Reactions involving fluoride ion. Part 37[*]. 'Proton Sponge' hydrofluoride as a fluoride ion donor[†]

Richard D. Chambers[a], Stewart R. Korn[b] and Graham Sandford[a††]
[a] *Department of Chemistry, University of Durham, South Road, Durham, DH1 3LE (UK)*
[b] *Zeneca F.C.M.O., North of England Works, P.O. Box A38, Leeds Road, Huddersfield, Yorkshire, HD2 1FF (UK)*

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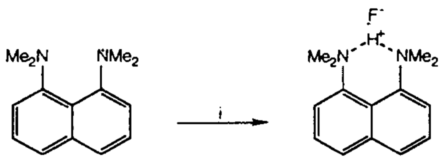
Abstract

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

Introduction

Fluoride ion is, of course, the most simple source of fluorine for the formation of carbon–fluorine bonds and the methodology is already extensive, e.g. the use of alkali metal fluorides in various forms [2], including complexes with crown polyethers [3], 'TAS' fluoride $(Me_2N)_3S^+\ Me_3SiF_2^-$ [4], etc. However, there is still a great need for a readily available system that is very soluble in organic solvents, especially if derived simply from hydrogen fluoride. Indeed, complexes of tertiary amines with hydrogen fluoride are valuable reagents, e.g. pyridinium polyhydrogen fluoride [5], $Et_3N \cdot 3(HF)$ [6], etc., and, with this background, we were prompted to explore the potential of 'Proton Sponge' hydrofluoride. The properties of 'Proton Sponge' (**1**) are very well documented [7] and it is possible that this base could strongly bind the proton from hydrogen fluoride and so release fluoride ion in a unique way, as illustrated in **2**.



1 **2**

i, HF, Et_2O, room temp.

Results and discussion

In a preliminary communication [8], we described how the hydrofluoride salt of **1** was prepared by the addition of a standardised solution of anhydrous hydrogen fluoride in diethyl ether to an ethereal solution of the base. A white crystalline solid was recovered whose elemental analysis corresponded to that of a monohydrofluoride salt.

The question arises as to whether this system exists as the monohydrofluoride salt **2** or as a mixture of the dihydrofluoride salt, together with the free base **1**. This is difficult to address experimentally. Mass spectrometry was unhelpful in that no parent peak was observed either on electron impact or in the FAB mode, but the infrared spectrum showed clearly that the system is protonated, both in the solid state and in solution. The infrared spectra of salts of **1** have been extensively investigated by other workers [9], the N–H stretch in the protonated species occurring between 460 and 600 cm^{-1}. A broad peak is observed in the spectrum of **2** centred at 580 cm^{-1}, clearly demonstrating that the starting material **1** is largely protonated and therefore cannot exist simply as a mixture of **1** and the corresponding dihydrofluoride. However, some free amine **1** is undoubtedly present because the Bohlmann bands (N–Me stretch) corresponding to **1** in the IR spectrum are substantially reduced on protonation but do not completely disappear [9]. This conclusion is consistent with the NMR spectra. A single sharp resonance occurs in the ^{19}F spectrum $\delta_F = -169$ ppm, and this value was little affected by concentration. Values anticipated for HF (δ_F *c.* 150–200 ppm) [10], HF_2^- (δ_F *c.* -145 ppm) [11] and F^- (δ_F *c.* -73 to -125 ppm) [12], depend

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[*] See ref. 1.

[†] Dedicated to Professor A.R. Katritzky on the occasion of his 65th birthday.

[††] Author to whom correspondence should be addressed.

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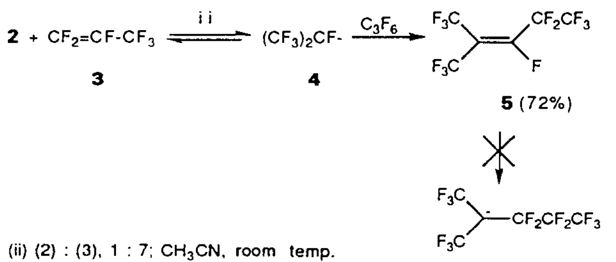
critically on a variety of factors including concentration, solvent, dryness, etc. and comparisons do not allow any firm conclusions to be drawn. The proton spectrum showed broad bands centred at δ_H 18.7 ppm (N^+–H) [13] and δ_H 13.6 ppm (HF), suggesting that some dissociation of **2** into **1** plus hydrogen fluoride occurs. Furthermore, *N*-methyl resonances occurred at δ_H 2.8 ppm (N–Me) [13] and δ_H 3.1 ppm (N^+–Me). Together these data imply that some dissociation occurs in the solid state, but that this is greater in solution.

We attempted to observe the NMR spectra at lower temperatures but salt **2** came out of solution at temperatures below −10 °C. However, related studies on the system tributylamine hydrogen fluoride showed that extensive dissociation occurred in that system even at −80 °C, and we have confirmed these spectroscopic observations [14].

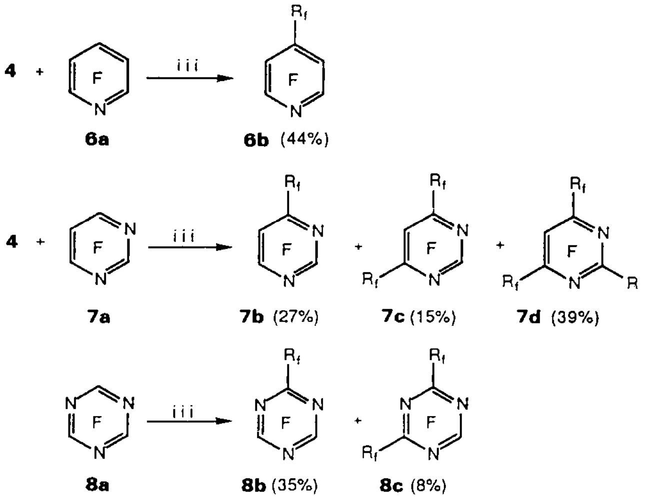
Salt **2** is extremely soluble in acetonitrile and a range of other organic solvents and this contrasts with the corresponding hydrochloride salt which is largely insoluble in these media. Hence, precipitation as the hydrochloride is a potentially simple way of recovering the base **1**.

The next question concerns the ability of **2** to act as a fluoride-ion donor and to examine this we defined a series of experiments based on the known reactions of alkali-metal fluorides. The oligomerisation reactions of fluorinated alkenes are important processes and well established [15]. For this reason, reactions of hexafluoropropene (**3**) in acetonitrile with **2** were investigated when it was observed that oligomerisation occurred at room temperature in what was a homogeneous system. The dimer **5** was the sole product which separates from the acetonitrile, enabling easy purification. Consequently, the solvent layer was recovered and recharged with hexafluoropropene (**3**) in a repeat process, without loss of reactivity. Several experiments were carried out to demonstrate that this process is catalytic.

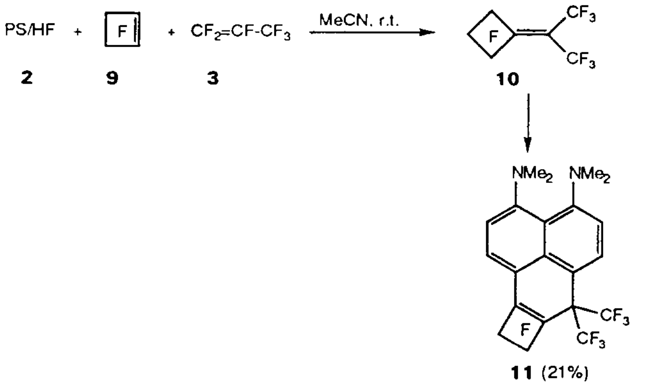


(ii) (2) : (3), 1 : 7; CH_3CN, room temp.

The same system may be used to promote polyfluoroalkylation reactions with activated perfluoroaromatic compounds [16]. Even at room temperature, reaction of the anion **4** with a series of perfluorinated heterocycles **6a**–**8a** occurs, giving the corresponding perfluoroalkylated products **6b**–**8c**. The lower yields derived from the triazine **8a** may be accounted for by some reaction of the free amine **1** in the system to give byproducts; the reactions of 'Proton Sponge' (**1**) with triazine **8a** have been described elsewhere [17]. Similarly, the use of **2** to promote reactions of hexafluoropropene (**3**) with perfluorocyclobutene (**9**) to give the interesting derivative **10** was precluded because of the further reaction of **10**, when produced, with free amine **1** to give the interesting anelated product **11**. The reaction of **1** with perfluorocycloalkene derivatives has been described elsewhere [18].

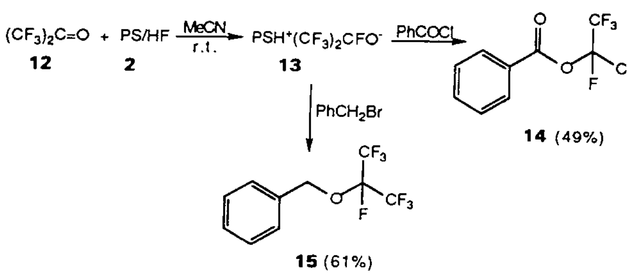


4 + CH_3CN, room temp.
= $-CF(CF_3)_2$

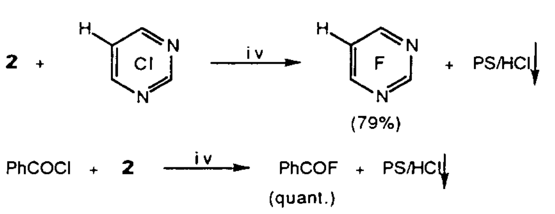


We have also attempted to generate observable anions by the use of **2** as the fluoride-ion source, e.g. the reaction of **5** with **2** in sulpholane to give **5a**. This process proceeds slowly with caesium fluoride [19], but we were unable to observe **5a** in the presence of **2**. Obviously, the equilibrium is unfavourable for this process.

Hexafluoroacetone (**12**) reacts with alkali-metal salts to give the anion **13** and we have generated this anion from **2** and trapped it with benzoyl chloride and benzyl bromide, giving the corresponding products **14** and **15**.



Halogen-exchange processes involving potassium fluoride are important both in the laboratory and on the industrial scale for the synthesis of fluoroaromatic compounds, and the salt **2** will act in this type of process. For example, trichloropyrimidine reacts even at room temperature to give a high yield of trifluoropyrimidine (**17**) and, similarly, benzoyl chloride was converted quantitatively to benzoyl fluoride.



(iv) CH_3CN, room temp., overnight

We have thus demonstrated that **2** acts as a fluoride-ion donor in a range of processes and could have advantages over alkali-metal fluorides in some situations because the 'Proton Sponge' could in fact be recycled and the merits of a homogeneous system are obvious. Applications to other systems remain to be explored.

Experimental

All materials were obtained commercially and used as received. 'Proton Sponge' is a trade mark of the Aldrich Chemical Co. and denotes 1,8-bis-(dimethylamino)naphthalene. All solvents were dried prior to use by standard procedures. NMR spectra were recorded on a Bruker AC250 spectrometer operating at 250 MHz for ^1H NMR and at 235 MHz for ^{19}F NMR spectra, mass spectra on a Varian VG7070E spectrometer, UV spectra on a Perkin-Elmer Lambda 3 spectrophotometer and infrared spectra on a Perkin-Elmer 577 grating spectrophotometer. Elemental analyses were obtained on a Perkin-Elmer 240 Elemental Analyser. Melting points were recorded at atmospheric pressure and are uncorrected.

Preparation of 'Proton Sponge' hydrogen fluoride complex (PS/HF) (2)

Anhydrous hydrogen fluoride gas was bubbled under anhydrous conditions through dry diethyl ether (100 ml) contained in an ice-cooled FEP bottle. **Face masks, gloves and an efficient fume hood are essential when handling anhydrous HF!** The concentration of HF was determined by titrating an aliquot of the ether solution with a standard solution of sodium hydroxide using phenolphthalein as the indicator, e.g. a 1 ml aliquot of HF/ether solution required 5.65 ml of 1.192 M NaOH solution giving a solution containing 0.134 g HF per ml.

'Proton Sponge' (**1**) (1.5 g, 7 mmol) was dissolved in the minimum amount of dry diethyl ether and the required 1:1 stoichiometric amount of the HF/ether solution (0.134 g HF per ml) (1.05 ml, 7 mmol) was added by pipette. A white solid immediately precipitated and the ether was carefully removed under reduced pressure to leave 'Proton Sponge' hydrofluoride (**2**) (1.62 g, 98%), m.p. 117–118 °C. Analysis: Found: C, 69.7; H, 8.5; N, 11.5%. $C_{14}H_{19}N_2F$ requires: C, 71.8; H, 8.1; N, 11.95%. ^1H NMR (CD_3CN) δ: 2.8 (N–Me); 3.1 (N^+–Me); 6.8–8.2 (Ar–H); 13.6 (HF); 18.7 (N^+–H) ppm. ^{19}F NMR (CD_3CN) δ: -169 ppm. MS *m/z* (FAB^+): 215 (100%).

The preparation was repeated many times as the material was required usually on the 3 g scale, but was scaled up to 25 g without any problems. In all the following reactions, 'Proton Sponge' hydrogen fluoride complex (**2**) will be referred to as PS/HF.

Dimerisation of hexafluoropropene (3)

A Carius tube was charged with PS/HF (**2**) (1.63 g, 7 mmol) and acetonitrile (35 ml), and hexafluoropropene (**3**) (7.34 g, 49 mmol) was transferred under vacuum to the tube which was cooled in liquid air. The tube was sealed and allowed to warm to room temperature in a steel casing and then agitated on a rotating arm for 48 h at room temperature. The tube was opened to reveal a lower fluorocarbon layer which was collected and determined by GC methods to be the thermodynamic dimer of hexafluoropropene (**5**) (5.3 g, 72%) as the only product ^{19}F NMR ($CFCl_3$) δ: -60 (m, 3F, CF_3); -63 (m, 3F, CF_3); -86 (m, 3F, CF_3); -100.5 (s, br, 1F, CF); -119 (m, 2F, CF_2) ppm. MS *m/z* (El^+): 281 (M^+-F, 24%). These data compare well with the literature values [20] [^{19}F NMR δ: -60.2 (m, 3F, CF_3); -62.8 (m, 3F, CF_3); -86.4 (m, 3F, CF_3); -100.1 (s, br, 1F, CF); -119.6 (m, 2F, CF_2) ppm. MS *m/z* (El^+): 281 (M^+-F, 27%)].

Perfluoroalkylation of pentafluoropyridine (6a)

A flask was charged with PS/HF (**2**) (0.75 g, 3 mmol), pentafluoropyridine (**6a**) (2.20 g, 13 mmol) and dry sulpholane (20 ml), and then cooled in liquid air and evacuated. After warming to room temperature, hexafluoropropene (**3**) (3.4 g, 23 mmol) was added via an expandable gas reservoir and the mixture stirred vigorously for 7 d at room temperature. The volatile products were removed from the reaction mixture by flash distillation (4.8 g). GC–MS methods showed three main products, which were separated using an SE30 column at 100 °C and identified as the hexafluoropropene dimer **5** (2%), pentafluoropyridine (**6a**) (49%) and perfluoro-4-isopropylpyridine (**6b**) (44%). For the latter, the following data were obtained. ^{19}F NMR (CF_3CN) δ: −75.4 (6F, s, CF_3); −86.7 (2F, s 2,6-ring F); −135.3, 137.5 (2F, d, 3,5-ring F); −180.5 (1F, m. C–F) ppm. MS *m/z* (El$^+$): 319 (M^+, 41%); 250 (15, $M-CF_3$); 200 (100, $M-C_2F_5$), as compared to the literature data [16] ^{19}F NMR δ: −74.3 (6F, s, $2CF_3$); −87.3 (2F, s, 2,6-ring F); −135.1 (2F, s, 3,5-ring F); −178.5 (1F, s, CF) ppm. MS *m/e*: 319 (M)]. Trace amounts of perfluorodi-isopropylpyridine (2%) [MS *m/z* (El$^+$): 469 (M^+, 18%)] and perfluorotri-isopropylpyridine (1%) [MS *m/z* (El$^+$): 619 (M^+, 16%)] were also observed by GC–MS.

Perfluoroalkylation of tetrafluoropyrimidine (7a)

A flask was charged with PS/HF (**2**) (1.40 g, 6 mmol), tetrafluoropyrimidine (**7a**) (2.30 g, 15 mmol) and dry sulpholane (30 ml), and then cooled in liquid air and evacuated. After warming to room temperature, hexafluoropropene (**3**) (5.23 g, 35 mmol) was added via an expandable gas reservoir and the mixture stirred vigorously for 3 d at room temperature. The volatile products were removed from the reaction mixture by flash distillation (6.1 g). The product mixture was analysed by GC–MS methods and by ^{19}F NMR spectroscopy and found to consist of perfluoro-4-isopropylpyrimidine (**7b**) (27%) [^{19}F NMR (CD_3CN) δ: −48.7 (2-ring F); −72 (6-ring F); −76.1 (CF_3 groups); −154 (5-ring F); −186.9 (CF) ppm. MS *m/z* (El$^+$): 302 (M^+, 35%); 283 (20 $M-F$); 233 (18, $M-CF_3$); 183 (51, $M-C_2F_5$), as compared to the literature data [21], i.e. ^{19}F NMR δ: −48.7 (2-ring F); −72.5 (6-ring F); −78.1 (CF_3); −154.5 (5-ring F); −188.7 (CF) ppm. MS *m/e* (El$^+$): 302 (M^+, 65%); 283 (36, $M-F$); 233 (20, $M-CF_3$); 183 (57, $M-C_2F_5$)]; perfluoro-2,4-di-isopropylpyrimidine (**7c**) (15%) [^{19}F NMR (CD_3CN) δ: −48.7 (2-ring F); −76.2 (CF_3); −133.5 (5-ring F); −186.9 (CF) ppm. MS *m/e* (El$^+$): 452 (M^+, 22%), 433 (33, $M-F$); 383 (16, $M-CF_3$); 333 (40 $M-C_2F_5$), as compared to the literature data [21], i.e. ^{19}F NMR δ: −48.6 (2-ring F); −76.5 (CF_3); −132.5 (5-ring F); −186.3 (CF) ppm. MS *m/e* (El$^+$): 452 (M^+, 42%); 433 (44, $M-F$); 383 (22, $M-CF_3$); 333 (37, $M-C_2F_5$)]; and perfluoro-2,4,6-tri-isopropylpyrimidine (**7d**) (39%) [^{19}F NMR (CD_3CN) δ: −76.2 (CF_3); −124.1 (5-ring F); −182 (CF); −186.9 (CF) ppm. MS *m/e* (El$^+$): 602 (M^+, 5%); 583 (9, $M-F$); 533 (4, $M-CF_3$); 452 (14, $M-C_3F_6$), as compared to the literature data [21], i.e. ^{19}F NMR δ: −76.5 (CF_3); −123.1 (5-ring F); −182.1 (CF); −186.3 (CF) ppm. MS *m/e* (El$^+$): 602 (M^+, 46%); 583 (50, $M-F$); 533 (22, $M-CF_3$)].

Perfluoroalkylation of trifluoro-s-triazine (8a)

A flask was charged with PS/HF (**2**) (0.70 g, 3 mmol), trifluoro-s-triazine (**8a**) (1.80 g, 13 mmol) and dry sulpholane (20 ml), and then cooled in liquid air and evacuated. After warming to room temperature, hexafluoropropene (**3**) (7.5 g, 50 mmol) was added via an expandable gas reservoir and the mixture stirred vigorously for 3 d at room temperature. The volatile products were removed from the reaction mixture by flash distillation (8.2 g). The product mixture was analysed by ^{19}F NMR spectroscopy and GC–MS method and found to consist of two main products, i.e. perfluoroisopropyl-s-triazine (**8b**) (35% by GC) [MS *m/z* (El$^+$): 285 (M^+, 100%); 266 (98, $M-F$); 197 (88, $M-FCF_3$); 166 (51, $M-C_2F_5$)] and perfluorodi-isopropyl-s-triazine (**8c**) (8%) [MS *m/z* (El$^+$): 435 (M^+, 65%); 416 (100, $M-F$); 347 (38, $M-FCF_3$); 316 (11, $M-C_2F_5$)]. ^{19}F NMR spectroscopy of the product mixture revealed perfluoroalkylation [δ_F (CD_3CN): −33 (N=C–F); −73 (CF_3); −183.8 (CF) ppm, as compared to the literature data [22], i.e. δ_F: −30.4 to −30.6 (ring F); −74.4 to −75.4 (CF_3 groups); −183.8 to −186.5 (CF) ppm].

*Preparation of 3,4-bis[dimethylamino]-8,8,9,9-tetrafluoro-5,5-(trifluoromethyl)-8,9-dihydro-7*H*-cyclobuta[*a*]phenalene (11)*

A Carius tube was charged with PS/HF (**2**) (2.5 g, 10.6 mmol) in acetonitrile (20 ml) and perfluorocyclobutene (**9**) (6.7 g, 41 mmol) and hexafluoropropene (**3**) (5.0 g, 33 mmol) were transferred under vacuum to the tube which was cooled in liquid air. After agitating on a rotating arm at room temperature for 2 d, the tube was opened to reveal a red solvent layer. On adding water (20 ml), an orange solid precipitated and was collected by filtration. TLC showed that the solid contained two components. The solid was evaporated on to chromatographic alumina and elution with light petroleum gave 3,4-bis[dimethylamino]-8,8,9,9-tetrafluoro-5,5-(trifluoromethyl)-8,9-dihydro-7*H*-cyclobuta[*a*]phenalene (**11**) (1.1 g, 21%) as orange crystals, $R_F = 0.5$, m.p. 128 °C (from aqueous ethanol). Analysis: Found: C, 52.2; H, 3.4; N, 5.6; F, 38.0%. $C_{21}H_{16}N_2F_{10}$ requires: C, 51.9; H, 3.3; N, 5.8; F, 39.0%. IR $\lambda_{max.}$ (CH_3CN) (nm): 273.6 ($\log_{10}\epsilon$ 3.78); 367.6 (3.45); 451.2 (3.78). IR $\nu_{max.}$ (cm^{-1}): 1680 (C=C). ^{1}H NMR (CD_3CN) δ: 2.81 (6H, s, 3-NMe_2); 2.88 (6H, s, 4-NMe_2); 6.79, 7.45 (2H, AX, $J_{AX} = 8.3$ Hz, 1-H and 2-H); 6.98, 7.85 (2H, AX, $J_{AX} = 8.8$ Hz, 5-H and 6-H) ppm. ^{19}F NMR (CD_3CN) δ: −67.2 (6F, s, CF_3); −105.1 (2F, s, 9-CF_2); −112.5 (2F, s, 8-CF_2) ppm. ^{13}C NMR (CD_3CN) δ: 43.5 (s, br, N–Me); 107.7 (s, C-6a); 108.9 (s, C-2); 111.5 (s, C-5); 115–120 (many overlapping peaks, CF_2 and CF_3); 116.7 (s, C-9b); 121.4 (s, C-3a); 123.7 (s, C-9a); 126.0 (s, C-7a); 126.9 (s, C-1); 130.4 (s, C-6); 134.1 (s, C-9c); 152.9 (s, C-3); 153.0 (m, C-7); 156.1 (s, C-4) ppm. MS *m/z* (CI^+, NH_3): 487 ($M^+ + 1$, 20%).

A red solid was also isolated (0.05 g) which is, as yet, unidentified. IR $\nu_{max.}$ (cm^{-1}): 1790 (C=O). ^{19}F NMR (CD_3CN) δ: -68.9 (s, 6F); -110.5 (s, 2F) ppm. MS *m/z* (EI^+); 464 (M^+, 83%).

*Attempted formation of a stable perfluorinated carbanion **5a***

A flask was charged with the hexafluoropropene dimer **5** (1.8 g, 6 mmol), PS/HF (**2**) (1.4 g, 6 mmol) and sulpholane (5 ml) under a plume of dry nitrogen, and the mixture stirred for 1 week at room temperature. ^{19}F NMR spectroscopic studies of the mixture revealed only starting material. The reaction was repeated in tetraglyme and acetonitrile but only starting material was observed by ^{19}F NMR spectroscopy.

Reaction between hexafluoroacetone and PS/HF

A Carius tube was charged with PS/HF (**2**) (5.1 g, 22 mmol) in acetonitrile (20 ml) and hexafluoroacetone (**12**) (5.3 g, 32 mmol) was transferred under vacuum to the trap which was cooled in liquid air. The tube was sealed and allowed to stand at room temperature overnight. The solution went pale yellow in colour. The tube was opened when ^{19}F NMR spectroscopy revealed the desired carbinolate species **13** [^{19}F NMR (CH_3CN) δ: -80.33 (6F, s, CF_3); -107.88 (1F, s, br, CF) ppm]. There was no peak at -164 ppm indicating that all the PS/HF had reacted and hence that the solution contained 22 mmol of the carbinolate species. The reaction solution was used in the two following trapping reactions.

Preparation of heptafluoroisopropyl benzoate (14)

Benzoyl chloride (1.7 g, 12 mmol) was added dropwise to the carbinolate solution prepared as above (10 ml, 11 mmol) and the mixture stirred overnight. The volatiles were transferred under vacuum and analysed by GC–MS methods and ^{19}F NMR spectroscopy. There were two products, i.e. benzoyl fluoride (51%) and heptafluoroisopropyl benzoate (**14**) (49%) which was isolated by preparative scale GC using a 30% SE30 column at 150 °C. ^{19}F NMR (CH_3CN) δ: -78.1 (6F, s, CF_3); -141.1 (1F, s, CF) ppm. MS *m/z* (EI^+): 290 (M^+, 22%); 105 (100, Ar–C=O); 77 (60, C_6H_5); 69 (11, CF_3).

Preparation of heptafluoroisopropyl benzyl ether (15)

Benzyl bromide (2.3 g, 13 mmol) was added dropwise to the carbinolate solution prepared as above (10 ml, 11 mmol) an the mixture stirred overnight at room temperature. All volatile materials were transferred under vacuum and analysed by GC–MS methods and ^{19}F NMR spectroscopy. There were two components, i.e. benzyl bromide (39%) and heptafluoroisopropyl benzyl ether (**15**) (61%) which was isolated by preparative scale GC using a 30% SE30 column at 150 °C. IR $\nu_{max.}$ (cm^{-1}): 1230 (C–O–C stretch). ^1H NMR (250 MHz, $CDCl_3$, TMS) δ: 5.01 (2H, s, CH_2); 7.42 (5H, m, Ar–H) ppm. ^{19}F NMR ($CDCl_3$) δ: -79.5 (6F, s, CF_3); -142.6 (1F, s, CF) ppm. MS *m/z* (EI^+): 276 (M^+, 33%); 91 (100, Ar–CH_2).

Reaction of PS/HF (2) with 2,4,6-trichloropyrimidine

A mixture containing PS/HF (**2**) (0.63 g, 2.6 mmol), 2,4,6-trichloropyrimidine (0.15 g, 0.8 mmol) and acetonitrile (5 ml) was allowed to stand at room temperature for 24 h. A white solid, 'Proton Sponge' hydrochloride (PS/HCl), precipitated. The mixture was filtered and benzotrifluoride (0.20 g, 1.37 mmol) was added as an NMR marker. ^{19}F NMR spectroscopy revealed 2,4,6-trifluoropyrimidine (79% yield by integration); δ_F (CH_3CN): -50 to -60 ppm as compared to the literature data [23] (δ_F -50.6 and -59.7 ppm).

Reaction of PS/HF (2) with benzoyl chloride

A mixture containing PS/HF (**2**) (1.07 g, 4.5 mmol), benzoyl chloride (0.70 g, 5 mmol) and acetonitrile (5 ml) was allowed to stand at room temperature for 24 h. A white solid, 'Proton Sponge' hydrochloride (PS/HCl), precipitated. The mixture was filtered and benzotrifluoride (0.17 g, 1.16 mmol) was added as an NMR marker ^{19}F NMR spectroscopy revealed benzoyl fluoride (76% yield by integration); δ_F (CH_3CN): $+17.0$ (1F, s, COF) ppm as compared to the literature data [23] (δ_F $+17.1$ ppm).

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