

Communication

1,4-Difluoro-1,4-diazoniabicyclo[2.2.2]octane salts

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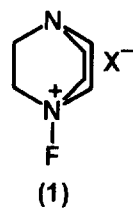
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Abstract

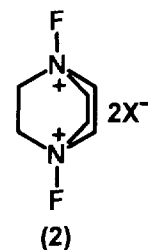
1,4-Difluoro-1,4-diazoniabicyclo[2.2.2]octane salts, $F^+N(CH_2CH_2)_3N^+-F 2X^-$ (**2**) where $X^- = BF_4^-, PF_6^-, FSO_3^-, CF_3SO_3^-$, have been synthesised by direct fluorination of 1:1 or 1:2 Lewis acid adducts of 1,4-diazabicyclo[2.2.2]octane with boron trifluoride, phosphorus pentafluoride or sulfur trioxide, and of 1,4-bis(trimethylsilyl)-1,4-diazoniabicyclo[2.2.2]octane ditriflate, respectively, in cold acetonitrile. The bis(tetrafluoroborate) salt (**2**; $X^- = BF_4^-$) has also been obtained via fluorination of 1-heptafluoro-*n*-butyryl-1,4-diazoniabicyclo[2.2.2]octane-trifluoromonoborane tetrafluoroborate.

Keywords: Difluorodiazoniabicyclo-octane salts; NMR spectroscopy; Direct fluorination; Lewis acid adducts

During pioneering work on the development of site-selective electrophilic fluorinating agents of the F-TEDA salt class (TEDA = triethylenediamine, i.e. 1,4-diazabicyclo[2.2.2]octane) [1], it was found impossible to isolate either the 1-fluoro-4-aza-1-azoniabicyclo[2.2.2]octane salts **1** or the corresponding bis (*N*-fluoro) compounds **2a,b** following fluorination of TEDA in cold $CFCl_3$ ($-78^\circ C$) or CH_3CN ($-35^\circ C$), with or without addition of LiOTf, as appropriate [2]. In every case, low-temperature work-up of products provided white solids which readily oxidised iodide ion to iodine and reacted with phenylmagnesium bromide in diethyl ether to give low yields of fluorobenzene, but when allowed to warm to room temperature 'decomposed' to red/yellow non-oxidising materials containing appreciable amounts of *N*-hydro salts [$N(CH_2CH_2)_3N^+-H X^-$, $H^+N(CH_2CH_2)_3N^+-H 2X^-$ ($X = F^-$ or TfO^-)]. Since monoquaternization of TEDA enables fluorination under the above conditions to proceed smoothly, e.g. $CH_3^+N(CH_2CH_2)_3N^- TfO^- + F_2-LiOTf \rightarrow CH_3^+N(CH_2CH_2)_3N^- F^- 2TfO^- + LiF$ [1,3], it was inferred that the mono(N^+-F) salts **1** are inherently unstable. This deduction receives support from the success of the method reported here for the synthesis of the first TEDA bis(N^+-F) salts.



$X^- = F^-$ or TfO^-



$X^- =$ (a) F^- , (b) TfO^- ,

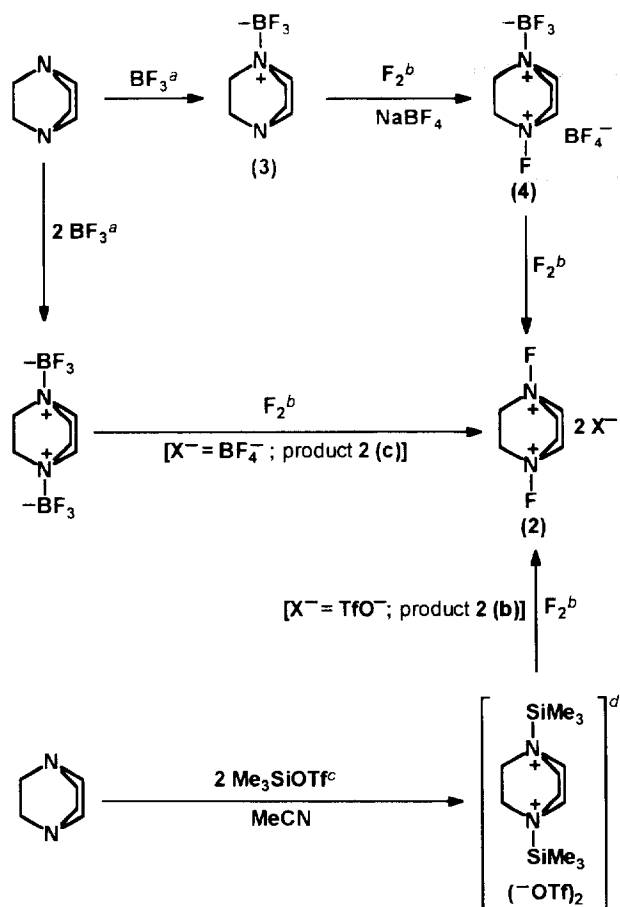
(c) BF_4^- , (d) PF_6^- ,

(e) FSO_3^-

The stratagem adopted was to directly fluorinate TEDA derivatives in which nitrogen lone pairs were 'tied up' with Lewis acids or organosilyl (or related) functions capable of displacement during the halogenation process. The results are exemplified in Scheme 1.

Loss of oxidising power with concomitant release of fluoride ion was noted for all of the white bis- ^+NF TEDA salts [**2(a)–(e)**] once they were exposed to moist air (this hydrolysis was followed by ^{19}F NMR spectroscopy using a solution of the salts in D_2O), and it proved impossible to obtain acceptable elemental analyses (C, H, N, F) except in the case of the bis(tetrafluoroborate) **2(c)** prepared from the heptafluoro-

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Scheme 1. ^a Other Lewis acids used were PF_5 [final product = 2(d), $\text{X}^- = \text{PF}_6^-$] and SO_3 [\rightarrow 2(e), $\text{X}^- = \text{FSO}_3^-$]; ^b Fluorinations were carried out in cold (-35°C) anhydrous MeCN, using F_2 diluted with N_2 (ca. 10% F_2 by vol.) except for the synthesis of the mono(N^+-F) salt 4, in which neat F_2 at ca. 20 mmHg pressure was employed; ^c $n\text{-C}_3\text{F}_7\text{CO}$ was also used as a fluoride-removable protecting group: $\text{N}(\text{CH}_2\text{CH}_2)_3\text{N}^+-\text{BF}_3^-$ (3) + $n\text{-C}_3\text{F}_7\text{COCl}$ + NaBF_4 in MeCN \rightarrow $n\text{-C}_3\text{F}_7\text{CO}-\text{N}^+(\text{CH}_2\text{CH}_2)_3\text{N}^+-\text{BF}_3^-\text{BF}_4^- \rightarrow$ with F_2/N_2 in MeCN (-40°C) \rightarrow 4 + 2(c) [4]; ^d Not isolated.

robutyryl-protected TEDA- BF_3 complex (see footnote c, Scheme 1). Neither was it possible to achieve consistent data when the salts were subjected to iodimetric estimation of their oxidising capacities ($2^+ \text{N}-\text{F} + 4\text{I}^- \rightarrow 2\text{I}_2$ [5]), although this was not unexpected in view of the perceived instability of the unknown mono-NF TEDA salts (1); using an inverse addition method [addition of 2(a)–(e) in MeCN to vigorously stirred acidified (HCl) KI aq.], values in the range 71%–88% were obtained.

The assignment of structures to the bis-NF salts rests, therefore, on NMR data. The ^{19}F spectra of solutions of all the

salts in acetonitrile showed $^+ \text{N}-\text{F}$ absorptions within the narrow region +115.0 to +116.3 ppm [relative to $\text{CF}_3\text{CO}_2\text{H}$; cf. $\text{ClCH}_2-\text{N}^+(\text{CH}_2\text{CH}_2\text{CH}_2)_3\text{N}^+-\text{F} (\text{BF}_4^-)_2$, +125.6 ppm] with counteranion signals of expected relative intensities falling at standard values. The ^1H , ^{13}C and ^{11}B data for the bis(tetrafluoroborate) [2(c)], for example, were as follows: δ_{H} 5.01 (br.m, $6 \times \text{CH}_2$) ppm; δ_{C} 62.22 (br.s, $6 \times \text{CH}_2$) ppm; δ_{B} -20.9 (s, $2 \times \text{BF}_4^-$, relative to BF_3) ppm; the absorption patterns and chemical shifts in the ^1H and ^{13}C NMR spectra were common to all the bis- $^+ \text{NF}$ salts.

The analytical problems (combustion and iodimetric methods) were not encountered with bis- $^+ \text{NF}$ TEDA- BF_4 precursor 1-fluoro-4-aza-1-azoniabicyclo[2.2.2]octane-trifluoromonoborane tetrafluoroborate (4) derived from the 1:1 TEDA- BF_3 adduct (3) and an equivalent of fluorine (see Scheme 1). This mono-NF salt (m.p. $172\text{--}173^\circ\text{C}$) was isolated in 67% yield and was characterized by elemental and iodimetric analysis [Found: C, 25.0; H, 4.8; F^+ , 6.6; N, 9.3%. Calc. for $\text{C}_6\text{H}_{12}\text{B}_2\text{F}_8\text{N}_2$: C, 25.2; H, 4.2; F^+ , 6.7; N, 9.8%] and NMR (^1H , ^{13}C , ^{19}F and ^{11}B) spectroscopy (δ_{H} 4.20 (br.m, $6 \times \text{CH}_2$) ppm; δ_{F} +125.0 (br.s, N^+-F), -70.50 (s, BF_4-BF_3) ppm relative to TFA; δ_{C} 57.35 (br.s, $3 \times \text{CH}_2-\text{N}^+-\text{F}$), 38.44 (s, $3 \times \text{CH}_2\text{NBF}_3$) ppm; δ_{B} -18.1 (s, BF_4-BF_3) ppm relative to BF_3).

Site-selective fluorinations with bis- $^+ \text{NF}$ TEDA salts are under investigation, and will be reported in a full paper; in reactions examined so far, fluorine delivery seems restricted to only one-half of the available ' F^+ ' per molecule of salt; again this supports our views on the in-built decomposition mode of a mono-NF cation (1) [2]. The mechanism of this decomposition will be presented later.

Acknowledgement

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- [4] Work carried out by S.N. Mohialdin-Khaffaf.
- [5] See R.E. Banks, R.A. Du Boisson, W.D. Morton and E. Tsiliopoulos, *J. Chem. Soc., Perkin Trans. 1*, (1988) 2805.