambda^3$ (P)- and $\sigma^5\lambda^5$ (P)-compounds, while phosphorus oxychloride as an example of a $\sigma^4\lambda^5$ (P)-compound was unreactive towards **1**.

Keywords: Triphenylmethyl fluoride; Phosphorus–fluorine compounds; Chlorine–fluorine exchange

1. Introduction

Owing to their often unique properties, fluorinated compounds have found broad interest in chemistry, e.g. [1]. A key step in their synthesis is, in many cases, the exchange of a suitable leaving group (e.g. –Hal, –OTos, $-OSiMe_3$) for fluorine [1].

The reagents employed in effecting such exchange are frequently beset with disadvantages. Ionic reagents are poorly soluble in many common organic solvents and special solvents or additional reagents, e.g. crown ethers which contaminate the product may be required. On the other hand many covalent reagents are of high reactivity but low selectivity. Further problems may arise from toxicity, sensitivity to moisture, and handling difficulties. The synthesis of selective reagents of more complex structure is often difficult, and may require special laboratory equipment. The few selective reagents which are commercially available are expensive throughout, so that their application is limited to cases in which only small amounts of them are needed.

For that reason we wish to present our observations regarding the potential of triphenylmethyl fluoride **1** as a reagent useful for halogen–fluorine exchange in phosphorus chemistry. Triphenylmethyl fluoride **1** is only slightly sensitive to moisture. A new synthesis of **1**, based on cheap starting materials, and also suitable on a large scale, without any special equipment, is indicated.

*Corresponding author. Tel.: +49-531-391-5304; fax: +49-531-391-5387; e-mail: r.schmutzler@tu-bs.de

2. Results and discussion

Owing to the effective electron charge delocalization over its three phenyl rings, the triphenylmethyl group is known to form carbocations of unique stability [2], which explains the enhanced ionic character of many triphenylmethyl-element compounds. When we tried to use TrtF **1** (Trt=triphenylmethyl, CPh_3) as an alkylating agent in phosphorus chemistry [3], we observed that in several cases, exchange of chlorine for fluorine rather than alkylation, had taken place.

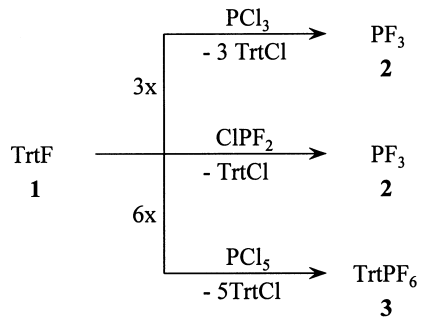
Phosphorus trichloride was readily converted to phosphorus trifluoride **2** upon treatment with three equivalents of **1** at r.t. (Scheme 1). No mixed fluorinated species were observed. The same product, **2** was obtained in the reaction of difluorochlorophosphine and **1**.

Triphenylmethyl fluoride **1** failed to act as a chlorine–fluorine exchange reagent on phosphorus oxychloride. Not even traces of the desired phosphorus oxyfluoride $P(:O)F_3$ or mixed halogenated compounds were observed in the reaction mixture after 18 h at r.t.

Phosphorus pentachloride, on the other hand, upon treatment with six equivalents of **1**, was quantitatively converted to triphenyl-methylcarbenium hexafluorophosphate **3** within 15 min at r.t. In this case the metathesis, which produced the strong Lewis acid PF_5 [4] as a putative intermediate, was followed by abstraction of fluoride ion from **1** by phosphorus pentafluoride (Scheme 1).

An attempt to exchange chlorine for fluorine in dichlorophosphines, e.g. *tert*-$BuPCl_2$ and $(Et_2N)PCl_2$, was unsuccessful. Surprisingly, the reaction between diphenyl-

0022-1139/98/$ – see front matter
PII: S0022-1139(98)00272-3



Scheme 1.

chlorophosphine and **1** was quite complex. We propose a reaction pathway as outlined in Scheme 2, which is based on a stoichiometry in which all of the starting materials, **1** and Ph_2PCl, were consumed.

Subsequent to the successful chlorine–fluorine exchange in Ph_2PCl, the resulting diphenylfluorophosphine disproportionated in the usual way described in the literature for many fluorophosphines [5], giving Ph_2PF_3 **4**, and tetraphenyldiphosphine. The P–P bond in the latter was cleaved by triphenylmethyl fluoride **1**, whereupon diphenylfluorophosphine and triphenylmethyl(diphenyl)phosphine **5** were formed. Oxidative addition of **1** to diphenylfluorophosphine finally yielded triphenylmethyl(diphenyl)difluorophosphorane **6**. Although the reaction was continuously followed by ^{31}P NMR spectroscopy, only the components of the final product mixture (**4**, **5**, **6**) as shown in Fig. 1, were observed during the reaction.

Although not totally clear in every detail, the following mechanism for the Cl–F-metathesis using triphenylmethyl fluoride seems to be conclusive:

$\sigma^3\lambda^3(P)$*-compounds*. In the first step tritylation of the nucleophilic phosphorus center took place, which led to Umpolung of the latter. In the next step it was attacked by the remaining "naked" fluoride which is known to be a strong nucleophile [6], and replaced chloride. Subsequently detritylation gave triphenylmethyl chloride, and the corresponding P–fluorinated species which may take part in further metathesis reactions. Whether **1** is effective in chlorine–fluorine metathesis depends on the nucleophilicity of the phosphorus compound employed (cf. *tert*-$BuPCl_2$, $(Et_2N)PCl_2$ vs. Ph_2PCl).

$\sigma^5\lambda^5(P)$*-compounds*. As Lewis acids they abstract the fluoride anion from **1** yielding, apparently, thermodynamically unstable, $\sigma^6\lambda^5$(P)-species which may "eliminate" triphenylmethyl chloride or scramble to give another $\sigma^5\lambda^5$(P)-species which is able to abstract fluoride from **1** again. This happens as long as, finally, $[PF_6]^-$ is formed as a stable species (with $[Trt]^+$ as counterion).

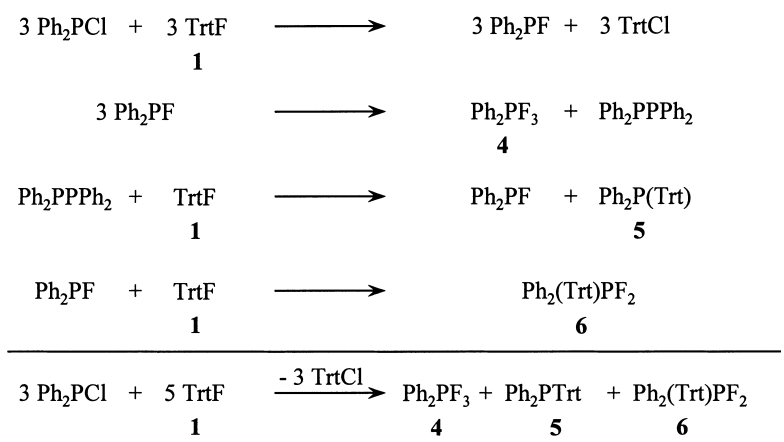
This mechanism would also explain why $\sigma^4\lambda^5$(P)-compounds, which are neither good nucleophiles nor Lewis acids, are unreactive towards **1**. On the other hand a mechanism which would involve the formation of minimal amounts of free fluoride anion from **1** in an equilibrium does not seem very plausible.

3. Experimental

Working conditions were as described elsewhere [7]. The following compounds were synthesized according to literature procedures: PF_2Cl [8], $PhPF_4$ [9], *tert*-$BuPCl_2$ [10], $(Et_2N)PCl_2$ [11]. Several compounds were identified by comparison of their ^{31}P NMR parameters with literature data which were taken from the following references: PF_3 **2** [12], $TrtPF_6$ **3** [13], Ph_2PF_3 **4** [14], $TrtPPh_2$ **5** [15]. The synthesis of **5** is described in [16].

3.1. Triphenylmethyl fluoride 1 (new route to TrtF)

To a suspension of 10.0 g (35.9 mmol) of triphenylmethyl chloride in 50 ml of acetonitrile, and 4.5 g (107.1 mmol) of sodium fluoride were added at r.t. a few drops of boron trifluoride etherate, and a few drops of the crown ether 15-crown-5. The mixture was stirred for 3 days at r.t., and extracted with hexane (3×150 ml). Evaporation of the hexane solution gave pure **2** which was dried for 2 h at 50°C in vacuo. Yield: 7.5 g (79.7%); m.p. 105°C ([17], 104°C).



Scheme 2.

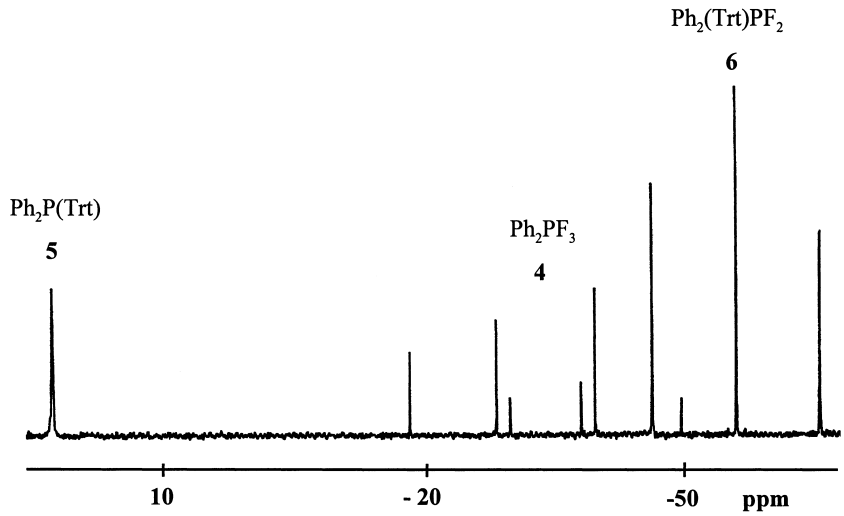


Fig. 1. ^{31}P NMR-spectrum of the reaction mixture of Ph_2PCl and TrtF in C_6D_6 (molar ratio: 3:5).

Alternatively, cooling of the hexane solutions to −20°C was used to precipitate **1**, which was subsequently collected by filtration, and dried in vacuo.

3.2. *Reaction of triphenylmethyl fluoride* **1** *with phosphorus trichloride, formation of phosphorus trifluoride* **2**

To 0.1 g (0.38 mmol) of **1** placed in a 5 mm NMR tube was added at −30°C a solution of 0.017 g (0.12 mmol) of phosphorus trichloride in 1 ml of $CDCl_3$. After 2 min the mixture was investigated by ^{31}P NMR spectroscopy. It revealed the quantitative formation of phosphorus trifluoride **2** which was identified by its ^{31}P NMR parameters.

^{31}P NMR ($CDCl_3$): δ=105.4 [q, ^{1}J(PF) 1402.0].

3.3. *Reaction of triphenylmethyl fluoride* **1** *with difluorochlorophosphine, formation of phosphorus trifluoride* **2**

A solution of 3.1 g (11.8 mmol) of **1** in 8 ml of toluene, and a few drops of phenyltetrafluorophosphorane were placed in a heavy-walled glass tube (200 ml). On this mixture were condensed at −196°C 1.7 g (16.3 mmol) of difluorochlorophosphine. The mixture was allowed to warm up to r.t. within 1 h, and stirred for 3 h. Investigation of the mixture by ^{31}P NMR spectroscopy revealed the exclusive formation of phosphorus trifluoride **2**, and only traces of the starting difluorochlorophosphine and phenyltetrafluorophosphorane were observed.

3.4. *Attempted reaction of triphenylmethyl fluoride* **1** *with phosphorus oxychloride*

To 0.1 g (0.38 mmol) of **1** placed in a 5 mm NMR tube was added at r.t. a solution of 0.020 g (0.13 mmol) of phosphorus oxychloride in 1 ml of $CDCl_3$. After 18 h at r.t, ^{31}P NMR spectroscopy revealed that no reaction had taken place.

3.5. *Reaction of triphenylmethyl fluoride* **1** *with phosphorus pentachloride, formation of triphenylmethylcarbenium hexafluorophosphate* **3**

To a solution of 0.1 g (0.38 mmol) of **1** in 1 ml of acetonitrile-d_3 were added 0.016 g (0.08 mmol) of phosphorus pentachloride. The ^{31}P NMR inspection of the reaction mixture after 15 min at r.t. revealed the quantitative formation of **3**.

^{31}P NMR (CD_3CN): δ=−143.5 [sept, ^{1}J(PF) 706.9].

3.6. *Attempted reaction of triphenylmethyl fluoride* **1** *with tert-butyldichlorophosphine and diethylaminodichlorophosphine*

The experiments were conducted as described for phosphorus oxychloride. Not even traces of products resulting from chlorine–fluorine exchange were detectable.

3.7. *Reaction of triphenylmethyl fluoride* **1** *with diphenylchlorophosphine*

At r.t. were added to a solution of 1.0 g (3.8 mmol) of **1** in 5 ml of dichloromethane 0.5 g (2.3 mmol) of diphenylchlorophosphine. The course of the reaction was monitored by ^{31}P NMR spectroscopy which revealed that the diphenylchlorophosphine was consumed after 18 h. Prolonged storage did not lead to further change in the composition of the mixture.

^{31}P NMR (C_6D_6): δ=−56.8 [t, ^{1}J(PF) 809.0; $TrtPPh_2F_2$ (**6**)], −33.9 [dt, $^1J(PF_{ax})$ 836.1, $^1J(PF_{eq})$ 970.2; Ph_2PF_3 (**4**)], 26.2 [s, $TrtPPh_2$ (**5**)].

References

[1] M.R.C. Gerstenberger, A. Haas, Angew. Chem. 93 (1981) 659; Angew. Chem. Int. Ed. Engl. 20 (1981) 647.
[2] A. Streitwieser, C.H. Heathcook, M. Kosower, Organische Chemie, VCH Publishers, New York, 1994, p. 638.
[3] V. Plack, H. Thönnessen, A. Fischer, P.G. Jones, J.R. Goerlich, R. Schmutzler, in preparation.
[4] R. Schmutzler, Advances in Fluorine Chemistry, vol. 5, Butterworths, London, 1965, p. 31.
[5] R. Schmutzler, O. Stelzer, J.F. Liebman, J. Fluorine Chem. 25 (1984) 289.
[6] V.V. Grushin, Angew. Chem. 110 (1998) 1042; Angew. Chem. Int. Ed. Engl. 37 (1998) 994.
[7] J.R. Goerlich, A. Fischer, P.G. Jones, V. Plack, R. Schmutzler, Z. Naturforsch. 48B (1993) 341.
[8] W. Albers, W. Krüger, W. Storzer, R. Schmutzler, Synth. React. Inorg. Met.-Org. Chem. 15 (1985) 187.
[9] R. Schmutzler, Inorg. Chem. 3 (1964) 410.
[10] M. Fild, O. Stelzer, R. Schmutzler, Inorg. Synth. 14 (1973) 4.
[11] K. Issleib, W. Seidel, Chem. Ber. 92 (1959) 2681.
[12] S. Berger, S. Braun, H.-O. Kalinowski, NMR-Spektroskopie von Nichtmetallen, vol. 3, Georg Thieme Verlag, Stuttgart, 1994, pp. 70, 147.
[13] Lit. [12], pp. 84, 147.
[14] E.L. Muetterties, W. Mahler, R. Schmutzler, Inorg. Chem. 2 (1963) 613.
[15] V. Plack, R. Schmutzler, Unpublished results.
[16] K. Issleib, B. Walther, Chem. Ber. 97 (1964) 3424.
[17] G.A. Olah, J.T. Welch, Y.D. Vankar, M. Nojima, I. Kerekes, J.A. Olah, J. Org. Chem. 44 (1979) 3872.