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The effect of basicity on fluorodenitration reactions using tetramethylammonium salts.

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Abstract: The fluorodenitration of several nitroaromatics with tetramethylammonium salts has been found to be dependent on the basicity of the fluorinating species. Tetramethylammonium fluoride is highly basic and is capable of inducing H-D exchange in 1,3-dinitrobenzene, as well as deprotonating *N,N*-dimethylacetamide. Reaction of the fluoride with phthalic anhydride forms the bifluoride *in situ*. Tetramethylammonium bifluoride gives higher yields of the required fluoroaromatic, but slower reaction rates than the corresponding fluoride.

Keywords: Basicity; Fluorine and compounds; Halogenation.

Introduction

Fluoroaromatics have applications in many sectors, including the pharmaceutical and agrochemical industries due to the unusual properties of the C-F bond [1, 2, 3]. One method of forming fluoroaromatics is by fluorodenitration, exploiting the low cost and ready availability of nitroaromatics along with the good leaving ability of the aromatic nitro group [4].

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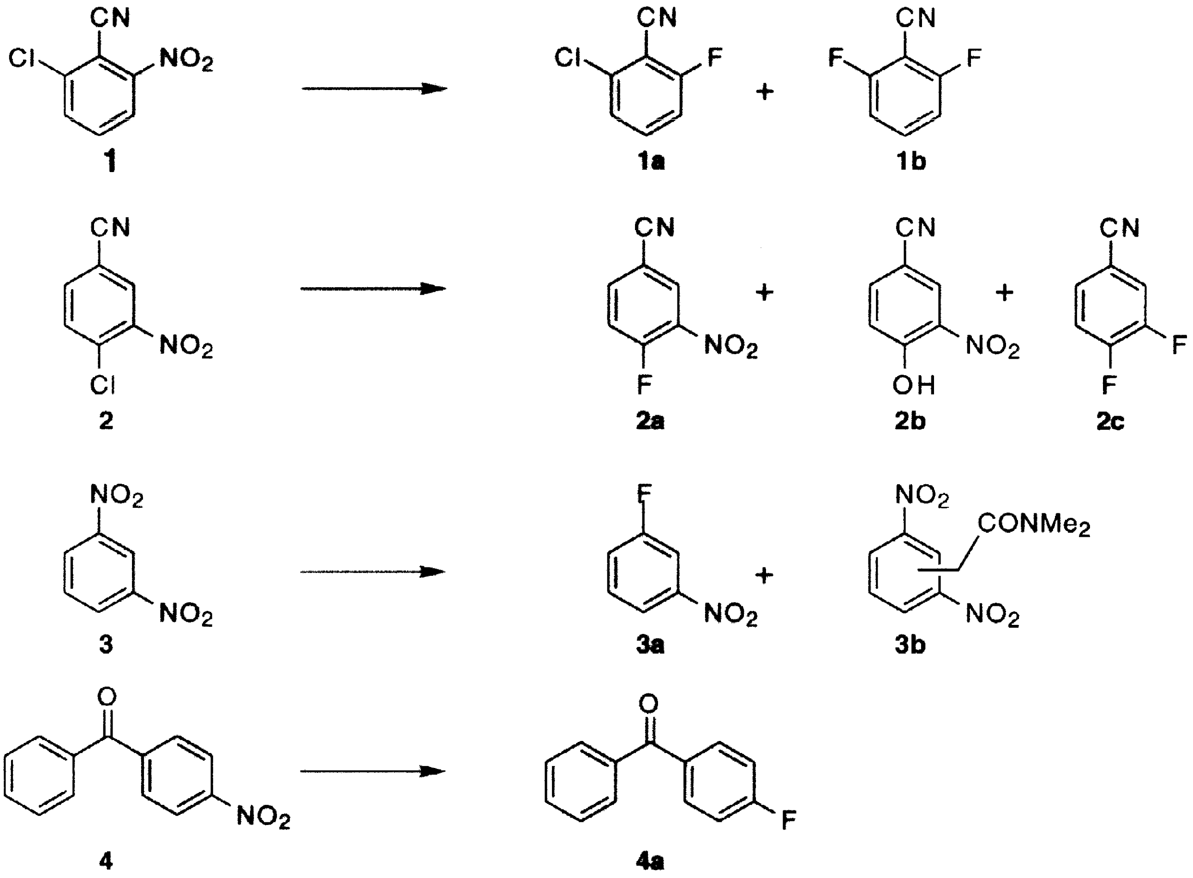
Fluorodenitration has the potential for complementing halogen exchange, one of the current methods of forming fluoroaromatics. The preparation of fluoroaromatics with only one other group *meta* to the fluorine is difficult to achieve by halogen exchange, but the greater inductive effect of the nitro group compared to the chloro group makes its displacement favourable when similarly activated. Thus, 1,3-dinitrobenzene is a much more likely, if still very demanding, substrate for the preparation of 3-fluoronitrobenzene than 3-chloronitrobenzene due to the larger inductive effect of the nitro group [5]. There are many reports in the literature of the fluorodenitration of a wide range of substituted nitroaromatics. It is known that for substitution to occur, at least one electron-withdrawing group is required on the ring, with CN, CF_3, SO_2CF_3, NO_2, CO, CHO and COOMe being used [6, 7, 8]. Alternatively, several inductively activating groups can be used, for example in the fluorodenitration of pentachloronitrobenzene. Tetraalkylammonium fluorides have been successfully used for the fluorodenitration of several substituted nitroaromatics [9, 10]. These have advantages over other alkali metal fluorides in that they are more soluble in the reaction media, allowing milder reaction conditions and shorter reaction times. The basicity of the fluoride ion is known to be highly dependent on the countercation, the level of hydration and the reaction solvent [11]. In protic solvents such as alcohols, fluorides form strong hydrogen bonds. However, fluorodenitration is generally carried out in dipolar aprotic solvents, where hydrogen bonding is of minor importance and the basicity and nucleophilicity of the fluoride is much increased [11]. Christie *et al.* have shown that anhydrous tetramethylammonium fluoride (TMAF) is capable of abstracting a proton from acetonitrile [12]. Similarly, we have found that the reaction of TMAF in DMSO with a variety of chloro and nitroaromatic compounds led to products which were attributed to the basicity of the fluoride in this medium [13]. These products were in addition to the expected phenol and ether by-products, formed by hydrolysis of the C-F bond [9] and / or nucleophilic attack by the displaced nitrite anion [5]. Nitroaromatics are known to be capable of interacting with bases in a variety of ways [14]. These include proton abstraction leading to carbanions, the formation of σ-adducts *via* covalent bond formation and electron transfer, leading to the formation of radical anions. All these may lead to unwanted by-products in fluorodenitration reactions [15, 16] and other S_NAr reactions [17]. Hence, we decided to examine further the use of tetramethylammonium salts in a number of fluorodenitration reactions to determine whether the basicity of the fluoride source has any effect on the overall reaction.

Results and discussion

TMAF reacts with a wide range of nitroaromatics to form the corresponding fluoroaromatics, Scheme 1. The nitroaromatics **1-4** used in this study were chosen to include a range of different activating groups as well as to examine competitive denitration and dehalogenation within the same molecule. **3** was chosen as an example of *meta*-denitration, which is of interest due to the difficulty of forming such fluoroaromatics *via* halogen exchange, an established industrial method of forming fluoroaromatics [2]. In examining the fluorodenitration of simple aromatics using TMAF, it was found that analysis of the reactions by simple GC methods was unsatisfactory due to a number of involatile products which were not detected by GC. The incorporation of an internal standard demonstrated that yields were often lower than previously reported [8, 9]. We found that higher yields of the desired products were obtained when the reactions were carried out with TMAF.$^4/_3H_2O$ in *N,N*-dimethylacetamide (DMAc), rather than the azeotropically-dried TMAF / DMSO system described previously when repeated with an internal standard [8].

The fluorodenitration reactions of both **1** and **4** with TMAF.$^4/_3H_2O$ in DMAc resulted in relatively high yields of the required fluoroaromatics (83 and 81 % respectively; 1 % **1b** was also detected in the fluorination of **1**). Analysis of the product mixture by mass spectroscopy showed that the compounds not detectable by GC were ethers, formed either by hydrolysis of the fluoroaromatics and subsequent phenoxide attack on further product [8] or by attack of the displaced nitrite anion [5]. The phenol **2b** (9 %) was also detected in the halogen exchange of **2**, with halogen exchange occurring in preference to fluorodenitration to give **2a** in 41 %. However, in the case of **3**, a complex product mixture was formed when it was reacted with two equivalents of TMAF at 140 °C in DMAc. ^{19}F-NMR spectroscopy showed that the only fluorine-containing product was **3a** (27 %), with **3b** (12 %) being the only other GC detectable product. If hydrolysis of the fluoroaromatic were leading to by-product formation in the



Scheme 1: Fluorodenitration reactions selected for investigation.

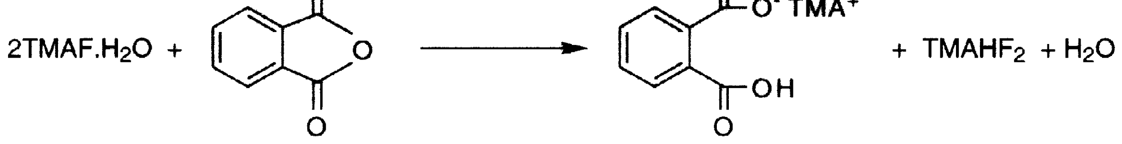
fluorodenitration of **3**, addition of water to the reaction mixture would be expected to lead to a reduction in the amount of **3a** formed. In agreement with other work [18], even the addition of six mole equivalents of water with respect to substrate was found to have no effect on the outcome of this fluorodenitration. Likewise, doping the system with another protic compound, propan-2-ol, was also found to have no effect on the fluorodenitration of **3**, although, in the case of **2**, it was found that 4-*iso*propoxy-3-nitrobenzonitrile was formed in place of the phenol. Nucleophilic attack of the displaced nitrite anion is also generally believed to lead to by-products [5]. However, no reaction was found to occur between pre-formed tetramethylammonium nitrite and **3** under the same reaction conditions as above. When one of the fluorodenitration products, **3a**, was reacted separately with tetramethylammonium nitrite, only 6 % **3** was formed in 24 hours at 140 °C. These results demonstrate that neither hydrolysis of the C-F bond nor attack of the displaced nitrite anion can account for the large amounts of by-products formed in this reaction.

Although the reaction of **3** leads to a complex mixture of by-products (as shown by TLC and ^{1}H-NMR), only one of these was detectable by GC. The identity of this product was attributed to **3b** arising from reaction of the solvent with **3**. The splitting pattern of the mass spectrum of this product is consistent with this assignment, with a base peak at 72 amu, as described by Lee *et al.* [19] for a range of substituted phenylacetamides. Unlike the 3-nitrophenylacetamide, there is a peak at 207 amu, rather than the 208 observed by Lee *et al.*. Further evidence for the formation of this product *via* deprotonation of DMAc was obtained from the fact that this product could also be prepared from the reaction of **3** in DMAc with another strong base, potassium hydroxide, in DMAc, but not from the reaction with TMAF.$^4/_3H_2O$ in DMF. The nucleophilic aromatic substitution of hydrogen from nitroaromatics by a variety of nucleophiles is well known [20], and is thought to arise from oxidation of the intermediate σ-complexes [21] by the nitroaromatic itself. Hence, part of the starting material is reduced (the ability of nitroaromatics such as **3** to accept electrons is well-documented [22]).

Addition of phthaloyl dichloride (PDC) to fluorodenitration reactions has been reported as a way of improving yields [5, 18, 23]. These reports showed that, with KF and a phase transfer catalyst alone, yields from the fluorodenitration of *meta*-substituted nitroaromatics were low, but the addition of PDC resulted in substantial improvements. This was thought to be due to trapping of the displaced nitrite anion, thus reducing the propensity for nucleophilic attack by this ambident nucleophile. All of the above workers carried out their reactions in sulfolane. However, we found that, while PDC was stable in sulfolane, it reacted vigorously with DMAc, even in the absence of both fluoride and substrate, and formed a red solution from which phthalic anhydride (PA) precipitated. PDC was also found to react with DMSO, evolving dimethyldisulfide, dimethylsulfide and *bis*(methylthio)methane along with precipitation of PA. Markezich *et al.* [24] described how nitrite anion trapping was observed in the fluorodenitration of 4-nitrophthalic anhydride, where some of the substrate reacted with the displaced nitrite anion to give 4-nitrophthalic acid. It was thus thought likely that addition of PA to a typical fluorodenitration reaction would remove nitrite anions and hence improve reaction selectivity.

We found that addition of one equivalent of PA to a typical fluorodenitration of **3** (2.2 equivalents of TMAF.$^4/_3H_2O$ at 140 °C in DMAc) resulted in the slower formation of the σ-complex (taking 90 seconds to form a purple solution characteristic of such a species [21] rather than instantaneously as in the case of fluoride alone). The rate of reaction was also much reduced, but the final yield of **3a** was found to be 49 % after 2 hours at 140 °C, almost double that achieved in the presence of fluoride alone (27 % after 10 minutes with no increase thereafter), with 30 % starting material also remaining (no starting material remained in the reaction with TMAF) . A slower rate of reaction would be consistent with a less nucleophilic fluoride and hence further investigations were carried out in an attempt to characterise the fluorinating species in this reaction.

It was found that addition of equimolar amounts of PA and TMAF.$^4/_3H_2O$ in acetonitrile at 50 °C resulted in complete dissolution of both species. Removal of the solvent gave a non-hygroscopic white solid which, unlike TMAF, was found to be readily soluble in DMSO. Spectroscopic analysis showed that the species was the tetramethylammonium salt of phthalic acid. Although the ^1H-NMR spectrum was identical to that from the solid formed by reaction of equimolar amounts of tetramethylammonium hydroxide and PA, the ^{19}F-NMR spectrum showed a single peak at -163 ppm in d^6-DMSO, which is not consistent with either TMAF or the tetramethylammonium bifluoride ($TMAHF_2$). It would appear that reaction occurs between PA and the water of hydration associated with the TMAF to form the tetramethylammonium salt of the acid and HF, which reacts with the glassware producing a fluorosilicate, consistent with the ^{19}F-NMR value obtained here [25]. In the case of a 2:1 ratio of TMAF.$^4/_3H_2O$ to PA, it would be expected that the HF formed would react with another molecule of TMAF to form $TMAHF_2$, Scheme 2.



Scheme 2: Reaction of TMAF with phthalic anhydride to give the corresponding bifluoride.

Indeed, using this ratio, the reaction between TMAF.$^4/_3H_2O$ and PA gave a hygroscopic white solid, the ^{19}F-NMR spectrum of which was found to be identical to that of a pure commercial sample of $TMAHF_2$. All other analytical data agreed with that of a mixture of the tetramethylammonium salt of the phthalic acid and $TMAHF_2$. These results imply that the fluorinating species in the above fluorodenitration reaction of **3** was the bifluoride, formed *in situ* from the reaction of TMAF with PA.

The effects of basicity on fluorodenitration reactions.

Landini *et al.* [26] predicted that the basicity of a tetraalkylammonium fluoride will increase as the level of hydration decreases. The authors also showed that the fluoride is more basic than the corresponding bifluoride. Nucleophilicity of the fluoride was also found to follow this same trend. Hence, we examined the fluorodenitration of the nitroaromatics **1-4** using successively more basic fluoride sources, Table 1 [27].

TMAF has the advantage over other onium fluorides in that it can be dried to a completely anhydrous state [12]. In agreement with the predictions of Landini *et al.* [26], the rates of reaction for fluorodenitration using anhydrous TMAF were greater than the corresponding reaction with TMAF.$^4/_3H_2O$. However, yields were slightly reduced with this fluoride source compared to those achieved with the hydrated fluoride, which correlates with the predicted increased basicity of the anhydrous fluoride. In all cases, an excess (three equivalents) of $TMAHF_2$ was required to avoid excessive residual starting material. For example, with **4**, using 1.2 equivalents of $TMAHF_2$ at 140 °C, only a 56 % conversion to **4a** was achieved, with 36 % starting material remaining. Similar effects were observed by Brown *et al.* [28] and Rieux *et al.* [29], which they attributed to the formation of higher fluorides such as $TMAH_2F_3$. Addition of 3 or 4 equivalents of $TMAHF_2$ was found to give 81 and 83 % conversion to **4a** respectively, with 8 and 6 % starting material remaining. Residual starting material was also observed when successive additions of one equivalent of $TMAHF_2$ were added at hourly intervals, Figure 1.

Table 1: Yields of all GC detectable products from the fluorodenitration of some nitroaromatics using different fluoride sources.

Substrate	Fluoride Source	Reaction Temp / °C	Reaction Time / min	Products and yields[a]
1[b]	TMAF[d]	60	40	72 % **1a**, 5 % **1b**
	TMAF.H_2O[e]	60	60	83 (71) % **1a**, 1 % **1b**
	$TMAHF_2$[e]	60	180	84 % **1a**
2[b]	TMAF[d]	80	10	29 % **2a**, 11 % **2b**, 5 % **2c**
	TMAF.H_2O[e]	80	20	41 % **2a**, 9 % **2b**
	$TMAHF_2$[e]	80	20	58 % **2a**, 2 % **2b**, 12 % **2**
3[c]	TMAF[d]	140	10	26 % **3a**, 10 % **3b**
	TMAF.H_2O[e]	140	10	27 % **3a**, 12 % **3b**
	$TMAHF_2$[e]	140	120	66 % **3a**, 2 % **3**
4[b]	TMAF[d]	140	30	75 % **4a**
	TMAF.H_2O[e]	140	40	81 (70) % **4a**
	$TMAHF_2$[e]	140	120	83 % **4a**, 6 % **4**

[a] All yields quoted as percentage area by GC, corrected by the presence of an internal standard. Values in parentheses refer to unoptimised isolated yields. All reactions were carried out in DMAc.

[b] 1.1 equivalents of TMAF and TMAF.$^4/_3H_2O$ used, 3 equivalents $TMAHF_2$.

[c] 2.2 equivalents of TMAF and TMAF.$^4/_3H_2O$ used, 6 equivalents $TMAHF_2$.

[d] TMAF dried by the method of Christie*et al.* [12]

[e] Dried under vacuum at 60 °C for two days.

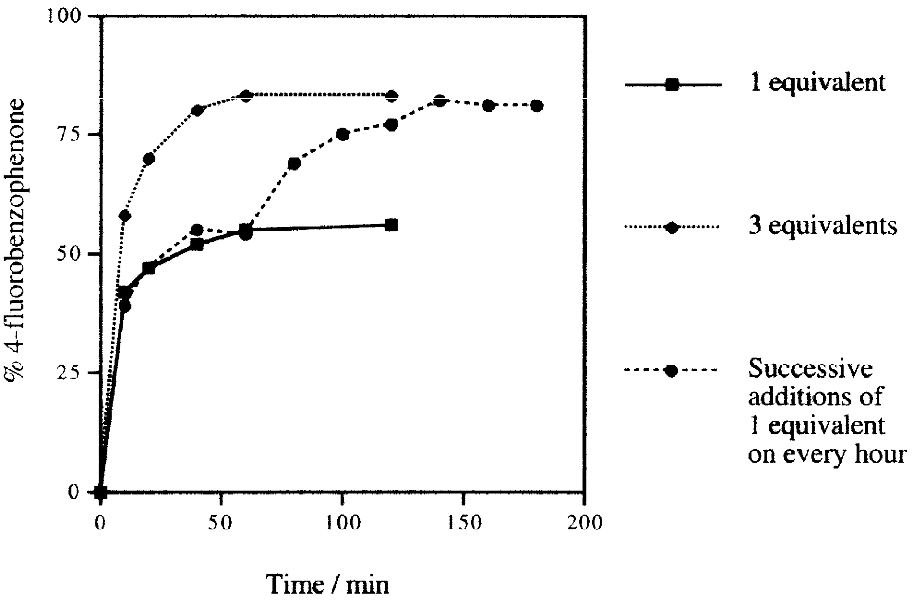


Figure 1: Effect of amount of $TMAHF_2$ on the fluorodenitration of **4**.

In general, the rates of reaction were much reduced when using $TMAHF_2$ compared to the fluoride, but yields of the required fluoroaromatics were greater. The reduced basicity of the fluoride salt prevents deprotonation of the solvent and so eliminates one of the pathways to by-product formation, with no **3b** being formed in the fluorodenitration of **3**. Reaction selectivity is thus improved. This was shown *via* the high yields obtained in the fluorination of many nitro and chloroaromatics using $TMAHF_2$ [27]. These included the fluorodenitration of 3,5-dinitrobenzonitrile, where a 39 % yield of the 3,5-difluorobenzonitrile could be obtained using $TMAF.{}^4/_3H_2O$, but a much higher yield of 85 % could be obtained with $TMAHF_2$ (albeit in large excess). Again, this can be attributed to the reduced basicity of the fluoride used. Interestingly, the amount of hydrolysis by-product detected in the reaction of **2** is reduced when $TMAHF_2$ is used, giving an added advantage to using the fluoride in such reactions.

Conclusions

In summary, fluorodenitration with tetramethylammonium salts is affected by the basicity of the fluoride source. TMAF.$^4/_3H_2O$ can be used successfully to fluorodenitrate nitroaromatics, but the use of this fluoride results in many side reactions occurring with some nitroaromatics. We have also found that TMAF is sufficiently basic to deprotonate DMAc, a solvent commonly used for nucleophilic aromatic fluorination reactions. The use of anhydrous TMAF has been found to result in the formation of more by-products than the hydrated fluoride. However, while the use of $TMAHF_2$ in fluorodenitration reactions results in decreased reaction rates over those with TMAF, the yields of the required fluoroaromatics are improved, most notably in difficult *meta*-fluorodenitrations. A reduction in the yields of both hydrolysis and base-induced by-products is also observed.

Experimental

Solvents were obtained from Aldrich Chemical Co. and dried over a mixture of 3 Å and 4 Å molecular sieves for at least three days before use. All other chemicals were obtained from Aldrich Chemical Co. or Lancaster Chemicals and used without further purification, except for TMAF, which was obtained from Apollo Scientific Ltd. The commercially available tetrahydrated TMAF was dried either by heating under a dynamic vacuum for two days at 60 ^oC to give a salt containing 19.4 % w/w water (TMAF.$^4/_3H_2O$) by Karl-Fischer analysis or by the method of Christie *et al.* [12] to give an anhydrous salt. Tetramethylammonium bifluoride was heated at 60 ^oC for two days under a dynamic vacuum. Gas chromatography was performed on a HP5 column in a Hewlett Packard HP6890. GC-mass spectra were obtained on a Varian 3400CX gas chromatograph interfaced to a Finnigan Mat Magnum mass spectrometer (which has a mass range of $m/z = 50$ to 650, calibrated daily using perfluorotrioctylamine). The other mass spectrometry techniques described were carried out on a VG *Autospec* mass spectrometer. Infrared transmission spectra were recorded using a Perkin Elmer 1720 FT-IR spectrometer interfaced to a PC data station, with a resolution of 2 cm^{-1}. Solution state nuclear magnetic resonance spectra were obtained on a Jeol EX270 spectrometer (operating at 270 MHz for ^1H and 254 MHz for ^{19}F). ^1H-NMR spectra were referenced to tetramethylsilane and ^{19}F-NMR spectra referenced to $CFCl_3$. All products except **3b** were characterised by comparison of their mass spectra and GC retention time to those of authentic samples. Fluorinated products were also characterised by ^{19}F-NMR.

Preparation of tetramethylammonium nitrite: Tetramethylammonium nitrite was prepared by slowly adding silver nitrite solution dropwise to a solution of tetramethylammonium chloride in water until no further precipitate formed. The precipitate was removed by filtration and the water removed on a rotary evaporator. The solid was then dried under vacuum at 60 oC.

Tetramethylammonium nitrite: IR (KBr disc) ν max (cm^{-1}): 3023 (w), 1493 (s), 1410 (w), 1273 (s), 947 (s).

General procedure for the fluorination of 1-4: To a solution of **1** (0.182 g, 1 mmol) in DMAc (10 ml) was added biphenyl (0.077 g, 0.5 mmol) as an internal standard and the solution heated to the 60 oC. TMAF.$^4/_3$H$_2$O (0.144 g, 1.2 mmol) was added to the solution and the reaction monitored by GC. After the starting material had been consumed, the reaction mixture was cooled to room temperature and diluted with ether. The solution was washed with dilute acid and water, the solvent removed and the crude product purified by column chromatography (DCM) to give **1a**. Reactions with anhydrous TMAF (1.2 mmol) and TMAHF$_2$ (3 mmol) or tetramethylammonium nitrite (1.2 mmol) were carried out similarly. When required, water or phthalic anhydride were added to the reaction mixture *prior* to the fluoride.

1a: MS (*m/z*, %) M$^+$ 155; 155 (100), 123 (23), 100 (13), 75 (9), 93 (6); ^{1}H-NMR (CDCl$_3$) δ 7.45 (ddd), 7.36 (m), 7.18 (ddd) ppm; ^{19}F-NMR (CDCl$_3$) δ -103.0 ppm; m.p. 56-7 oC. Analysis for C_7H_3NFCl requires C, 54.20 %; H, 1.40 %; N, 8.72 %. Found C, 53.99 %; H, 1.86 %; N, 8.77 %. **1b**: MS (*m/z*, %) M$^+$ 139; 139 (100), 112 (12), 88 (10), 75 (5), 125 (3); ^{1}H-NMR (DMSO) δ 7.87 (m), 7.41 (t); ^{19}F-NMR (CDCl$_3$) δ -104.0 ppm; IR (KBr disc) ν max (cm^{-1}): 3114 (w), 3081 (w), 2251 (m), 1633 (s), 1489 (s), 1295 (m), 1252 (s), 1007 (s), 796 (s), 660 (s).

2a: MS (*m/z*, %) M$^+$ 166; 166 (100), 150 (62), 100 (62), 108 (58), 120 (30), 75 (13), 136 (12), 95 (10); ^{1}H-NMR (CD$_3$CN) δ 8.54 (d), 8.51 (d), 8.11 (m), 8.07 (m), 7.60 (d), 7.56 (d) ppm; ^{19}F-NMR (CDCl$_3$) δ = -103.0 ppm; IR (KBr disc) ν max (cm^{-1}): 3105 (w), 3063 (m), 2242 (s), 1616 (m), 1540 (s), 1506 (m), 1354 (s), 1278 (m), 1253 (m), 1091 (m), 931 (m), 855 (m), 744 (m); **2b**: MS (*m/z*, %) M^+ 165; 165 (100). 63 (22), 148 (16), 131 (9), 88 (5); ^{1}H-NMR (DMSO) δ 8.41 (d), 7.94 (d), 7.91 (d), 7. 24 (d) ppm; IR (KBr disc) ν max (cm^{-1}): 3258 (m), 3097 (m), 2243 (s), 1633 (s), 1540 (s), 1430 (m), 1379 (s), 1337 (s), 1261 (s), 1168 (s), 1117 (s), 931 (s), 855 (s), 736 (s), 576 (s).

3a: MS (*m/z*, %) M^+ 141; 125 (100), 141 (51), 83 (28), 111 (17), 63 (7); ^{1}H-NMR (DMSO) δ 8.01 (m), 7.97 (m), 7.68 (m) ppm; ^{19}F-NMR ($CDCl_3$) δ -109.5 ppm; IR (KBr disc) ν max (cm^{-1}): 3105 (w), 1531 (s), 1354 (s), 1278 (w), 1227 (w), 922 (w), 813 (m), 752 (m); **3b**: MS (*m/z*, %) M^+ 254; 72 (100), 207 (52), 254 (6), 161 (4), 135 (4), 89 (3), 107 (3), 191 (2).

4a: MS (*m/z*, %) M^+ 200; 123 (100), 105 (78), 200 (77), 77 (44), 95 (43), 51 (23); ^{1}H-NMR (DMSO) δ 7.80 (m), 7.71 (m), 7.69 (m), 7.66 (m), 7.63 (m), 7.54 (m), 7.35 (m) ppm; ^{19}F-NMR (DMSO) δ -106.0 ppm; IR (KBr disc) ν max (cm^{-1}): 3063 (w), 1659 (s), 1608 (s), 1515 (m), 1447 (m), 1295 (m), 1227 (m), 1151 (m), 846 (m), 796 (m), 736 (s), 711 (s); m.p. 45.5 - 46.5 °C. Analysis for $C_{13}H_9OF$ requires C, 78.00 %; H, 4.50 %. Found C, 77.63 %; H, 4.12 %.

Reaction of 3 with a solution of potassium hydroxide in DMAc: A solution of potassium hydroxide (0.3 g, 5.4 mmol) in DMAc (10 ml) was heated to 140 °C. The solution gradually became yellow and partial dissolution of the pellets occurred. To this solution, **3** (0.168 g, 1.0 mmol) was added. This was stirred for ten minutes and then a sample removed and analysed by GC and GC-MS.

Reaction of phthaloyl dichloride with DMAc: Phthaloyl dichloride (7.75 ml, 10.91 g, 53.70 mmol) was added slowly to DMAc (5 ml). The solution became red and gelatinous and a white solid precipitated. Water was added and the solid collected by filtration. After washing well with water, the solid was dried under vacuum overnight.

A similar reaction was carried out with DMSO on a tenth of the scale.

Dimethyldisulfide: MS (*m/z*, %) M^+ 94: 63 (100), 94 (96), 45 (3).

Dimethylsulfide: MS (*m/z*, %) M^+ 63: 63 (100), 47 (48), 35 (32).

Bis(methylthio)methane: MS (*m/z*, %) MS^+ 107: 61 (100), 107 (53), 45 (31), 35 (18).

Reaction of TMAF with phthalic anhydride: Phthalic anhydride (0.296, 2.0 mmol) was placed in a flask with acetonitrile (10 ml). TMAF.$^4/_3H_2O$ (0.240g, 2.0 mmol) was added and the mixture heated to 50 °C, resulting in the formation of a homogeneous solution. The solvent was removed to give a non-hygroscopic white solid. Similar reactions were carried out with tetramethylammonium hydroxide and two equivalents of TMAF.

Tetramethylammonium hydrogen phthalate: MS (*m/z*, %) M^+ 242; 104 (100), 76 (84), 58 (56), 149 (29), 91 (26), 163 (24), 242 (5), 197 (4); Electrospray MS shows 165.2 + n(239); ^{1}H-NMR (DMSO) δ 8.17 (dd), 7.50 (dd) ppm; IR (KBr disc) ν max (cm^{-1}) 3092 (broad, m), 1859 (broad, s), 1761 (s), 1703 (s), 1605 (w), 1479 (m), 1410 (m), 1362 (m), 1342 (w),1293 (w), 1264 (s), 1176 (w), 1118 (w), 1079 (w), 1010 (w), 913 (s), 845 (w), 806 (w), 747 (w), 718 (s), 681 (w), 650 (w), 562 (w), 538 (s).

^{19}F-NMR analysis from the reaction of TMAF with phthalic anhydride shows a solvent dependent signal: ^{19}F-NMR (DMSO) δ -163.0 ppm; ^{19}F-NMR (D_2O) δ -141.0 ppm

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