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A new method for the preparation of fluoro-λ^6-sulfanenitriles: reaction of sulfimides with Selectfluor™

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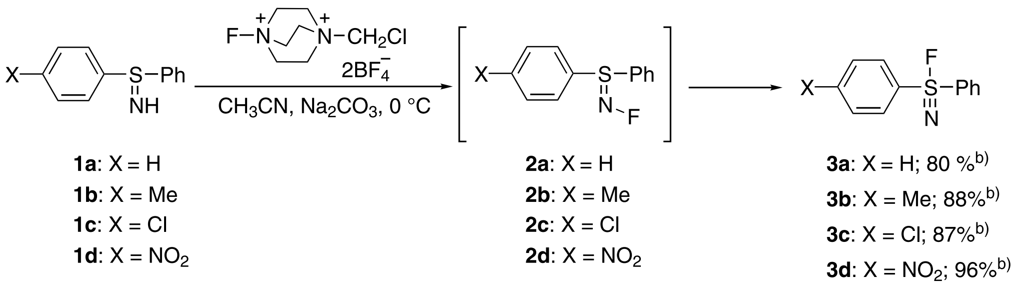
Abstract—Several diaryl(fluoro)-λ^6-sulfanenitriles **3** were synthesized by the reaction of *S*,*S*-diarylsulfimides **1** with Selectfluor™. This reaction also allows the first preparation of heterocyclic fluoro-λ^6-sulfanenitrile, 5-fluoro-10,10-dioxo-5,10-dihydro-5λ^6,10λ^6-thianthren-5-nitrile (**5**) and its molecular structure was determined by X-ray crystallographic analysis.

N-Halosulfimides ($R_2S=NX$, X = F, Cl, Br, I) have attracted much attention because of their unique structures and reactivities.[1–5] We recently have found that diaryl(fluoro)-λ^6-sulfanenitriles ($Ar_2FS\equiv N$) bearing an SN triple bond are obtained by the reaction of *N*-bromosulfimides with a fluoride anion, and we have also prepared several types of λ^6-sulfanenitriles by using the fluoro-λ^6-sulfanenitriles as the starting materials.[5,6] In fluorine and inorganic chemistry, *S*,*S*-difluoro-*N*-fluorosulfimide and its structural isomer, trifluoro-λ^6-sulfanenitrile ($F_3S\equiv N$), were prepared several decades ago.[7,8] In contrast, *S*-alkyl and -aryl substituted *N*-fluorosulfimides are less well-known. *S*,*S*-Diaryl-*N*-chloro-, -*N*-bromo-, and -*N*-iodo-sulfimides were prepared by halogenation of *S*,*S*-diarylsulfimides ($Ar_2S=NH$) **1**.[4] We, therefore, have examined reaction of **1** with an electrophilic fluorinating reagent, Selectfluor™ (1-chloromethyl-4-fluoro-1,4-diazoniabicyclo-[2,2,2]octane bis(tetrafluoroborate)).[9] This work led us to the finding that the resulting *S*,*S*-diaryl-*N*-fluorosulfimides **2** readily undergo 1,2-migration of the fluorine atom to form the corresponding diaryl(fluoro)-λ^6-sulfanenitriles **3**. In addition, we also found that the reaction of heterocyclic sulfimide, 10,10-dioxo-10*H*-5λ^4,10λ^6-thianthren-5-ylideneamine (**4**) with Selectfluor™ affords a new type of heterocyclic fluoro-λ^6-sulfanenitrile **5**.

The reaction of *S*,*S*-diphenylsulfimide (**1a**) with Selectfluor™ was carried out in CH_3CN at 0°C for 3 h (Scheme 1). A large amount of Na_2CO_3 was added to avoid protonation of **1**. Separation and purification from the resulting mixture gave fluoro(diphenyl)-λ^6-sulfanenitrile (**3a**) in 80% yield,[5b,10] and the expected *S*,*S*-



Scheme 1. (a) **1** (1 mmol), Selectfluor™ (1 mmol), Na_2CO_3 (5 mmol), CH_3CN (90 ml). (b) Isolated yields.

Keywords: fluoro-λ^6-sulfanenitriles; sulfimides; Selectfluor™; fluorination; heterocycles; X-ray crystallographic analysis.

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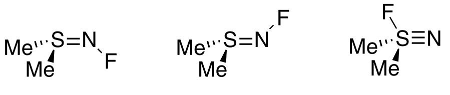
diphenyl-*N*-fluorosulfimide (**2a**) was not obtained even in trace amounts. Similar treatment of arylsulfimides **1b–d** also gave the corresponding fluoro-λ^6-sulfanenitriles **3b–d** (Scheme 1).[5b,10] It is well known that the nitrogen atom of sulfimides has a nucleophilic character,[4a,b] and hence, the formation of **3** can be explained by assuming the initial formation of *N*-fluorosulfimides **2**, which undergo 1,2-migration of the fluorine atom.

In order to verify the above proposed possibilities, we carried out the reaction of sulfimides **1a**, **1b**, and **1d** with Selectfluor™ in CD_3CN at −40°C. In the reaction of **1a** and **1b**, the starting materials immediately disappeared, and the peaks due to fluoro-λ^6-sulfanenitriles **3a** and **3b** appeared, while in the reaction of **1d** the reaction mixture showed the same peaks of the starting materials in the ^{1}H and ^{19}F NMR spectrum. Up to −20°C, the ^{19}F NMR peak of Selectfluor™ at δ 46.1 (N–F) gradually diminished and two resonance signals at δ −125.2 and 87.4 appeared. The latter signal was assigned to that of λ^6-sulfanenitriles **3d**. The former new signal increased gradually but disappeared soon and the spectra changed to that of **3d**, being indicative of the existence of intermediate, *S*-(4-nitrophenyl)-*S*-phenyl-*N*-fluorosulfimide (**2d**) in the present reaction. As mentioned above, $F_2S{=}NF$ and $F_3S{\equiv}N$ were reported by Glemser and Mews et al.[7,8] Theoretical calculations also indicated that their energy difference is small.[2] We therefore performed calculations on *cis*- and *trans*-*S*,*S*-dimethyl-*N*-fluorosulfimide (**2A-*cis*** and **2A-*trans***) and dimethyl(fluoro)-λ^6-sulfanenitrile (**3A**) as the model compounds of **2** and **3**.[11] It was revealed that *N*-fluorosulfimides **2A-*cis*** and **2A-*trans*** are 12.1 and 18.0 kcal/mol higher in energy compared to **3A** at the B3LYP/6-311++G(3df, 2pd)//B3LYP/6-31G(d) level (Fig. 1). These results imply that diary-*N*-fluorosulfimides **2** should be converted to thermodynamically stable fluoro-λ^6-sulfanenitriles **3**.



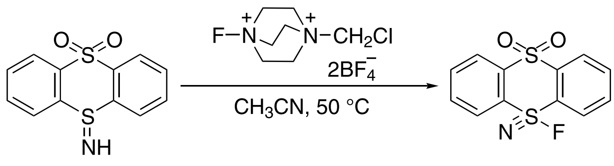
2A-*cis* 12.1^a)^

2A-*trans* 18.0^a)^

3A 0.0^a)^

Figure 1. Calculated relative energies of **2A** and **3A**. (a) B3LYP/6-311++G(3df,2pd)//B3LYP/6-31G(d), ZPE corrected values (kcal/mol).

Further, the reaction of heterocyclic sulfimide, 10,10-dioxo-5*H*-5λ^4,10λ^6-thianthren-5-ylideneamine (**4**)[12] with Selectfluor™ gave the corresponding fluoro-λ^6-sulfanenitrile **5** in 65% yield (Scheme 2).[13] Interestingly, this reaction should be applicable to the formation of cyclic-fluoro-λ^6-sulfanenitriles, because the conversion of cyclic-*N*-bromosulfimides with a fluoride anion to the corresponding λ^6-sulfanenitriles is difficult. The new cyclic-fluoro-λ^6-sulfanenitrile **5** was characterized by its analytical and spectroscopic data.[14] The molecular structure of **5** was determined by X-ray crystallographic analysis (Fig. 2).[15] The thianthrene ring system is found in the expected boat conformation. The S1–N1 and S1–F1 bond lengths (1.435(2) and 1.584 (2) Å) in **5** are somewhat shorter than those of fluoro(4-nitrophenyl)(phenyl)-λ^6-sulfanenitrile **3d** (S–N; 1.444(2) Å, S–F; 1.638 (2) Å).[16]



4

5 (65 %^b)^)

Scheme 2. (a) **4** (1 mmol), Selectfluor™ (0.5 mmol), CH_3CN (45 ml). (b) Isolated yields (based on Selectfluor™).

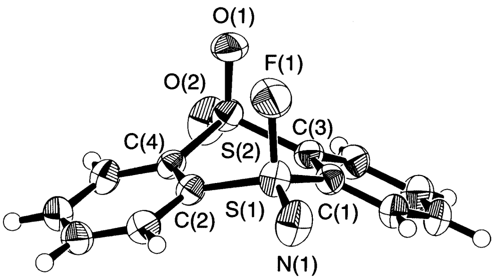


Figure 2. The molecular structure of **5**. Selected bond distances (Å) and bond angles (°): S(1)–F(1), 1.584(2); S(1)–N(1), 1.435(2); S(1)–C(1), 1.778(2), S(1)–C(2), 1.780(2); S(2)–O(1), 1.466(2); S(2)–O(2), 1.434(2); S(2)–C(3), 1.765(2); S(2)–C(4); 1.771(2); F(1)–S(1)–N(1), 118.6(1), F(1)–S(1)–C(1), 99.98(9); F(1)–S(1)–C(2), 98.19(9); N(1)–S(1)–C(1), 117.1(1); N(1)–S(1)–C(2), 116.5(1); C(1)–S(1)–C(2), 103.38(8); O(1)–S(2)–O(2), 119.0(1); O(1)–S(2)–C(3), 107.24(10), O(1)–S(2)–C(4), 105.25(9); O(2)–S(2)–C(3), 110.8(1); O(2)–S(2)–C(4), 110.3(1); C(3)–S(2)–C(4), 102.95(8).

In summary, we have demonstrated the formation of acyclic and cyclic fluoro-λ^6-sulfanenitriles from the reaction of the corresponding sulfimides with Selectfluor™. Our current efforts include elucidation of the mechanism for the migration of the fluorine atom and application of this reaction system to the preparation of other heterocyclic fluoro-λ^6-sulfanenitriles.

Acknowledgements

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13. A nucleophilicity of sulfimide **4** is relatively low. The reaction **4** with Selectfluor™ in the presence of Na_2CO_3 was carried out in CH_3CN at 50°C, which gave the intractable complex mixture.
14. For **5**: mp 234–236°C (decomp.); ^1H NMR (400 MHz, $CDCl_3$) δ 7.88–7.95 (m, 4H), 8.28–8.32 (m, 2H), 8.54–8.59 (m, 2H); ^{13}C NMR (100 MHz, $CDCl_3$) δ 125.9, 127.2, 133.8, 134.4, 138.7, 139.5 (d, $J_{CF}=22.2$ Hz); ^{19}F NMR (376 MHz, $CDCl_3$) δ 120.6; IR (KBr) 1376 cm^{-1} (SN), 1324 cm^{-1} (SO), 1170 cm^{-1} (SO); FABMS (m/z) 282 (M^++1); Calcd. for $C_{12}H_8FNO_2S_2$: C, 51.23; H, 2.87; N, 4.98. Found: C, 51.29; H, 2.93; N, 5.02.
15. Crystal data of **5**: $C_{12}H_8FNO_2S_2$, $M=281.32$, monoclinic $a=11.172(1)$, $b=8.143(1)$, $c=13.171(1)$ Å, $\beta=102.850(9)°$, $U=1168.2(3)$ Å^3, $T=296$ K, space group $P2_1/c$ (no. 14), $Z=4$, μ(Mo Kα)$=4.60$ cm^{-1}, 3812 reflections measured, 3421 unique ($R_{int}=0.007$). The final R values was 0.039. Crystallographic data for the structural analysis has been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 211241 for compound **5**.
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