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A NEW METHOD OF PREPARATION OF TRIALKYLDIFLUOROPHOSPHORANES

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SUMMARY

Trialkyldifluorophosphoranes are obtained in good yields by the fluorination of bromotrialkylphosphonium bromides with sodium fluoride in acetonitrile.

INTRODUCTION

Relatively few methods of synthesis of difluorophosphoranes, based mostly on the oxidative fluorination of the appropriate phosphorus(III) compound, are known [1]. Of the metathetical methods, the sulfur/fluorine exchange in phosphine sulfides, R_3PS, by means of AsF_3 and, especially, SbF_3 [1-6] is of some importance while simple exchange of halogen such as chlorine and bromine by fluorine in triorganohalophosphonium halides has not been used as a synthesis method for difluorophosphoranes.

RESULTS

We now wish to report a particularly simple synthesis of difluorophosphoranes, 2a - 2c, which consists in bromine/fluorine exchange in trialkylbromophosphonium bromides, 1a - 1c

$$[R_3PBr]Br + 2\ NaF \xrightarrow{CH_3CN} R_3PF_2 + 2\ NaBr$$

1a :	R = Et	2a :	R = Et
1b :	R = Pr^i	2b :	R = Pr^i
1c :	R = Bu^n	2c :	R = Bu^n

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The starting compounds, 1, are readily obtained from the reaction of the corresponding tertiary phosphines with the stoichiometric quantity of bromine. Fluorination of 1 with sodium fluoride in boiling acetonitrile furnishes 2 in high yield. This is true also for 2b for which the yields, using the phosphine sulfide method, were both low and erratic [6]. As further advantages over other methods the cheap fluorinating agent, NaF, as against AsF_3 or SbF_3, and the facile recovery of the products from the reaction mixture should be noted. The present method proved unsuitable for the synthesis of Me_3PF_2 [4], presumably due to the poor solubility of $[Me_3PBr]Br$, and $Bu^t{}_3PF_2$ [5] where the bulk of the Bu^t groups may have been a disadvantage. In order to illustrate the scope and use of the present method, the synthesis of 2a - 2c, all previously known compounds, will be described in the following (Tab. 2). Compound characterization was by ^{19}F and ^{31}P NMR spectroscopy (see Table 1). The observed n.m.r. parameters were in agreement with literature values [1,9].

TABLE 1.

^{19}F and ^{31}P NMR Data for Difluorophosphoranes, 2a - 2c.

Compound	δ_F (p.p.m.)	J(PF) (Hz)	δ_P (p.p.m.)
2a	+ 42.6	575	+ 13.5
2b	+ 60.1	649	+ 17.1
2c	+ 33.5	588	+ 15.0

EXPERIMENTAL

Compounds 1a (R = Et); 1b (R = Pr^i), and 1c (R = Bu^n) were obtained by bromination of the corresponding tert. phosphines [7,8].

NMR spectra (JEOL C 60 HL) were recorded on the neat liquids at 56.4 MHz (^{19}F) and 60 MHz (^1H), respectively; internal CCl_3F and 85% H_3PO_4 (ext.) were used as references. Low field shifts are listed with negative, high field shifts with positive sign.

The preparation of 1a will be described as typical.

Preparation of triethyldifluorophosphorane (1a)

The reaction was conducted in a three-necked flask, fitted with a mechanical stirrer and a reflux condenser, topped by a drying tube. In a countercurrent of nitrogen sodium fluoride was added with stirring to the solution of 1a in acetonitrile. The reaction mixture was stirred for 3 days at reflux temperature. After cooling to room temperature insoluble products were removed by filtration, and the residue was washed with small amounts of acetonitrile. The solvent was removed by distillation at atmospheric pressure. Fractionation of the higher-boiling residue in vacuo furnished 2a.

The preparation of tri-i-propyldifluorophosphorane (2b) and tri-n-butyldifluorophosphorane (2c) was effected in an identical manner (see Table 2).

TABLE 2.
Preparation of Difluorophosphoranes, 2a - 2c

Reactants (mol)	Reaction Conditions	Yield	b.p. (^{o}C)
1a (8 g; 0.029 mol) NaF (3.0 g; 0.07 mol) in MeCN (200 ml)	3 d (90^{o})	62% (2a)	53 (20 mm) [a]
1b (40 g; 0.125 mol) NaF (14 g; 0.33 mol) in MeCN (200 ml)	3 d (90^{o})	70% (2b)	60 (5 mm) [b]
1c (109 g; 0.3 mol) NaF (30 g; 0.71 mol) in MeCN (200 ml)	3 d (90^{o})	85% (2c)	75 (5 mm) [c]

[a] Lit. [2] b.p. 53^{o} (20 mm)
[b] Lit. [6] b.p. 56^{o} (4 mm)
[c] Lit. [2] b.p. 72^{o} (4 mm)

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