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Reactions Involving Fluoride Ion. Part 40[1]. Amines as Initiators of Fluoride Ion Catalysed Reactions

Richard D. Chambers*[a], William K. Gray[a], and Stewart R. Korn[b]

[a]*Department of Chemistry, University of Durham, South Road, Durham. DH1 3LE*

[b]*Zeneca Specialities, Leeds Road, Huddersfield. HD2 1FF*

(Dedicated to our dear friend, Professor H. Suschitzky, on the occasion of his 80th Birthday)

Abstract: Tetrakis(dimethylamino)ethene (TDAE) and trimethylamine react with anhydrous unsaturated fluorocarbons to produce, 'in situ', powerful fluoride- ion sources. These are used to initiate carbon- carbon bond forming reactions eg. oligomerisation and polyfluoroalkylation, and many of these reactions occur efficiently in the *absence of a solvent*.

INTRODUCTION

We and other workers[2-6] have demonstrated that fluoride-ion induced formation of carbanions, from reactions with fluorinated alkenes, provides useful methodology for carbon-carbon bond formation:

$$\text{eg. } F^- + CF_2 = CFCF_3 \rightleftharpoons (CF_3)_2CF^- \longrightarrow \text{etc.}$$

The source of fluoride ion poses a problem, in that anhydrous fluoride ion salts, soluble in organic media (eg. TASF [7], Me_4NF [8]), are not readily available. Previously[9-11], we have used anhydrous potassium and caesium fluorides, largely in suspension, in solvents like sulpholan or tetraglyme and these systems are very effective but the solvents themselves pose considerable problems for isolation of the products. In this paper, we describe methodology involving the use of tetrakis(dimethylamino)ethene (TDAE) and of the less reactive trimethylamine, to provide '*in situ*' formation of fluoride ion and, remarkably, these procedures can be used in the *absence of a solvent*.

TDAE (**1**) is a very strong electron donor[12; 13] and we have demonstrated that it will react with unsaturated fluorocarbons[14], to yield a fluoride salt that is soluble in a wide range of organic solvents. It seemed reasonable, therefore, to consider using a small amount of this amine, with an unsaturated fluorocarbon, to generate a source of fluoride ion eg. (**1a**) that should be very active, providing that the starting materials are anhydrous.

$$\begin{array}{lcl} \text{eg. } (Me_2N)_2C{=}C(NMe_2)_2 + CF_2 = CFCF_3 & \longrightarrow & (\overset{+}{TDAE})\text{-}CF = CFCF_3 \\ \qquad\qquad \textbf{(1) TDAE} & & \qquad F^-\ \textbf{(1a)} \end{array}$$

We describe the salt obtained from hexafluoropropene as (**1a**), because ^{19}F nmr data confirms the moiety derived from the fluorinated alkene, but the ^1H nmr data are too complex to define the amine derived moiety in (**1a**).

Oligomerisation of Fluorinated - Alkenes

We and other workers have described oligomerisations and co-oligomerisation reactions of fluorinated-alkenes and -cycloalkenes[10; 11; 15-17] using metal fluorides. Amines are known to react with fluorinated-alkenes and -cycloalkenes eg. trimethylamine and pyridine will oligomerise hexafluoropropene and perfluorocyclobutene respectively[6; 16; 18] in dipolar aprotic solvents, while perfluorocyclo-butene and -pentene form stable ylides with tributylamine[19] and pyridine[16] respectively, and Russian workers[20] have studied the interaction of amines with unsaturated fluorocarbons. In this paper we describe attempts to assess and develop convenient and general methodology for the use of amines as an alternative to anhydrous fluoride salts, for carbon-carbon bond forming reactions.

Indeed, reaction of TDAE (**1**) with hexafluoropropene occurred, at room temperature, simply by containing the alkene in the presence of a catalytic amount of the amine, in a Carius tube at room temperature. Under these conditions the dimer arising from kinetic control (**2**) was formed quantitatively, while at 60°C,

$$\underset{20\quad:}{CF_2=CFCF_3} + \underset{1(\mathbf{1})}{TDAE} \xrightarrow{\text{i}} \underset{\text{Quant. }(\mathbf{2})}{(CF_3)_2CFCF=CFCF_3}$$

$$\xrightarrow{\text{ii}} \underset{\text{Quant. }(\mathbf{3})}{(CF_3)_2C=CFCF_2CF_3}$$

i, No solvent, r.t.
ii, No solvent, 60°C

the product of thermodynamic control (**3**) is formed exclusively. Furthermore, these compounds may be isolated pure, simply by vacuum transfer.

If, however, acetonitrile is used as solvent, and a higher ratio of amine to alkene is used, then the dimer (**3**) is largely present as a stable anion, observable by ^{19}F nmr[21; 22]. The process clearly involves formation 'in situ' of a very active fluoride ion salt eg. (**1a**), which then forms an ion (**5**), and then dimer (**2**) which, in acetonitrile, forms a stable anion (**6**). Thus, the formation of (**6**) is clear evidence of the availability of fluoride ion in this mixture.

$$(\mathbf{1}) + \underset{(\mathbf{4})}{CF_2=CFCF_3} \overset{F^-}{\rightleftharpoons} \underset{(\mathbf{5})}{(CF_3)_2CF^-} \xrightarrow{(\mathbf{4})} (\mathbf{2}) \xrightarrow{F^-} \underset{(\mathbf{6})}{(CF_3)_2\bar{C}CF_2CF_2CF_3}$$

The nmr spectrum of the anion (**6**) is remarkably similar to that of the corresponding caesium salt[22], and demonstrates that fluorocarbon anion salts are most likely to be relatively 'free' carbanions, quite unlike many other such systems whose structures in solution may be highly associated.

Tetrafluoroethene (TFE) is much more difficult to oligomerise[15; 23]; the structure of the oligomers have been well described in the literature[15; 24] but relatively high temperatures (100°C) are used. We have been unable to oligomerise TFE with amines except under conditions that employ *DMF as solvent.* However, with this solvent, oligomerisation occurred *even at 60°C*, under pressure, to give the normal range of products, with the pentamer predominating.

$$CF_2 = CF_2 \xrightarrow{i} (C_2F_4)_n \text{, where } n = 1\text{-}6$$

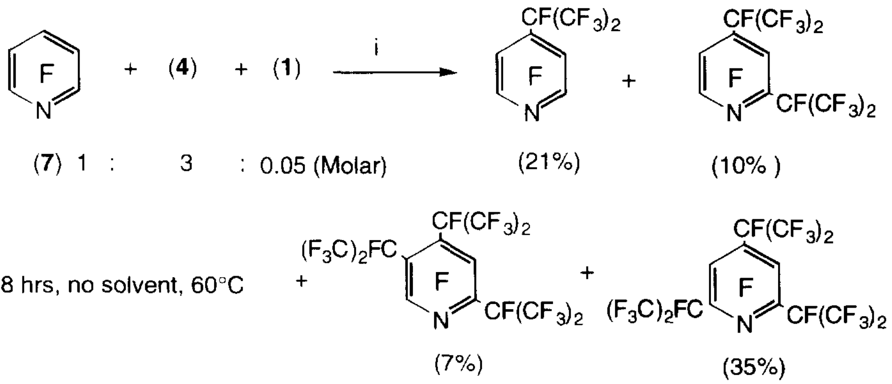
i, Me_3N, DMF, 60° C.

Polyfluoroalkylation

Reactions of fluorinated anions eg. (**5**) with activated fluoroaromatic compounds provide a simple method for introducing some sterically very demanding groups eg. perfluoroisopropyl[9; 25-27]. These reactions are very efficient but isolation of the products from solvent can be extremely difficult. However, we now find that these reactions can be effected in high yield, using amines to promote formation of fluoride ion and, importantly, *in the absence of any solvent.*

$$\text{eg. } \underset{(\mathbf{5})}{(CF_3)_2\bar{C}F} + \text{Ar-F} \longrightarrow \text{Ar-CF}(CF_3)_2 + F^-$$

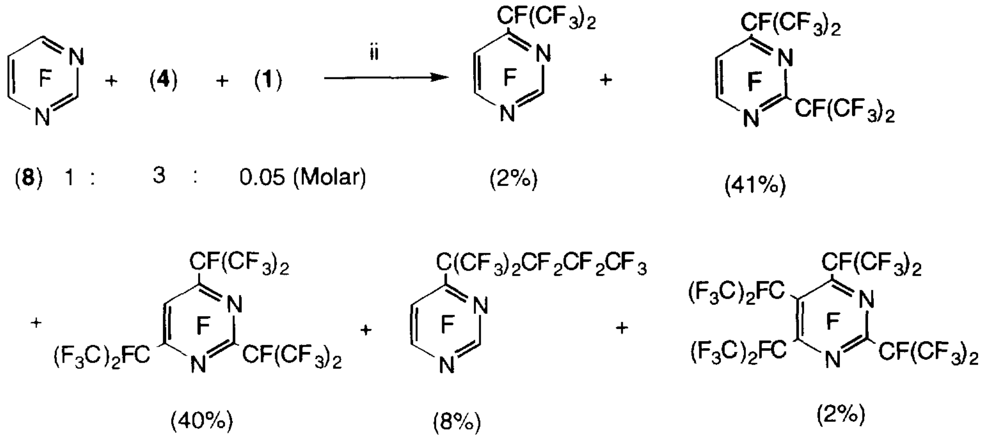
Examples of these reactions are shown below, using pentafluoropyridine (**7**), tetrafluoropyrimidine (**8**), and trifluoro-s-triazine (**9**). In the latter case TDAE proved too reactive and probably the derived fluoride formed a σ-complex[28] with the triazine (**9**) and was therefore not available for reaction with the fluoro alkene (**4**). However, trimethylamine worked very efficiently in this system, although if a solvent is used in the latter case, then σ-complexes of the products (**10**) and (**11**) are formed[28].



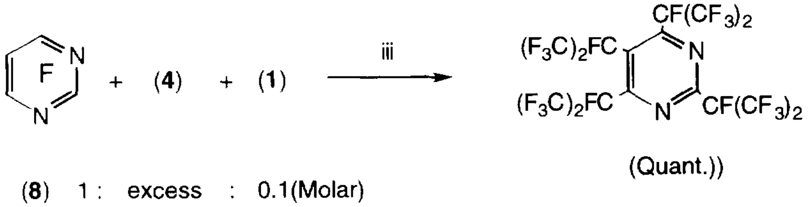
(**7**) 1 : 3 : 0.05 (Molar)

(21%) (10%) (7%) (35%)

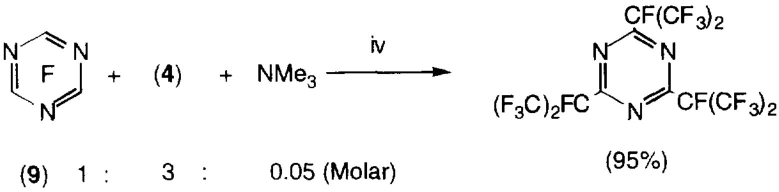
i. 48 hrs, no solvent, 60°C



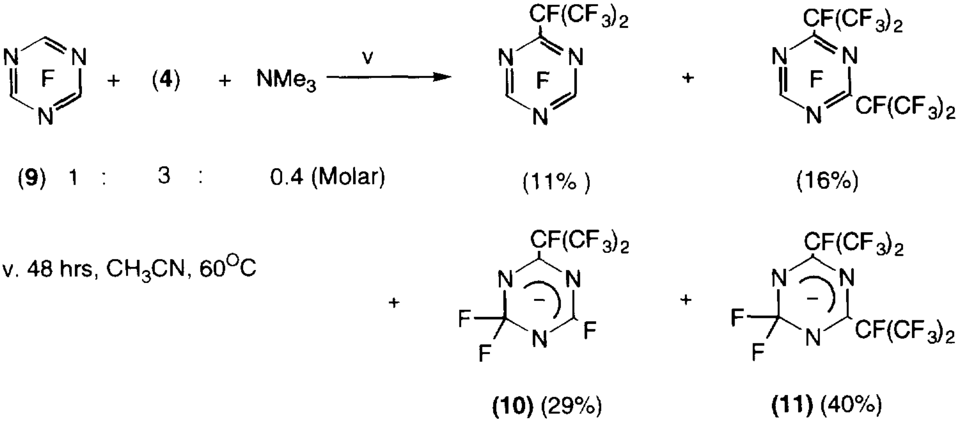
ii. 48 hrs, no solvent, 60°C



iii. 48 hrs, CH_3CN, r.t.

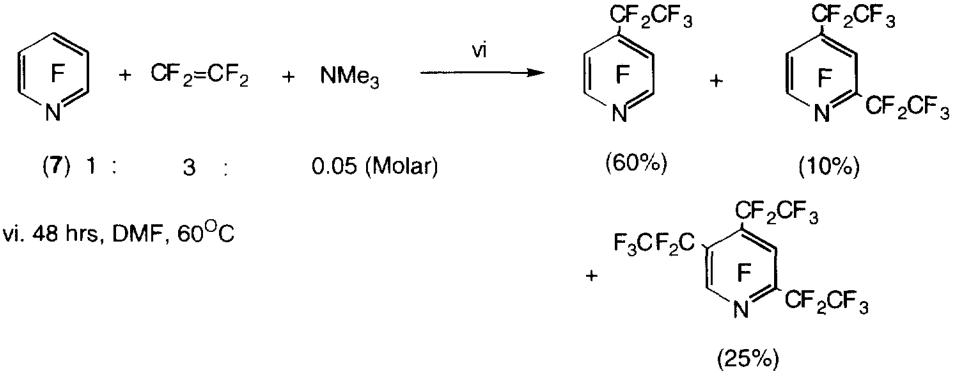


iv. 48 hrs, no solvent, 60°C



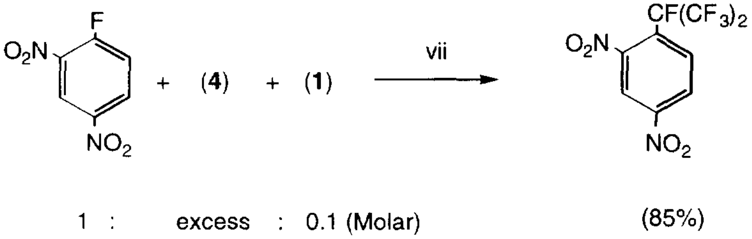
v. 48 hrs, CH_3CN, 60°C

Using TFE, with pentafluoropyridine, we found again that DMF was essential to the success of the fluoride initiation process, as it was with oligomerisation (see above); excellent yields were obtained even at 60°C.



vi. 48 hrs, DMF, 60°C

The effectiveness of the amine initiator was particularly significant with 2,4-dinitrofluorobenzene. Metal fluorides have previously been used for this process[25], but the high temperatures required (120°C) led to competing loss of the nitro group.



vii. 3 days, CH_3CN, 60°C

EXPERIMENTAL

All materials were obtained commercially (Aldrich) and used as received except tetrafluoropyrimidine which was made from tetrachloropyrimidine on heating to 480°C in an autoclave with KF. All solvents were dried prior to use by standard procedures. ^{19}F NMR spectra were recorded using either a Varian VXR 400S or a Bruker AC250 NMR spectrometer. ^{13}C NMR spectra were recorded on a Varian VXR 400S spectrometer. GLC mass spectra were obtained using a VG Trio1000 spectrometer linked to a Hewlett-Packard 5890 Series II gas chromatograph fitted with a 25m cross linked silicone capillary column. Accurate mass measurements were recorded on a VG ZAB-E instrument at the University of Swansea. Preparative scale GLC was performed on a Varian Aerograph Model 920 gas chromatograph, fitted with a 3m 104 SE30 packed column.

Dimerisation of hexafluoropropene (4) at room temperature

A Carius tube (60cm^3), charged with TDAE (**1**) (0.10g, 0.50mmol) and hexafluoropropene (6.00g, 40.00mmol), was sealed and agitated for 24 hrs on a rotating arm at room temperature. After this time the tube was opened and volatile material (5.70g) transferred to a cold trap under reduced pressure. After distillation (atmospheric pressure) the product was shown to contain one major fluorinated compound, which was identified by reference to an authentic sample[29] as perfluoro-4-methylpent-2-ene (**2**); (5.28g,17.65mmol, 88%) δ_F (235 MHz, CH_3CN, $CFCl_3$) -71.7 (3 F, d J 20.9 Hz, 1-CF_3), -78.0 (6F, s, 4',5-CF_3), -158.0 (1F, d J 139.8 Hz, 2-CF), -161.1 (1F, dd J 139.8 45.8 Hz, 3-CF), -189.8 (1F, d J 45.8 Hz, 4-CF).

Dimerisation of hexafluoropropene (4) at 60°C

A Carius tube (60cm^3), charged with TDAE (**1**) (0.10g, 0.50mmol) and hexafluoropropene (6.00g, 40.00mmol), was sealed and heated to 60°C in a protective metal tube for 24 hrs. After this time the tube was opened and volatile material (5.45g) transferred to a cold trap under reduced pressure. After distillation (atmospheric pressure) the product was shown to contain one major fluorinated compound, which was identified by reference to an authentic sample[29] as perfluoro-2-methylpent-2-ene (**3**); (4.90g,16.33mmol, 82%) δ_F (235 MHz, CH_3CN, $CFCl_3$) -60.3 (3 F, m, 1-CF_3), -63.0 (3F, m, 1'-CF_3), -86.4 (3F, m, 5-CF_3), -100.4 (1F, br.s, 3-CF), -119.5 (2F, m, 4-CF_2).

Formation of an observable anion from (2)

A Carius tube (60cm^3), charged with hexafluoropropene (5.25g, 35.00mmol) and a significantly larger quantity of TDAE (**1**) than used in the reaction above (2.00g, 10.00mmol) in acetonitrile (10cm^3), was sealed and agitated for 24 hrs on a rotating arm at room temperature. After this time the tube was opened and volatile material (0.60g) was isolated by transfer to a cold trap under reduced pressure and identified as perfluoro-4-methylpent-2-ene (2) (0.50g,1.67mmol, 10%). Examination of the residual liquid by ^{19}F NMR revealed the perfluoro-2-methyl pentaneyl anion (**6**)[22]; δ_F (235 MHz, CH_3CN, $CFCl_3$) -42.2 (6F, m, 1-CF_3), -91.6 (2F, m, 3-CF_2), -126.7 (2F, m, 4-CF_2), -81.4 (3F, m, 5-CF_3).

Oligomerisation of tetrafluoroethylene

A Carius tube (60cm^3), charged with, trimethylamine (0.1g, 1.69mmol) and tetrafluoroethene (3.00g, 30.00mmol) in dimethylformamide (10cm^3), was sealed and heated in a protective metal tube at 60°C for 48 hrs. After this time the tube was opened and volatile materials (2.78g) isolated by distillation under reduced pressure at 70°C. The isolated material was shown to contain five major fluorinated compounds, which were identified by reference to authentic samples[15] as dimer (6% by GLC), trimer (8% by GLC), tetramer (11% by GLC), pentamer (58% by GLC) and hexamer (12% by GLC). Reference compounds kindly supplied by Dr R. L. Powell (ICI Ltd.).

Perfluoroalkylation of pentafluoropyridine (7) using hexafluoropropene (4)

A Carius tube (60cm^3), charged with, TDAE (**1**) (0.10g, 0.50mmol), hexafluoropropene (**4**) (4.12g, 27.47mmol) and pentafluoropyridine (**7**) (1.5g, 8.88mmol), was sealed and heated in a protective metal tube at 60°C for 48 hrs. The tube was opened, volatile materials (5.65g) transferred to a cold trap under reduced pressure, fluorobenzene added as a marker and products analysed by GLC-MS and ^{19}F NMR. There were five main components in the mixture which could be characterised by comparison of spectra with those obtained previously[26]; perfluoro-4-isopropylpyridine (21% by ^{19}F NMR integration of ring fluorine resonances against that of fluorobenzene); m/z (EI^+) 319 (M^+ 25%); δ_F (235 MHz, CH_3CN, $CFCl_3$) -74.3 (6F, d J 6.0 Hz, 4-CF_3), -86.7 (2F, dd J 21.0, 29.4 Hz, 2,6-CF), -135.2 (1F, d J 85.1 Hz, 3-CF), 136.4 (1F, d J 85.0 Hz, 5-CF), -180.3 (1F, dq J 21.3, 6.0 Hz, 4-CF), perfluoro-2,4-diisopropylpyridine (10% by ^{19}F NMR integration of ring fluorine resonances against that of fluorobenzene); m/z (EI^+) 469 (M^+ 14%); δ_F -74.0 (6F, m, 4-CF_3), -74.0 (6F, m, 2-CF_3), -82.3 (1F, m, 6-CF), -119.0 (1F, dd J 20.3, 30.3 Hz, 3-CF), -121.3 (1F, d J 23.4 Hz, 5-CF), -177.3 (1F, dm J 85 Hz, 4-CF), -181.4 (1F, dm, J 60 Hz, 6-CF), perfluoro-2,4,5-triisopropylpyridine (7% by ^{19}F NMR integration of ring fluorine resonances against that of fluorobenzene); m/z (EI^+) 619 (M^+ 8%); δ_F -50.5 (1F, m, 6-CF), -72.6 (12F, m, 4,5-CF_3), -74.4 (6F, m, 2-CF_3), -110.5 (1F, ddsept. J 30.0, 58.2, 3.0 Hz, 3-CF), -166.6 (2F, dm, J 32.2 Hz, 4,5-CF), -184.2 (1F, dm J 58.0 Hz, 2-CF), perfluoro-2,4,6-triisopropylpyridine (35% by ^{19}F NMR integration of ring fluorine resonances against that of fluorobenzene); m/z (EI^+) 619 (M^+ 14%); δ_F -74.1 (12F, m, 2,6-CF_3), -74.8 (6F, m, 4-CF_3), -106.4 (1F, ddsept. J 19.2, 57.3, 3.0 Hz, 5-CF), -107.5 (1F, ddsept. J 58.3, 92.2, 3.0 Hz, 3-CF), -179.3 (1F, dm J 6.0 Hz, 4-CF), -185.2 (2F, d m J 6.0 Hz, 2,6-CF), and hexafluoropropene dimer.

Perfluoroalkylation of tetrafluoropyrimidine (8) using hexafluoropropene (4)

A Carius tube (60cm^3), charged with, TDAE (**1**) (0.10g, 0.50mmol), hexafluoropropene (**4**) (6.00g, 40.00mmol) and tetrafluoropyrimidine (**8**) (2.0g, 13.16mmol), was sealed and heated in a protective metal tube at 60°C for 48 hrs. The tube was opened, volatile materials (7.76g) transferred to a cold trap under reduced pressure, fluorobenzene added as a marker and products analysed by GLC-MS and ^{19}F NMR. There were six main components in the mixture which could be characterised by comparison of spectra with those obtained previously[27]; perfluoro-4-isopropylpyrimidine (2% by ^{19}F NMR integration of ring fluorine resonances against that of fluorobenzene); m/z (EI^+) 302 (M^+ 29%); δ_F (376 MHz, CH_3CN, $CFCl_3$) -47.7 (1F, d J 27.8 Hz, 2-CF), -69.9 (1F, d J 21.8 Hz, 6-CF), -74.8 (6F, d J 6.2 Hz, 4-CF_3), -151.7 (1F, m, 5-CF), -186.2 (1F, dm J 53.0 Hz, 4-CF), perfluoro-4,6-diisopropylpyrmiidine (41% by ^{19}F NMR integration of ring fluorine resonances against that of fluorobenzene); m/z (EI^+) 452 (M^+ 21%); δ_F -48.6 (1F, d J 27.8 Hz, 2-CF), -74.5 (12F, m, 4,6-CF_3), -134.1 (1F, dd J 5.0, 30.4 Hz, 5-CF), -185.7 (2F, d sept J 6.8, 53.0 Hz, 4,6-CF), perfluoro-2,4,6-triisopropylpyrimidine (40% by ^{19}F NMR integration of ring fluorine resonances against that of fluorobenzene); m/z (EI^+) 602 (M^+ 14%); δ_F -74.2 (12F, m, 4,6-CF_3), -74.9 (6F, m, 2-CF_3), -122.7 (1F, t J 51.1 Hz, 5-CF), -181.1 (2F, sept J 6.0 Hz, 2-CF), -185.5 (1F, sept J 6.0 Hz, 4,6-CF), perfluoro-2,4,5,6-tetraisopropylpyrimidine (2% by ^{19}F NMR integration of tertiary fluorine resonances against that of fluorobenzene); m/z (EI^+) 752 (M^+ 3%); δ_F -70.0 (3F, m, 5-CF_3), -71.9 (3F, dd J 18.4, 30.0 Hz, 4-CF_3), -72.8 (3F, m, 6-CF_3) -74.7 (3F, d J 7.5 Hz, 2-CF_3), -150.7 (1F, d sept sept J 125.9, 17.3, 3.0 Hz, 5-CF), -176.5 (1F, dm J 126.3 Hz, 6-CF), -181.4 (1F, sept m J 43.6, 4-CF), -183.3 (1F, sept J 6.8 Hz, 2-CF), the previously uncharacterised **perfluoro-4-(1',1'-dimethyl)butylpyrimidine** (8% by ^{19}F NMR integration) a sample of which was isolated by preparative scale GLC; (Found: C, 26.5; F, 67.3; N, 6.19%. M^+, 451.981, $C_{10}F_{16}N_2$ requires C, 26.5; F, 67.3; N, 6.19%. M^+, 451.981), m/z (EI^+) 452 (M^+ 16%); i.r. (film) λ_{max} 750, 980, 1250, 1360, 1450, 1500, 1600 and 1650 cm^{-1}; δ_F -47.4 (1F, s, 2-CF), -59.1 (6F, m, 4-CF_3), -67.6 (1F, d J 21.1 Hz, 6-CF), -81.2 (3F, m, 4'-CF_3), -104.5 (2F, m, 2'-CF_2), -122.6 (2F, m, 3'-CF_2), -142.8 (1F, m, 5-CF) and hexafluoropropene dimer.

Formation of perfluoro-2,4,5,6-tetraisopropylpyrimidine from crude products of perfluoroalkylation

To an evacuated round bottomed flask (50ml) containing the crude product of the reaction above (5.50g) and TDAE (**1**) (0.20g, 1.00mmol) in acetonitrile (10cm^3) was attached an expandable gas bladder (2 litre), fitted with a tap, and charged with hexafluoropropene (**4**) (9.00g, 60.00mmol). The bladder was opened to the flask and the hexafluoropropene allowed to diffuse into the sealed system. The flask was agitated, using a magnetic stirrer, for 48 hrs at room temperature. After this time the lower fluorocarbon layer was isolated and the products distilled to give perfluoro-2,4,5,6-tetraisopropylpyrimidine (4.66g, 6.20 mmol) and hexafluoropropene dimer.

Perfluoroalkylation of trifluoro-s-triazine (9) using hexafluoropropene (4)

A Carius tube (60cm^3), charged with, trimethylamine (0.10g, 1.69mmol), hexafluoropropene (**4**) (3.60g, 24.00mmol) and trifluoro-s-triazine (**9**) (1.0g, 7.40mmol), was sealed and heated in a protective metal tube at 60°C for 48 hrs. The tube was opened, volatile materials (4.23g) transferred to a cold trap under reduced pressure, fluorobenzene added as a marker and products analysed by GLC-MS and ^{19}F NMR. There were two main components in the mixture which could be characterised by comparison of spectra with those obtained previously[30]; perfluoro-2,4,6-triisopropyl-s-triazine (95% by ^{19}F NMR integration); m/z (EI^+) 585 (M^+ 13%), δ_F (376 MHz, CH_3CN, $CFCl_3$) -75.5 (18F, d J 7.5 Hz, 2,4,6-CF_3), -186.4 (3F, sept. J 7.5 Hz, 2,4,6-CF), δ_C (100 MHz, CH_3CN, $Si(CH_3)_4$) 88.6 (3C, dsept. J 215.3, 33.4 Hz, 2,4,6-CF), 118.3 (6C, qd J 286.4, 26.5 Hz, 2,4,6-CF_3), 166.6 (3C, d J 22.0 Hz, 2,4,6-CF) and hexafluoropropene dimer.

Perfluoroalkylation of trifluoro-s-triazine (9) using hexafluoropropene (4) in a solvent

A Carius tube (60cm^3), charged with, trimethylamine (0.20g, 3.38mmol), hexafluoropropene (**4**) (3.00g, 22.22mmol) and trifluoro-s-triazine (**9**) (1.0g, 7.40mmol), was sealed and heated in a protective metal tube at 60°C for 48 hrs. The tube was opened, the clear lower layer isolated, volatile materials (1.30g) transferred to a cold trap under reduced pressure, fluorobenzene added as a marker and products analysed by GLC-MS and ^{19}F NMR. There were three main components in the mixture which could be characterised by comparison of spectra with those obtained previously[28]; perfluoro-2-isopropyl-s-triazine (11% by ^{19}F NMR integration); m/z (EI^+) 285 (M^+ 24%), δ_F (376 MHz, CH_3CN, $CFCl_3$) -30.4 (2F, s, 4,6-CF), -74.4 (6F, d J 7.5 Hz, 2-CF_3), -188.8 (1F, sept. J 7.5 Hz, 2-CF), perfluoro-2,4-isopropyl-s-triazine (16% by ^{19}F NMR integration); m/z (EI^+) 435 (M^+ 7%), δ_F -30.0 (1F, s, 6-CF), -75.7 (12F, d J 7.5 Hz, 2,4-CF_3), -186.4 (2F, sept. J 7.5 Hz, 2,4-CF) and hexafluoropropene dimer. The orange upper layer was also examined by ^{19}F NMR, after addition of a marker, and shown by comparison of spectra with those obtained previously to contain two fluorinated components; perfluoro-2-isopropyl-s-triazine σ-complex (29% by ^{19}F NMR integration); δ_F (376 MHz, CH_3CN, $CFCl_3$) -2.3 (2F, br.s, 4-CF_2), -50.4 (1F, s, 6-CF), -74.2 (6F, d J 7.5 Hz , 2-CF_3), -183.4 (1F, sept. J 7.5 Hz, 2-CF), perfluoro-2,4-isopropyl-s-triazine σ-complex (40% by ^{19}F NMR integration); δ_F -1.5 (2F, br.s, 6-CF_2), -74.3 (12F, d J 7.5 Hz, 2,4-CF_3), -183.8 (2F, sept. J 7.5 Hz, 2,4-CF).

Perfluoroalkylation of pentafluoropyridine (7) using tetrafluoroethene

A Carius tube ($60cm^3$), charged with, trimethylamine (0.1g, 1.69mmol), tetrafluoroethene (2.80g, 28.00mmol) and pentafluoropyridine (**7**) (1.50g, 8.88mmol) in dimethylformamide ($10cm^3$), was sealed and heated in a protective metal tube at 60°C for 48 hrs. The tube was opened, volatile materials (4.15g) transferred to a cold trap under reduced pressure and, fluorobenzene added as a marker and products analysed by GLC-MS and ^{19}F NMR. There were three main components in the mixture which could be characterised by comparison of spectra with those obtained previously[31]; perfluoro-4-ethylpyridine (60% by ^{19}F NMR integration of ring fluorine resonances against that of fluorobenzene); m/z (EI^+) 269 (M^+ 16%), δ_F (235 MHz, CH_3CN, $CFCl_3$) -86.0 (3F, t J 6.4 Hz, 4-CF_3), -89.7 (2F, dd J 13.7, 8.3 Hz, 2,6-CF), -113.6 (2F, t J 28.6 Hz, 4-CF_2), -141.1 (2F, br.m, 3,5-CF), perfluoro-2,4-diethylpyridine (10% by ^{19}F NMR integration of ring fluorine resonances against that of fluorobenzene); m/z (EI^+) 369 (M^+ 6%), δ_F -83.8 (1F, m, 6-CF), -84.9 (3F, m, 4-CF_3), -86.6 (3F, m, 4-CF_3), -113.2 (2F, t J 30.0 Hz, 4-CF_2), -116.9 (2F, t J 31.1 Hz, 2-CF_2), -118.5 (1F, br. m, 3-CF), -126.4 (1F, br. m, 5-CF), -140.3 (2F, m, 3,5-CF), perfluoro-2,4,5-triethylpyridine (25% by ^{19}F NMR integration of ring fluorine resonances against that of fluorobenzene); m/z (EI^+) 469 (M^+ 10%), δ_F -55.5 (1F, m, 6-CF), -81.4 (6F, m, 4,5-CF_3), -83.2 (3F, m, 2-CF_3), -103.2 (4F, br.m, 4,5-CF_2), -115.8 (1F, s, 3-CF), -116.0 (2F, m, 2-CF_2).

Perfluoroalkylation of 2,4-dinitrofluorobenzene using hexafluoropropene

To an evacuated round bottomed flask (50ml) containing 2,4-dinitrofluorobenzene (2.00g, 16.13mmol) and TDAE (**1**) (0.20g, 1.00mmol) in acetonitrile ($10cm^3$) was attached an expandable gas bladder (2 litre), fitted with a tap, and charged with hexafluoropropene (**4**) (9.00g, 60.00mmol). The bladder was opened to the flask and the hexafluoropropene allowed to diffuse into the sealed system. The flask was agitated, using a magnetic stirrer, for 3 days at 60°C. After this time solvent was removed under reduced pressure the residue shown to contain **2,4-dinitroheptafluoroisopropylbenzene** (85% by GLC integration) and 2,4-dinitrofluorobenzene. A sample of the product was isolated by preparative scale GLC (0.6g, 1.79mmol); (Found: C, 32.0; H, 0.8; N, 8.3%. $C_9H_3F_7N_2O_4$ requires C, 32.1; H, 0.9; N, 8.3%), m/z (EI^+) 336 (M^+ 10%); i.r. (film) λ_{max} 860, 990, 1250, 1365, 1450, 1550, 1620, 1850, 2060 and $3050cm^{-1}$; δ_F (235 MHz, CH_3CN, $CFCl_3$) -74.2 (6F, br.s, 1-CF_3), -182.9 (1F, m, 1-CF).

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