

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

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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