

Proton Sponge Hydrofluoride as a Soluble Fluoride Ion Source

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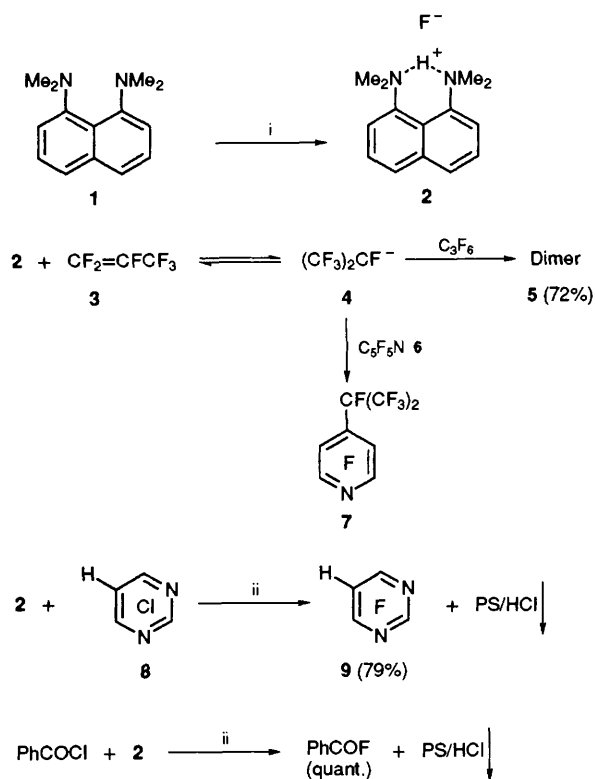
Proton Sponge (PS) hydrofluoride has been prepared and is totally soluble in acetonitrile; this system was used to generate carbanions from hexafluoropropene and to form carbon–fluorine bonds by reaction with 2,4,6-trichloropyrimidine and by reaction with benzoyl chloride (Proton Sponge hydrochloride 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 (Me₂N)₃S⁺Me₃SiF₂⁻,³ *etc.* 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 fluoride are valuable reagents, *e.g.* pyridinium polyhydrogen 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**

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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