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Direct fluorination of bis(trifluoromethanesulfonyl)imide and its lithium salt and related studies☆

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Dedicated to Dr. Karl O. Christe on the occasion of his 65th Birthday

Abstract

Studies on the direct fluorination of the acidic imide $(CF_3SO_2)_2NH$ and of its lithium salt $(CF_3SO_2)_2NLi$ have enabled us to establish a potentially-viable commercial route to *N*-fluorobis(trifluoromethanesulfonyl)imide, $(CF_3SO_2)_2NF$, and to carry out hazard testing on this well-known electrophilic fluorinating agent.

Keywords: Direct fluorination; *N*-fluorobis(trifluoromethanesulfonyl)imide; Fluorination of bis(trifluoromethanesulfonyl)imide; Fluorination of lithium bis(trifluoromethanesulfonyl)imide; Hazard tests on *N*-fluorobis(trifluoromethanesulfonyl)imide

1. Introduction

The DesMarteau reagent, *N*-fluorobis(trifluoromethanesulfonyl)imide (**1**), $(CF_3SO_2)_2NF$ (b.p. 90–91 °C) [1], is the most powerful of the growing class of site-selective, user-friendly, electrophilic fluorinating agents of the N–F type now being widely utilized in organic chemistry [2–4]. However, despite its merits and wide applicability, including ring fluorination of aromatic compounds, the perceived difficulties and hazards associated with the published method of preparation of this *N*-fluoroimide from neat $(CF_3SO_2)_2NH$ (**2**) and undiluted fluorine in a sealed metal "bomb" [1,5] have severely limited its wide-spread use, except in the originator's laboratory [6–10]. The easier method of carrying out this F for H exchange described here (treatment of the N–H compound (**2**) dissolved in a perfluorocarbon with nitrogen-diluted fluorine in a flow system) has enabled us to define a potentially-viable commercial route to **1**, and to carry out detailed hazard tests on this compound.

2. Results and discussion

2.1. Formation of *1* by different fluorination methods

Various fluorination procedures (including the Simons electrochemical method) were applied during attempts to develop a better (more easily achieved and less hazardous) laboratory procedure than that reported by DesMarteau et al. [1,5] for the provision of multi-gram quantities of **1**. These methods include both closed and open (i.e. flow method) vessel fluorination of the parent imide (**2**) and of its commercially-available lithio derivative, $(CF_3SO_2)_2NLi$ (**3**; 3M's FLUORAD™ HQ-115) with neat F_2 or F_2/N_2 blends, using solid-phase (e.g. **2** supported on NaF or CaF_2) or liquid-phase techniques (CH_3CN, $CHCl_3$ and $CFCl_3$ or blends of these, perfluorocarbon (PFC) fluids, H_2O and HF were employed as solvents or suspending media). Representative examples of these experiments are given in Table 1.

The best fluorination results were achieved by fluorinating the parent imide (**2**) (conveniently prepared from **3**+ H_2SO_4) dissolved in the PFC fluids APF-215 or APF-240 (Air Products MULTIFLUOR™ liquids, b.p. 215 and 240 °C, respectively) in a flow system at 80–120 °C. Reactions were carried out using 5–22 g of **2**, and up to a 600% excess of F_2. Isolated yields of the N–F product (**1**) varied from 63

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Table 1
Experimental conditions for the fluorination of $(CF_3SO_2)_2NH$ (**2**), $(CF_3SO_2)_2NLi$ (**3**), and $(CF_3SO_2)_2NNa$ (**4**)

No.	Substrate (concentration)[a]	Solvent	Fluorination temperature (°C)	Fluorine added (mmol)	Fluorination result
1	**3**	$CH_3CN/CHCl_3/CFCl_3$ (1:1:1 by volume)	−73 −50 to −30 −30 to −10	44	No reaction detected Attack on solvent only Minor amount of product—mostly derived from attack on solvent
2	**3**	CH_3CN/H_2O (9:1 by volume)	−40 to −20	50	Mostly attack on solvent occurred
3	**3**	H_2O	0	26	Low conversion to **1** (not isolated)
4	**3** (0.25 M)	H_2SO_4	40 80	19 19	98% Conversion to **1** (48% isolated yield)
5	**3** (16 M)	H_2O	Zero to ambient	69	Product collected at −100 °C exploded when warmed to room temperature[b]
6	**3**	APF-140	50–80	60	40% Conversion to **1**
7	**3**	APF-140 plus cat. Amt. H_2O	25–80	74	98% Conversion to **1** (15% isolated yield)
8	**3**	APF-215 plus cat. Amt. H_2O	75–90	100	100% Conversion to **1** (30% isolated yield)
9	**3** (0.15 M)	APF-215	80 100 120	35 52 24	100% Conversion to **1** (52% isolated yield)
10	**3** (0.32 M)	APF-240	80 110–120	167 139	100% Conversion to **1** (36% isolated yield)
11	**2** (0.15 M)	APF-215	80–120	106	92% Conversion to **1** (81% isolated yield)
12	**2** (0.08 M)	APF-240	80 120	59 36	100% Conversion to **1** (67% isolated yield)
13	**2** (0.15 M)	APF-240	80 110–120	119 72	100% Conversion to **1** (63% isolated yield)
14	**2** (4.5 g)	No solvent (**2** was evenly dispersed on powdered CaF_2)	Ambient	64	Low conversion to **1** (17% isolated yield)
15	**3** (3.0 g)	No solvent (**3** was supported between two layers of powdered NaF)	Ambient	37	Low conversion to **1** (15% isolated yield)
16	**3** (5.48 g)	No solvent (**3** was mixed with 75 g of Teflon® chips).	45	19	Approx. 5 ml of liquid collected at room temperature in a Teflon® FEP transfer line; this material exploded at room temperature without provocation.
17	**4** (0.07 M)	APF-240	80 110 120	30 59 52	Low conversion to **1** (13% isolated yield)

[a] Concentration of substrate is 0.1 M unless otherwise indicated.
[b] This experiment was done using 230.57 g of **3** dissolved in 50.83 g of H_2O. Approximately 20 g of a colourless liquid product was collected in a trap cooled to −100 °C. This material exploded when warmed to room temperature.

to 81% and were very much dependent on how efficiently the product could be isolated from the perfluorocarbon solvent (see Table 1, entries 11–13).

Other methods for preparing the N–F compound (**1**) were less successful than the liquid-phase fluorination of **2**. Fluorination of the lithium salt (**3**) in liquid-phase systems did, in most cases, produce the desired N–F compound (**1**) in modest yields (up to ≈52%) but in general, higher reaction temperatures were required because of the lower solubility of the lithium salt (**3**) compared to the imide (**2**). In one case (see Table 1, entry 5) fluorination of an aqueous solution of **3** led to the formation of an unidentified liquid product which detonated at room temperature (see Section 3).

Fluorination of solid-phase systems, comprising mixtures of either precursor **2** or **3** mixed with, or supported on, different fluorine-resistant materials (NaF, CaF_2, or Teflon® chips) was generally less productive than fluorinating liquid-phase systems. However, in some cases, low yields of **1** were produced (see Table 1, entries 14 and 15). In one particular case, fluorination of **3** mixed with Teflon® chips produced a colorless liquid which detonated at room temperature (see section below on explosion events). Simons electrochemical fluorination (ECF) of the lithium salt (**3**), and direct fluorination (with F_2) of the sodium salt of the parent imide, $(CF_3SO_2)_2NNa$ (**4**), in various liquid media failed to produce significant amounts of the desired product, e.g. see entry 17 in Table 1.

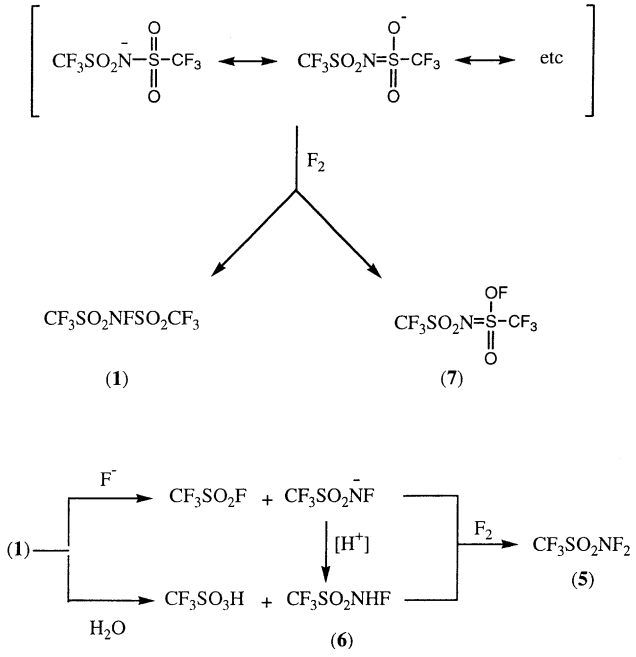
2.2. Thermal analysis of N-fluorobis(trifluoromethanesulfonyl)imide (1)

A series of thermal screening analyses were performed on the N–F compound (**1**) in order to establish that it could be produced and handled safely. These methods included differential scanning calorimetry (DSC) [11], the Radex–Solo thermal screening method (Radex) [12], and accelerating rate calorimetry (ARC) [13,14]. Data from these tests provided crucial information relating to, for instance, the onset temperature for self-sustaining decomposition (160 °C, by ARC using a 2.1 g sample, thermal inertia factor $\Phi \approx 3.32$) and the energy of decomposition (611 J/g, by DSC using a 2.3 mg sample). Overall, the thermal properties of the N–F compound (**1**) were found to be within a regime where safe operation of the process was assured. This was necessary to justify further developmental work, and to provide a measure of confidence in being able to handle gram quantities of this material safely.

3. Explosion events

While much of the experimental work described was completed without incident, and all of the work was done without serious personal injury or damage to property, there were three separate events which occurred quite unpredictably and are worth noting here. Separate attempts to prepare the N–F compound (**1**) from the lithium salt (**3**), either by Simons ECF (in HF) or by direct fluorination in a bed packed with Teflon® chips (Table 1, entry 16) or via a water-based liquid-phase method (Table 1, entry 5), led in each case to the formation of explosive products which were not identified. We speculate that the compounds $CF_3SO_2NF_2$ (**5**), CF_3SO_2NHF (**6**), and $CF_3SO_2N{=}S(OF)(CF_3){=}O$ (**7**) could have been involved in the explosions which occurred. The first two (**5** and **6**) are known compounds, having been prepared, respectively, by direct fluorination of trifluoromethanesulfonamide in admixture with sodium and potassium fluoride [15] and via hydrolysis of *N*-fluorobis-(trifluoromethanesulfonyl)imide (**1**) or its reaction with fluoride ion [16]; the gaseous NF_2 compound (**5**), b.p. 12–15 °C, explodes when heated or on impact [15], and its monofluoro analogue (**6**) carries a hazard warning (''. . .may be explosive under certain conditions'' [16]).

Scheme 1 indicates how *N*-fluorosulfonamides **5** and **6** could have been generated during our fluorination experiments; also shown is how the yet unknown novel hypofluorite **7** also might have arisen, i.e. via *O*-fluorination of the lithium salt $(CF_3SO_2)_2NLi$ (**3**), the anion of which is known to enjoy extensive delocalization of its negative charge [17,18]. Regarding the thermal stability of the hypothetical O–F compound **7**, ab initio (3-21G*) and DFT (6-31G**) calculations [19] reveal that the ground-state energy of **7** is more than 37 kcal/mol higher than that of its N–F isomer (**1**).



Scheme 1.

4. Experimental

4.1. Starting materials

Bis(trifluoromethylsulfonyl)imide (**2**), a white hygroscopic solid (m.p. 49–50 °C) which fumes in air, was prepared as described in the literature [1,20] except that lithium bis(trifluoromethanesulfonyl)imide (**3**) (a commercial sample of FLUORAD™ (3M Co.) battery electrolyte HQ-115, dried in vacuo at 130–140 °C) was used in the reaction with concentrated sulfuric acid in place of the sodium salt of the imide (**4**); it was stored under dry nitrogen until required. MULTIFLUOR® perfluorocarbon fluids (Air Products and Chemicals Inc.), APF-140 (perfluorodecalin, b.p. 140 °C), APF-215 (perfluorophenanthrene, b.p. 215 °C), or APF-240 [perfluoro (diisopropylnapthalene), b.p. 240 °C] were employed as the fluorination media. Fluorine was either generated as required using a 60 A ICI medium temperature (80–85 °C) cell (electrolyte KF·2HF) or taken from commercial cylinders as a 20% mixture (v/v) in N_2 (Air Products and Chemicals Inc.). Before use, F_2 was freed from HF by passage through a substantial bed of sodium fluoride pellets.

4.2. Fluorination techniques for the preparation of 1 from 2

4.2.1. Method A

Fluorination of bis(trifluoromethanesulfonyl)imide (**2**) dissolved in hot APF-215 (it dissolved completely only at temperatures >80 °C) was carried out with a fluorine–nitrogen blend in an 'open' system [21] incorporating a borosilicate glass (Pyrex) reactor (250 cm^3) and traps fitted with greaseless PTFE–Pyrex vacuum stopcocks; ground

glass joints were lubricated with chlorofluorocarbon grease [Voltalef (supplied by Fluorochem Ltd., UK)] or fitted with rigid Teflon® sleeves (Aldrich), and a bubbler containing APF-215 was attached to the exit from the train of three traps [the first cooled to 0 °C (ice), the others to −72 °C (CO_2-methylated spirit)]. The reactor was attached to the first trap via an air-cooled Pyrex reflux condenser, and where it was necessary to introduce some flexibility into the line, this was done with short lengths of VITON® (DuPont) fluoroelastomer tubing (Isoversinic supplied by Jencons Ltd., UK) whose inner surfaces had been fully passivated with fluorine in situ. Only properly trained personnel should attempt to reproduce the fluorination described below; and above all, sensible adequate prior arrangements must be made for medical treatment (HF burns) [22].

Fluorine (4.25 g, 112 mmol) diluted with dry nitrogen (F_2:N_2 ratio ca. 1:4 (v/v)) was bubbled into a hot (125–130 °C) stirred (magnetically) solution of **2** (10.25 g, 36.5 mmol) in APF-215 (175 cm^3) during 2.25 h (note: initially the reactor was filled with neat N_2 while the temperature was raised until the imide had dissolved completely (85 °C); passage of the F_2/N_2 blend was then commenced and continued until ca. three times the stoichiometric quantity of fluorine had been used (the need to use such an excess had been determined previously in trial runs). Some N–F product (**1**) collected in the 0 °C trap and the first −72 °C trap (the fragmentation product CF_3SO_2F was also found in the cooler trap, analysis being carried out by IR and ^{19}F NMR spectroscopy) but the majority remained dissolved in the APF-215 reaction medium and was recovered as follows. The F_2/N_2 flow was discontinued and replaced with a slow stream of dry nitrogen to purge fluorine from the system, and the reactor's heater was turned off. Once the temperature had decreased to ca. 65 °C [by which time the exit gas gave a negative test for F_2 (KI paper)], the original product traps were replaced by a single trap at −196 °C and connected to a vacuum system, the nitrogen line closed, and the dissolved N–F product (**1**) transferred at ca. 15 mmHg to the new collector; during this operation traces of unconverted N–H compound (**2**) (identified by NMR) collected on the walls of the air-cooled condenser, which had not been removed from the reactor. All of the crude N–F compound (**1**) from this run was mixed with that obtained in a similar fluorination involving 10.3 g (36.6 mmol) of **2** and 5.4 g (142 mmol) of F_2 and, after the combined products had been stored over dry powdered sodium fluoride (ca. 2 g) for 4 h at 20 °C, as recommended in the literature [5], was purified by trap-to-trap distillation to provide >96% purity (as determined by ^1H and ^{19}F NMR spectroscopy) **1** (14.8 g, 49.5 mmol, 68%) (no NMR signals assignable to **2** or an OF compound, e.g. **7**, were observed).

4.2.2. Method B

In a typical experiment, 5.03 g (17.9 mmol) of the N–H compound (**2**) and 220 ml of APF-240 were heated to 80 °C under nitrogen in a 300-ml 316-SS Parr Instrument Co. magnetically-stirred reactor while F_2/N_2 (20% v/v) was bubbled into the reaction mixture at a rate of 100 sccm via a sparge tube. The exit gas from the reactor was passed first through a Teflon® FEP U-tube cooled to 0 °C, then through a Teflon® FEP U-tube cooled to −100 °C, and finally through a soda-lime scrubber. After one molar equivalent of F_2 (17.9 mmol) had been introduced, the reaction temperature was raised to 120 °C during the addition of a further 40.8 mmol of F_2 (as 20% v/v F_2 in N_2). The hot reactor and contents were then purged with N_2 for 5 min before materials collected in the U-tubes were analyzed by ^{19}F NMR. Only APF-240 was found in the 0 °C tube; the −100 °C tube contained 3.6 g of pure $(CF_3SO_2)_2NF$ (**1**) (3.56 g, 11.9 mmol, 67% yield).

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