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Reactions of *N*-Fluoropyridinium Salts with Phosphorus- and Arsenic-containing Nucleophiles

Aleksander S. Kiselev,*† Andrei A. Gakh, Nikolai D. Kagramanov and Victor V. Semenov

N. D. Zelinskii Institute of Organic Chemistry, Academy of Sciences of the USSR, 117913 Moscow, USSR. Fax: 095 135 5328

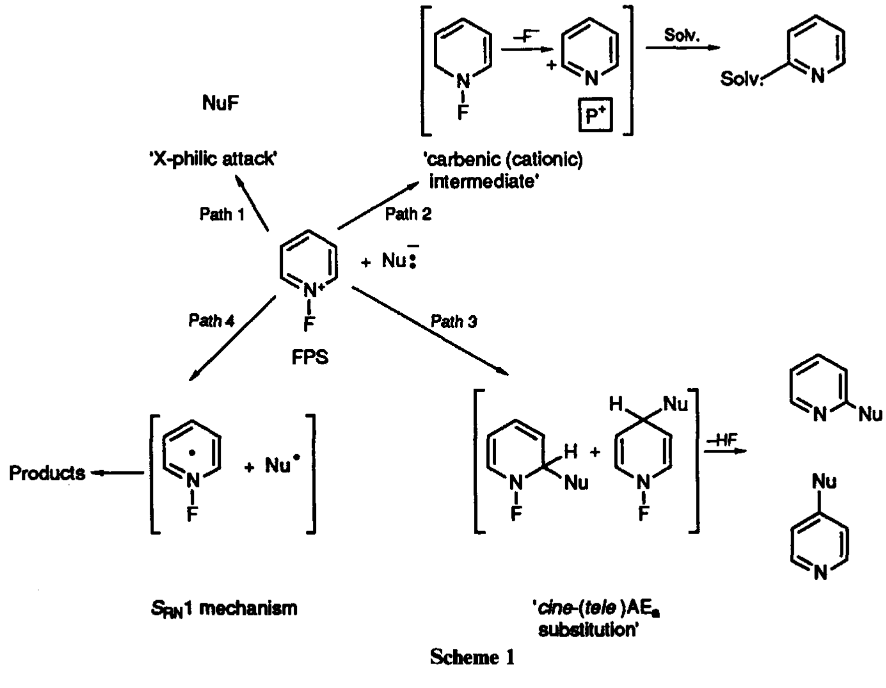
The direction of reaction of *N*-fluoropyridinium tetrafluoroborate with phosphorus- and arsenic-containing nucleophiles PR_3 and AsR_3 (*cine*-AE_a substitution or X-philic attack) has been found to depend on the nature of R.

The *N*-fluoropyridinium salts (FPS) have been of great interest over the last ten years. As shown by analyses of electron density distributions, FPS are multicentre electrophiles.[1] For example, they are used for electrophilic fluorination of various organic compounds: carbanions,[2–4] Grignard reagents,[3] aromatic substances,[3] silyl esters of enols and acetates[3] and alkenes[5] (X-philic attack, Scheme 1, path 1). In addition, FPS have been found to react with strong bases like triethylamine or Hunig base. It has been suggested that the reaction may proceed *via* formation of a carbenic (cationic) intermediate p^+, which then reacts with the solvent or a nucleophile.[7,8] As a result, 2-substituted pyridines are formed (path 2). In previous papers we have shown that this direction of reaction is predominant for the reaction of FPS with highly basic carbanions.[9–11] We have proposed a new type of reaction of FPS with carbanions: cine-(*tele*-) AE_a substitution (path 3).[9–13] The authors of ref. 5 propose that the reaction of FPS with carbanions and alkenes proceeds through the $S_{RN}1$ mechanism (path 4).

Table 1 Reaction of FPT with PR_3 and AsR_3

R	Yield of 1 (%)	
	Nu = PR_3	Nu = AsR_3
Pr^n	78	—
Pr^i	75	—
Bu^n	84	86
Ph	92	96
p-MeC_6H_4	88	—

We have studied the reactions of the readily available *N*-fluoropyridinium tetrafluoroborate (FPT) with phosphorus- and arsenic-containing nucleophiles. The direction of the reaction was found to depend on the nature of the nucleophile used.



Scheme 1

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† A. S. K. is currently working in the USA. Fax: 213 740 2701.

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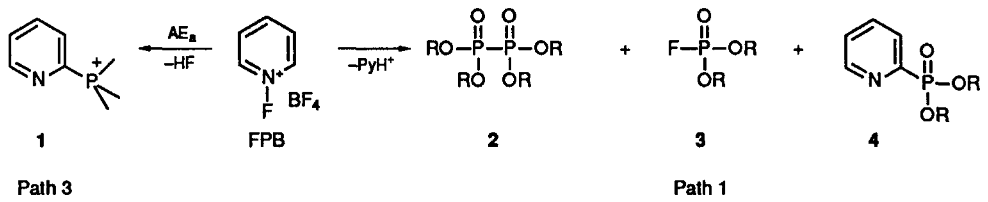

Scheme 2

Table 2 Reaction of FPT with $P(OR)_3$

R	Yield (%)		
	2	**3**	**4**
OMe	52	10	6
OEt	57	12	5
OPr^n	68	7	5
OPr^i	63	6	4

Nucleophiles PR_3 and AsR_3 (R = alkyl, aryl) were found to react with FPT with the formation of 2-substituted pyridine derivatives **1**, in almost quantitative yields (Table 1). These results allow us to propose *cine-(tele-)* AE_a substitution as a possible mechanism for this process.

The products of the reaction of FPT with trialkylphosphites $P(OR)_3$ are quite different from those obtained with PR_3. In this case the main products are the corresponding esters of bisphosphonic acid **2** and pyridinium tetrafluoroborate (Table 2). In addition we obtained fluorophosphites **3** and esters of 2-pyridinephosphonic acid **4** from the reaction mixtures. It can be seen that there are two possible directions of reaction. (*i*) The predominant one is X-philic attack. Formation of **2** as a major product of the process gives evidence for this conclusion. The appearance of **3** and **4** may also be explained in terms of this mechanism. The results obtained are presented in Scheme 2. (*ii*) The formation of **4** may be explained as a result of nucleophilic attack on the pyridinium ring. The intermediate **1′** then undergoes fluoride-anion attack, to form **4** (Scheme 3).

To summarize, the reactions of FPT with alkyl- and arylphospines and arsines are a convenient approach to phosphonium and arsenonium salts containing a pyridine substituent. The chemistry of pyridine derivatives activated toward nucleophilic attack by strongly electron-withdrawing substituents requires further investigation.[14]

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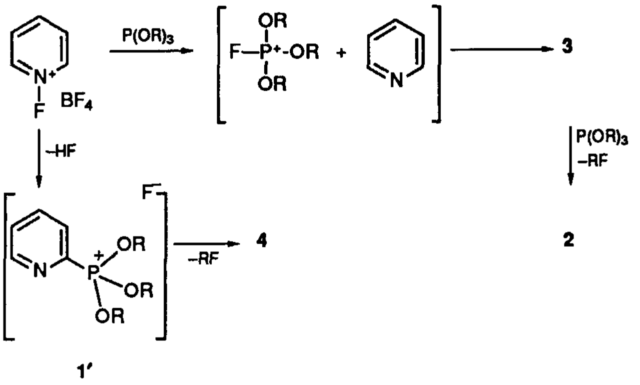

Scheme 3

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