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Proton Sponge Hydrofluoride as a Soluble Fluoride Ion Source

Richard D. Chambers,* a Thomas F. Holmes, a Stewart R. Korn^b and Graham Sandford a

^a Department of Chemistry, University of Durham, South Road, Durham, UK DH1 3LE ^b Zeneca Specialities, North of England Works, PO Box A38, Leeds Road, Huddersfield, Yorkshire, UK HD2 1FF

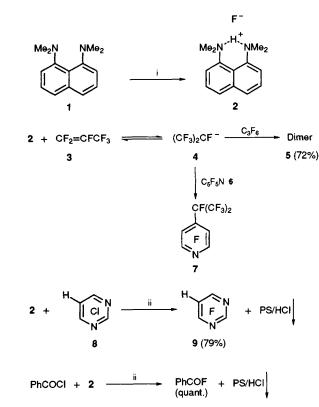
Proton Sponge (PS) hydrofluoride has been prepared and is totally soluble in acetonitrile; this system was used to generate carbanions from hexafluoropropene and to form carbon–fluorine bonds by reaction with 2,4,6-trichloropyrimidine and by reaction with benzoyl chloride (Proton Sponge hydrochloride is insoluble in acetonitrile).

Fluoride ion sources for use in synthesis have attracted a great deal of interest in recent years and a range of systems have been described, *e.g.* alkali metal fluorides in various forms,¹ including complexes with crown polyethers,² 'TAS' fluoride $(Me_2N)_3S+Me_3SiF_2^{-}, 3etc.$ However, there is still a great need for a readily available system that is very soluble in organic solvents. Complexes of tertiary amines with hydrogen fluoride⁴ and Et₃N(HF)₃,⁵ and this prompted us to explore the potential of Proton Sponge hydrofluoride. The properties of Proton Sponge are very well documented⁶ and it is possible that this

base could bind the proton from HF and release fluoride ion in a unique way as illustrated in 2.

We have now prepared the hydrofluoride salt of 1 by adding a standardised solution of anhydrous hydrogen fluoride in diethyl ether to an ethereal solution of the base. A white crystalline solid was recovered and elemental analysis indicated a monohydrofluoride salt. The IR spectrum (Nujol) was also consistent with a monohydrofluoride salt, rather than a mixture of free base and hydrogen difluoride salts.

In a series of test reactions in acetonitrile solution, we have established that the system 2 can be a useful fluoride ion donor



Scheme 1 Reagents and conditions: i, HF, Et₂O, room temp.; ii, MeCN, room temp., overnight

for forming carbon-fluorine bonds. Reaction with hexafluoropropene 3 gave a 72% yield of a dimer 5, thus demonstrating that a carbanion 4 is formed by donation of fluoride ion from 2 to 3. A further example of carbon-carbon bond formation, induced by 2, was demonstrated by trapping the carbanion 4

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with polyfluorinated aromatic compounds, e.g. pentafluoropyridine 6, to give perfluoroalkyl derivatives e.g. 7 plus products of further substitution.⁷ We have not, however, been able to generate stable carbanions in this way, although such species have been successfully generated in reactions between caesium fluoride and appropriate perfluorinated alkenes.8

This system may also be used for multiple carbon-fluorine bond formation by halogen exchange because conversion of 2,4,6-trichloropyrimidine 8 to 2,4,6-trifluoropyrimidine 9 occurs readily in high yield. Similarly, benzoyl chloride is converted quantitatively to benzoyl fluoride, with the precipitation in each case of Proton Sponge hydrochloride.

Thus, 2 is a potentially useful soluble fluoride ion source and, furthermore, the formation of a hydrochloride which is insoluble in acetonitrile, allows the base to be readily recovered.

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