Synthesis and Decomposition of Benzenediazonium Tris((trifluoromethyl)sulfonyl)methanide, $C_6H_5N_2^+(CF_3SO_2)_3C^-$, and Benzenediazonium Bis((trifluoromethyl)sulfonyl)amide, $C_6H_5N_2^+(CF_3SO_2)_2N^-$, and the Cyclic Analogue, $C_6H_5N_2^+\overline{SO_2(CF_2)_3SO_2N}^-$ [1]

Shi-Zheng Zhu[2] and D. D. DesMarteau*

H. L. Hunter Chemistry Laboratory, Clemson University, Clemson, South Carolina 29634-1905

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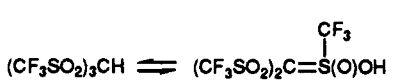
Phenyltris((trifluoromethyl)sulfonyl)methane $(CF_3SO_2)_3CC_6H_5$, and its isomeric ester $(CF_3SO_2)_2C{=}SCF_3(O)$-OC_6H_5 are formed by the thermal decomposition of benzenediazonium tris((trifluoromethyl)sulfonyl)methanide, $C_6H_5N_2^+\overline{SO_2(CF_2)_3SO_2N}^-$, which was prepared by treatment of tris((trifluoromethyl)sulfonyl)methane, $(CF_3$-$SO_2)_3CH$, with benzenediazonium chloride. Similarly, pyrolysis of benzenediazonium bis((trifluoromethyl)sulfonyl)amide, $C_6H_5N_2^+(CF_3SO_2)_2N^-$, and the cyclic analog $C_6H_5N_2^+\overline{SO_2(CF_2)_3SO_2N}^-$, prepared analogously from the corresponding sulfonimides, yields the *N*-phenyl and *O*-phenyl isomers $(CF_3SO_2)_2NC_6H_5$, $CF_3SO_2N{=}SCF_3(O)OC_6H_5$, $\overline{SO_2(CF_2)_3SO_2N}C_6H_5$, and $\overline{SO_2(CF_2)_3S(O)({=}N})OC_6H_5$, respectively.

Introduction

Tris(fluorosulfonyl)methane, $(FSO_2)_3CH$,[3,4] tris((perfluoroalkyl)sulfonyl)methanes, $(R_fSO_2)_3CH$,[1,5,6] and some similar compounds such as $\overline{SO_2(CF_2)_nSO_2C}HSO_2R_f$[1,5] have recently been reported. In addition, a variety of related nitrogen compounds, $(R_fSO_2)_2NH$[1,7] and $\overline{SO_2(CF_2)_nSO_2N}H$,[1,8] have been reported. These compounds are perhaps the strongest known carbon and nitrogen acids. For example, the acidity of $(FSO_2)_3CH$ has been estimated by means of Raman spectroscopy to lie between that of concentrated HNO_3 and that of $HOSO_2F$,[4] and the acidity of $(CF_3SO_2)_2NH$ in glacial acetic acid is much greater than that of HNO_3.[7a] Gas phase acidity measurements on $(CF_3SO_2)_3CH$ and $(R_fSO_2)_2NH$ have established these compounds as superacids, and the latter possess the highest acidity known.[9] This high acidity is obviously caused by the very strong electron-withdrawing groups bonded to the carbon and nitrogen atoms.[7,10] Yagupolskii has proposed tautomeric forms of the acid $(FSO_2)_3CH$ in which the proton is bonded to the oxygen atom. The ^{19}F NMR for $(FSO_2)_3$-CH, however, contained only one signal at 20 °C, indicating that the fluorosulfonyl groups are equivalent.[10]

When we synthesized $(CF_3SO_2)_3CH$, its ^{19}F NMR spectrum was studied at different temperatures.[1,5b] At 22 °C a single sharp signal at δ −76.4 ($CFCl_3$) was observed, but at −20 °C this peak broadens and at −50 °C two signals are observed with an intensity of 2:1 at δ −75.7 and −77.1, indicating two distinct CF_3 groups. We interpret these results in terms of an equilibrium involving the tautomeric forms of the acid which shifts to the right at low temperatures



$$(CF_3SO_2)_3CH \rightleftharpoons (CF_3SO_2)_2C{=}\overset{\displaystyle CF_3}{\overset{|}{S}}(O)OH$$

Yagupolskii reported the first stable compound of a similar isomeric form, i.e. $C_6H_5O(F)S(O){=}C(SO_2F)_2$, prepared by heating the phenyl diazonium tris(trifluorosulfonyl)methanide, $C_6H_5N_2^+C(SO_2F)_3^-$.[10] These findings together with the current electrochemical interest in superacids of carbon and nitrogen[11] led us to synthesize and study the title compounds.[12]

Results and Discussion

Phenyl diazonium tris((trifluoromethyl)sulfonyl)methanide, $C_6H_5N_2^+C(SO_2CF_3)_3^-$ (**1**), was easily prepared by treatment of an aqueous solution of $(CF_3SO_2)_3CH$ with $C_6H_5N_2^+Cl^-$. Compound **1** has a very low solubility in water and is easily separated by filtration as a white solid. Its structure was confirmed by the characteristic IR absorption at 2285 cm^{-1} for the $-N_2^+$ group along with absorptions typical for the $(CF_3SO_2)_3C^-$ anion.[5,6]

$$(CF_3SO_2)_3CH + C_6H_5N^+Cl^- \xrightarrow[0-22\ °C]{H_2O} \underset{\textbf{1}}{C_6H_5N_2^{+-}C(SO_2CF_3)_3}$$

1 can be stored at 0 °C for several weeks without decomposition. It decomposes rapidly at 75 °C in the absence of a solvent with quantitative release of nitrogen. In a polar solvent such as

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(1) Presented in part at: (a) IXth European Symposium on Fluorine Chemistry, Leicester (U.K.), Sept 4–8, 1989. Abstract: DesMarteau, D. D.; Zhu, S.; Pennington, W. T.; Gotoh, Y.; Witz, M.; Zuberi, S.; Singh, S. *J. Fluorine Chem.* **1989**, *45*, 24. (b) DesMarteau, D. D. ACS Ninth Winter Fluorine Symposium, St. Petersburg, FL, Jan 29–Feb 3, 1989; Abstract 69.

(2) Permanent address: Shanghai Institute of Organic Chemistry, 345 Lingling Lu, Shanghai 200032, PRC.

(3) Yagupolskii, Yu. L.; Savina, T. I. *J. Org. Chem. USSR* (*Engl. Transl.*) **1983**, *19*, 71.

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(5) (a) DesMarteau, D. D.; Zhu, S.-Z. 12th International Symposium on Fluorine Chemistry, Santa Cruz, CA, Aug 7–12, 1988; Abstract 218. (b) Manuscript in preparation.

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(7) (a) Foropoulos, J., Jr.; DesMarteau, D. D. *Inorg. Chem.* **1984**, *23*, 3720. (b) Singh, S.; DesMarteau, D. D. *Inorg. Chem.* **1990**, *29*, 2982.

(8) (a) DesMarteau, D. D.; Zuberi, S.; Huang, H.-N.; Singh, S.; Witz, M. ACS Eighth Winter Fluorine Conference, St. Petersburg, FL, Jan 25–30, 1987; Abstract 38. (b) Zuberi, S.; DesMarteau, D. D. Manuscript in preparation.

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(10) Yagupolskii, Yu. L.; Savina, T. I. *J. Org. Chem. USSR* (*Engl. Transl.*) **1986**, *21*, 1874.

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(12) Well after the completion of this work, two related publications have appeared regarding the decomposition of (a) C_6H_5-$N_2^+(CF_3SO_2)_3C^-$ and (b) $C_6H_5N_2^+(CF_3SO_2)_2N^-$. (a) Yagupolskii, Yu. L.; Pavlenko, N. V.; Yur'ev, I. I.; Iksanova, S. V. *J. Org. Chem. USSR* (*Engl. Transl.*) **1990**, *26*, 682. (b) Hass, A.; Yagupolskii, Yu. L.; Klare, C. *Mendeleev Commun.* **1992**, 70. In ref 12a, only the *O*-phenyl isomer was observed in contrast to the results reported here. In ref 12b both *O*- and *N*-phenyl isomers were observed, in reasonable agreement with the results reported here.

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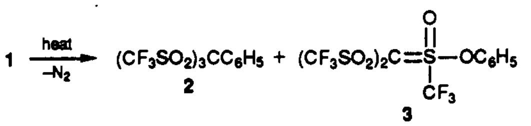
Table I. Properties of Benzenediazonium Salts 1 and 4

compd	IR (ν-N_2^+), cm^{-1}	mp, °C	*T* dec, °C	^{19}F NMR
1	2285	dec	75	−76.34 (s, CF_3)
4a	2284	dec	71	−78.96 (s, CF_3)
4b	2275	78	92	−78.95 (s, CF_3) −83.12 (m, F)
4c	2233	76–78	95	−78.92 (s, CF_3)

CH_3CN, the decomposition is evident at 50 °C. Under these conditions, two products were obtained with phenyltris((trifluoromethyl)sulfonyl)methane $(CF_3SO_2)_3CC_6H_5$ as the major product.



$$\mathbf{1} \xrightarrow[-N_2]{\text{heat}} \underset{\mathbf{2}}{(CF_3SO_2)_3CC_6H_5} + \underset{\mathbf{3}}{(CF_3SO_2)_2C{=}\overset{O}{\underset{CF_3}{S}}{-}OC_6H_5}$$

When **1** was heated at 70 °C for 5 min in CH_3CN, the ratio of **2** and **3** was 2:1 by ^{19}F NMR. In the case of $C_6H_5N_2^+C(SO_2F)_3^-$, pyrolysis under all conditions gave only $C_6H_5O(F)S(O){=}C(SO_2F)_2$ and no $(FSO_2)_3CC_6H_5$ was detected.[10]

The separation and purification of **2** and **3** was accomplished by column chromatography (see Experimental Section). Compound **3** was obtained as a yellow viscous oil, and **2** was obtained as a white crystalline solid. Compounds **2** and **3** were identified by their NMR, IR, and MS spectra. The ^{19}F NMR spectrum of **2** is a singlet at δ −76.3. The spectrum of **3** consists of two peaks with an intensity of 1:2 at δ −66.9 and −74.7 corresponding to the expected two different CF_3 groups. The MS spectrum of **3** exhibits an intense MH^+ ion (CI) in contrast to **2** and the base peak at *m/e* 93 in **3** ($C_6H_5O^+$) supports the aryl ester structure.

As mentioned above, the low-temperature ^{19}F NMR spectrum of $(CF_3SO_2)_3CH$ consisted of two peaks due to tautomeric forms of **1**. One might expect $(CF_3SO_2)_2NH$ to behave similarly, and the temperature dependence of the ^{19}F NMR spectrum of $(CF_3SO_2)_2NH$ was also checked; only one peak was observed down to the lowest possible temperature with CD_3CN (−85 °C). If the same tautomerism exists as in **1**, the proton shift must be fast even at −85 °C. However, it was possible to observe both *O*-phenyl and *N*-phenyl isomers in the decomposition of the respective benzenediazonium salts.

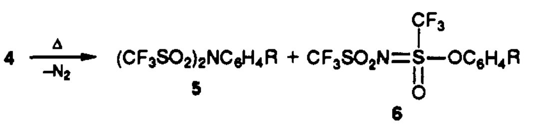
Three arenediazonium bis((trifluoromethylsulfonyl)amides were prepared by treatment of aryldiazonium chloride with $(CF_3SO_2)_2NH$, similar to the preparation of **1**.

$$RC_6H_4N_2^+Cl^- + (CF_3SO_2)_2NH \xrightarrow[0\text{–}22\,°C]{H_2O} \underset{\mathbf{4}}{RC_6H_4N_2^+(CF_3SO_2)_2N^-}$$

R = H (**4a**), *p*-F (**4b**), *p*-OH (**4c**)

Some properties of compounds **4** are compared with those of **1** in Table I.

The para substituents clearly cause a shift of the $\nu(N_2^+)$ absorption to lower frequencies with a corresponding increase in the decomposition temperature. The decomposition of **4** was studied in some detail and the product ratios were dependent on the reaction conditions.



$$\mathbf{4} \xrightarrow[-N_2]{\Delta} \underset{\mathbf{5}}{(CF_3SO_2)_2NC_6H_4R} + \underset{\mathbf{6}}{CF_3SO_2N{=}\overset{CF_3}{\underset{O}{S}}{-}OC_6H_4R}$$

R = H (**5–6a**); R = F, (**5–6b**)

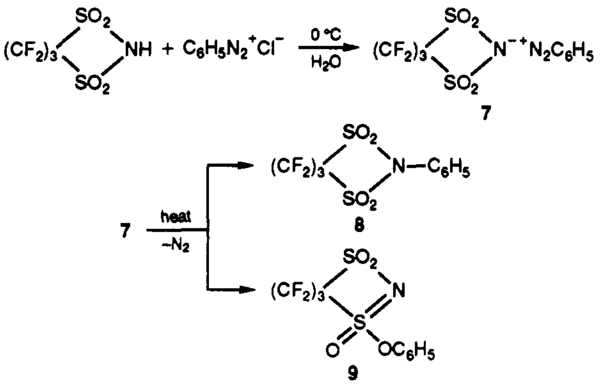
These results are summarized in Table II.

Table II. Decomposition of 4

compd	solvent	*T*, °C	time	product (% yield)[a]
4a		75	5 min	**5a** (48), **6a** (52)
4a	CD_3CN	70	5 min	**5a** (70), **6a** (30)
4a	$(CD_3)_2CO$	22	4 days	**5a** (33), **6a** (67)
4b,c	$(CD_3)_2CO$	22	1 week	**4b,c** (100)
4b		95	5 min	**5b** (<5), **6b** (95)
4b	CD_3CN	reflux	45 min	**4b** (100)

[a] By ^{19}F NMR.

In a very interesting extension of the above reactions, the diazonium salt of a cyclic sulfonimide was prepared and found to behave similarly to $PhN_2^+(CF_3SO_2)_2N^-$.



As in the decomposition of **1** and **4**, the pyrolysis of **7** gave two products when heated in CH_3CN at 90 °C for 5 min, **8** (62%) and **9** (38%). In the absence of a solvent, the yield of **9** increased to 90%.

It is interesting to speculate on the mechanism of the decomposition of **1**, **4**, and **7**. In structural studies of metal derivatives of the acids $(R_fSO_2)_2NH$,[1,13] $(R_fSO_2)_2CH_2$,[1,14] and $(R_fSO_2)_3CH$,[1,5,6] there are strong interactions in the solid state between the sulfonyl oxygens and the nitrogen in $(R_fSO_2)_2N^-$ and only the sulfonyl oxygens in $(R_fSO_2)_2CH^-$ and $(R_fSO_2)_3C^-$. This reflects the delocalized nature of the charge in these anions and is consistent with the high Bronsted acidity. The lack of significant interactions of the methanide carbon with the metal cations compared to nitrogen can be rationalized on the basis of the lower electronegativity of carbon. If the decomposition of **1**, **4**, and **7** in solution involves a phenyl cation intermediate, it might then be reasonable for the cation to combine with the anion via both nitrogen and oxygen in the case of $(R_fSO_2)_2N^-$ and more to oxygen than carbon in $(CF_3SO_2)_3C^-$. This reasoning seems to fit in the case of the sulfonimides but the high percentage of the *C*-phenyl isomer in the case of **1** indicates that other factors are important. Similarly, the ratio of isomers in the case of **4** and **7** is highly dependent on reaction conditions, and no simple rationale can explain the observed product distribution.

Experimental Section

General Procedures. All the work was carried out in ordinary glassware. The compounds $(CF_3SO_2)_3CH$,[5,6] $(CF_3SO_2)_2NH$,[7a,15] and $\overline{SO_2(CF_2)_3SO_2N}H$[8] were prepared from the respective sulfonyl fluorides, CF_3SO_2F and $FSO_2(CF_2)_3SO_2F$. All other reagents were commercially available and were purified before use as appropriate. IR spectra were obtained using KCl plates. ^{19}F NMR and ^{1}H NMR were recorded using $CFCl_3$ and TMS as internal standards and CD_3CN as a lock solvent. Mass spectra were obtained by direct insertion for EI (70 eV) and CI (CH_4). Only the higher mass and most intense fragments are given. Melting points are uncorrected. Purity of new compounds was determined

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(14) DesMarteau, D. D.; Pennington, W. T.; Sung, K. S.; Zhu, S.-Z.; Scott, R. *Eur. J. Solid State Inorg. Chem.* **1991**, *28*, 905.

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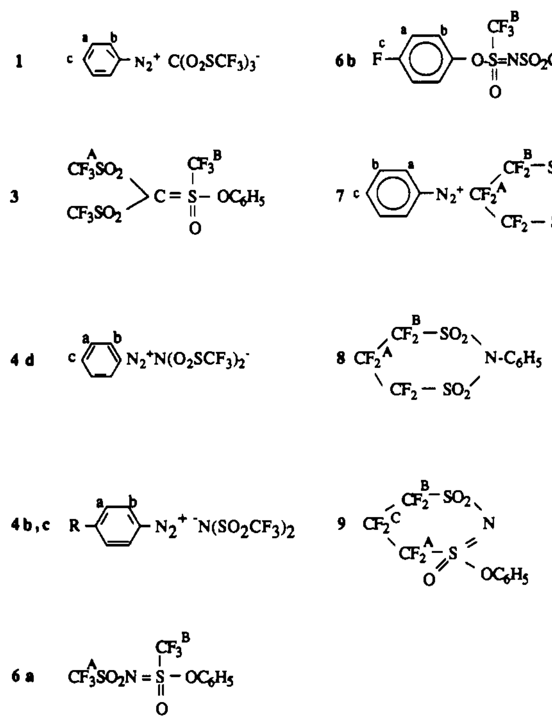
Table III. Structures for NMR Assignments



by ${}^1H$ and ${}^{19}F$ NMR. Structures for NMR assignments are given in Table III, as appropriate.

Preparation of 1. Hydrochloric acid (37%), 1.5 mL, was added to a 50-mL flask which contained a solution of aniline (0.5 g, 5.4 mmol) and 5 mL of distilled water. The flask was cooled by an ice–methanol solution. Sodium nitrite (0.35 g, 5 mmol) in 2 mL of water was added dropwise, keeping the temperature of the reaction mixture below 0 °C. After being stirred for 30 min, a solution of $(CF_3SO_2)_3CH$ (2.06 g, 5 mmol) in 5 mL of H_2O was added. The mixture was stirred for 30 min and allowed to warm to 22 °C. The white precipitate was then filtered off, washed with water, and dried over P_2O_5 under vacuum for 24 h, giving **1** (2.0 g, 77%).

IR: 3100 cm^{-1} (m), 2285 (m), 1567 (m), 1459 (m), 1371 (s), 1342 (m), 1308 (w), 1202 (vs), 1125 (s), 1071 (m), 974 (s), 755 (s), 687 (m), 664 (m), 625 (m), 578 (m), 509 (m) cm^{-1}. ${}^1H$ NMR: δ(a) 8.43–8.48 (2H); δ(b) 7.89–7.97 (2H); δ(c) 8.24–8.31 (1H). ${}^{19}F$ NMR: –76.34 (s, CF_3). MS (CI): *m/e* 489 ($MH^+ - N_2$, 55.1%), 162 ($C_6H_5CF_3O^+$, 87.8%), 109 ($C_6H_5S^+$, 100%). MS (EI): *m/e* 419 ($M^+ - N_2CF_3$, 2.0%), 162 ($CF_3OC_6H_5^+$, 62.8%), 93 ($C_6H_5O^+$, 100%), 69 (CF_3^+, 74.6%), 65 ($C_5H_5^+$, 73.0%).

Pyrolysis of $C_6H_5N^+C(O_2SCF_3)_3^-$ (1). A solution of **1** (1.0 g, 2 mmol) in 2 mL of CH_3CN in a 15-mL flask equipped with a gas outlet tube and magnetic stirring bar was heated to 65 °C, and nitrogen gas was evolved. After 5 min, the release of nitrogen stopped. TLC analysis and ${}^{19}F$ NMR showed that there were two products. The solvent was removed by distillation, and the residue was chromatographed on a silica gel column using light petroleum (bp 36–40 °C) and methylene chloride as the eluent. Compound **3** (0.25 g, 26%) was eluted first as a viscous yellow oil and could not be solidified.

3. IR: 3057 (w), 1594 (m), 1545 (m), 1493 (m), 1481 (m), 1400 (m), 1379 (s), 1318 (s), 1203 (vs), 1122 (s), 1012 (m), 996 (m), 963 (m), 899 (m), 757 (m), 694 (m), 622 (s), 503 (m) cm^{-1}. ${}^1H$ NMR: 7.58 (s, C_6H_5). ${}^{19}F$ NMR: δ(B) –66.89 (s, 3F); δ(A) –74.70 (s, 6F). MS (CI): *m/e* 489 (M^+H, 36.9%); 162 ($CF_3OC_6H_5^+$, 96.8%); 136 ($C_6H_4COS^+$ or CF_3SOF^+, 73.8%), 109 ($C_6H_5S^+$, 100%). MS (EI): *m/e* 419 ($M^+ - CF_3$, 1.3%), 201 ($C_6H_5OCSO_2^+$, 43.0%), 93 ($C_6H_5O^+$, 100%), 77 ($C_6H_5^+$, 7.4%), 69 (CF_3^+, 48.4%), 65 ($C_5H_5^+$, 62.1%).

$(CF_3SO_2)_3CC_6H_5$ (2) (0.4 g, yield 42%), mp 80–83 °C. IR: 3064 (w), 1588 (m), 1483 (m), 1373 (s), 1342 (w), 1199 (s), 1124 (s), 974 (s), 767 (m), 701 (m), 623 (s), 575 (m), 506 (m) cm^{-1}. ${}^1H$ NMR: δ 7.91–6.96 (m, C_6H_5). ${}^{19}F$ NMR: δ –76.36 (s, CF_3). MS (CI): *m/e* 287 ($MH^+ - CF_3SO_2 - CF_3$, 27.3%), 259 ($C_2F_6SCC_6H_5^+$, 95.9%), 257 ($CF_3S_3O_4C^+$, 24.0%), 201 ($S_2O_3CC_6H_5^+$, 29.8%), 153 ($SO_2CC_6H_5^+$, 32.2%), 137 ($SOCC_6H_5^+$, 31.4%), 153 ($O_2S{=}C^+C_6H_5$, 32.2%), 137 ($SOCC_6H_5^+$, 31.4%), 136 ($C_6H_5CSO^+$ or CF_3SOF^+, 100%), 133 ($CF_3SO_2^+$, 80.2%), 101 (CF_3S^+, 45.5%). MS (EI): *m/e* ($C_2F_6SCC_6H_5^+$, 3.1%), 101 (CF_3S^+, 19.2%), 93 ($C_6H_5O^+$, 60.6%), 87 ($C_6H_5C^+$, 13.0%), 77 ($C_6H_5^+$, 16.1%), 69 (CF_3^+, 22.3%), 65 ($C_6H_5^+$, 29.0%), 41 ($C_3H_5^+$, 100%).

Preparation of 4a. A solution of $(CF_3SO_2)_2NH$ (2.8 g, 10 mmol) in 10 mL of H_2O was treated with $C_6H_5N_2^+Cl^-$, prepared from $C_6H_5NH_2$ (0.95 g, 10.2 mmol), 3 mL of HCl (37%) and $NaNO_2$ (0.7 g, 10 mmol) as above. The white precipitate was filtered, washed with water, and dried under vacuum over P_2O_5, giving **4a** (2.7 g, 71%).

IR: 3099 (m), 2284 (s), 1565 (m), 1458 (m), 1353 (vs), 1345 (s), 1331 (m), 1198 (vs), 1137 (s), 1058 (s), 935 (w), 793 (m), 762 (m), 740 (m), 664 (m), 620 (s), 597 (m), 564 (m), 508 (m) cm^{-1}. ${}^{19}F$ NMR: δ –69.96 (s, CF_3). ${}^1H$ NMR: δ(a) 8.49–8.44 (m, 2H); δ(c) 8.31–8.24 (m, 1H); δ(b) 7.98–7.90 (m, 2H). MS (CI): *m/e* 358 ($MH^+ - N_2$, 46.3%), 224 ($CF_3SO_2NC_6H_5^+$, 14.0%), 164 ($C_6H_5N_2SO_2^+$, 100%), 162 ($CF_3OC_6H_5^+$, 92.6%), 141 ($SO_2C_6H_5^+$, 40.7%), 139 ($C_6H_5NSO^+$, 14.7%), 131 (CF_3SON^+, 18.6%). MS (EI): *m/e* 357 ($M^+ - N_2$, 3.2%), 162 ($CF_3OC_6H_5^+$, 30.0%), 93 ($C_6H_5O^+$, 100%), 69 (CF_3^+, 63.4%), 65 ($C_5H_5^+$, 91.7%).

Preparation of 4b and 4c. $(CF_3SO_2)_2NH$ (2.8 g, 10 mmol) in 10 mL of H_2O was treated with 10 mmol of *p*-$RC_6H_4N_2^+Cl^-$ prepared from *p*-$RC_6H_4NH_2$, $NaNO_2$, and HCl solution as above, giving **4b** (R = F) (yield 71%) and **4c** (R = OH) (yield 82%), respectively.

4b. ${}^{19}F$ NMR: δ –79.95 (s, CF_3); –83.1 (m, aryl F). ${}^1H$ NMR: δ(a) 8.65–8.50 (m, 2H), δ(b) 7.76–7.57 (m, 2H). IR: 3098 (m), 2275 (m), 1579 (s), 1481 (m), 1427 (w), 1355 (s), 1319 (s), 1257 (s), 1215 (s), 1192 (s), 1160 (m), 1140 (s), 1091 (m), 1097 (m), 1056 (s), 849 (m), 788 (m), 739 (m), 638 (m), 614 (s), 598 (m), 512 (m) cm^{-1}. MS (CI): *m/e* 376 ($MH^+ - N_2$, 38.6%), 111 ($FC_6H_4O^+$, 100%). MS (EI): *m/e* ($M^+ - N_2$, 2.6%), 111 ($FC_6H_4O^+$, 100%), 83 ($C_5H_4F^+$, 83.1%), 69 (CF_3^+, 29.7%).

4c. ${}^1H$ NMR: δ(a) 8.35–8.28 (m, 2H); δ(b) 7.28–7.20 (m, 2H). IR: 3341 (broad), 3100 (m), 2233 (m), 1587 (s), 1567 (s), 1449 (w), 1349 (s), 1323 (s), 1309 (s), 1239 (m), 1193 (vs), 1139 (s), 1118 (s), 1087 (m), 1057 (s), 846 (m), 791 (m), 741 (m), 614 (s), 510 (m) cm^{-1}. MS (CI): *m/e* 374 ($MH^+ - N_2$, 6.6%), 109 ($HOC_6H_4O^+$, 100%). MS (EI): *m/e* 373 ($M^+ - N_2$, 0.5%), 109 ($HOC_6H_4O^+$, 100%), 81 ($HOC_5H_4^+$, 29.4%), 69 (CF_3^+, 71.5%).

Pyrolysis of 4a. Compound **4a** (1.9 g, 5 mmol) in a 15-mL flask was heated to 70 °C. After 5 min, the release of N_2 stopped. The reaction mixture was distilled under vacuum, giving **6a** (0.7 g, 40%). The residue was purified by column chromatography and gave crude **5a** (0.6 g, yield 34%). Pure **5a** was obtained by vacuum sublimation.

6a. Bp: 50–55 °C (3×10^{-3} mmHg). IR: 3067 (w), 1600 (w), 1578 (m), 1481 (m), 1442 (w), 1391 (s), 1340 (s), 1226 (vs), 1131 (s), 1078 (vs), 1021 (m), 915 (m), 890 (s), 768 (m), 752 (m), 717 (m), 684 (m), 647 (m), 602 (s), 490 (m) cm^{-1}. ${}^{19}F$ NMR: δ(A) –78.0 (s, CF_3); δ(B) –72.7 (S, CF_3). ${}^1H$ NMR: 7.63–7.40 (m, C_6H_5). MS (CI): *m/e* 358 (MH^+, 100%); 293 ($M^+ - SO_2$, 13.2%), 272 ($M^+ - CF_3O$, 12.5%), 162 ($CF_3OC_6H_5^+$, 52.8%), 141 ($C_6H_5SO_2^+$, 69.9%), 107 ($C_6H_5ON^+$, 10.3%). MS (EI): *m/e* 357 (M^+, 2.7%), 93 ($C_6H_5O^+$, 93.0%), 69 (CF_3^+, 97%), 65 ($C_5H_5^+$, 100%).

$(CF_3SO_2)_2NC_6H_5$ (5a). Bp: >60 °C (3×10^{-3} mmHg[16]). Mp: 89–91 °C. IR: 3066 (w), 1631 (m), 1586 (m), 1485 (m), 1346 (s), 1192 (vs), 1133 (s), 1056 (s), 790 (m), 758 (m), 741 (m), 701 (m), 654 (m), 615 (m), 566 (m), 506 (m) cm^{-1}. ${}^{19}F$ NMR: δ –78.9 (s, CF_3). ${}^1H$ NMR: δ 7.65–7.44 (m, C_6H_5). MS (CI): *m/e* 281 ($MH^+ - C_6H_5$, 14.4%); 136 (CF_3SOF^+, 100%). MS (EI): *m/e* 211 ($CF_3SO_2NSO_2^+$, 1.3%), 133 ($CF_3SO_2^+$, 7.5%), 118 (CF_3SOH^+, 16.7%), 93 ($C_6H_5O^+$, 93.9%), 77 ($C_6H_5^+$, 12.1%), 69 (CF_3^+, 100%), 65 ($C_5H_5^+$, 10.9%).

Pyrolysis of 4b. One gram (2.5 mmol) of **4b** was heated to 95 °C in a 10-mL flask. After the evolution of N_2 stopped, vacuum distillation gave **6b** (0.7 g, 75%); bp 50–55 °C (3×10^{-3} mmHg). IR: 3116 (w), 3077 (w), 1591 (m), 1493 (s), 1442 (m), 1392 (s), 1342 (s), 1229 (vs), 1129 (s), 1078 (s), 1011 (m), 892 (s), 842 (m), 788 (m), 771 (m), 744 (m), 707 (m), 641 (m), 604 (s), 494 (m) cm^{-1}. ${}^{19}F$ NMR: δ(A) –77.9 ppm (3F, s); δ(B) –72.5 (3F, s); δ(C) –110.9 (1F, m). ${}^1H$ NMR: 7.15–7.51 (m, aryl H). MS (CI): *m/e* 376 (MH^+, 19.5%); 111 ($FC_6H_4O^+$, 100). MS (EI): *m/e* 375 (M^+, 1.3), 111 ($FC_6H_4O^+$, 100), 83 ($C_5H_4F^+$, 56.3), 69 (CF_3^+, 37.3).

Preparation of 7. Reaction of 2.9 g (10 mmol) of $\overline{SO_2(CF_2)_3SO_2N}H$ with $C_6H_5N_2^+Cl^-$ (10 mmol) in H_2O (15 mL) at 0 °C gave **8** (3 g, 76%). **8** decomposed at 94 °C. IR: 3099 (m), 2286 (m), 1568 (m), 1458 (m),

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[16] (a) Gandelsman, L. Z.; Dronkina, M. I.; Nazaretyan, V. P.; Yagupolskii, L. M. *Zh. Org. Khim.* **1972**, *8*, 1659. (b) Hendrickson, J. B.; Bergeron, R. *Tetrahedron Lett.* **1973**, 4609. No spectral data.

1353 (vs), 1330 (s), 1306 (m), 1277 (m), 1256 (m), 1220 (m), 1168 (vs), 1158 (vs), 1093 (m), 1073 (m), 1042 (s), 996 (m), 904 (m), 794 (s), 750 (m), 662 (m), 605 (m), 537 (m) cm^{-1}. ^{1}H NMR: δ(a) 7.70–7.98 (2H, m); δ(b) 8.44–8.49, (2H, m); δ(c) 8.23–8.31 (1H, m). ^{19}F NMR: δ(A) −119.3 (4F, t); δ(B) −125.7 (2F, m). MS (CI): *m/e* 370 ($MH^+ - N_2$, 100%). MS (EI): *m/e* 369 ($M^+ - N_2$, 13.7), 141 ($C_6H_5NCF_2^+$, 16.0), 139 ($C_6H_5NSO^+$, 14.9), 110 $(SO)_2N^+$, 15.0), 100 ($C_2F_4^+$, 19.9), 93 ($C_6H_5O^+$, 100), 91 ($C_6H_5N^+$, 16.7), 77 ($C_6H_5^+$, 17.1), 65 ($C_5H_5^+$, 72.2).

Pyrolysis of 7 (in CH_3CN). Compound **7** (1 g, 2.5 mmol) and 5 mL of CH_3CN were heated in a 15-mL flask for 5 min at 90 °C. By ^{19}F NMR the yields of **8** and **9** were 62% and 38%, respectively. After the solvent was removed, **9** was distilled out under vacuum, bp ~75–82 °C (6×10^{-3} mmHg). IR: 3069 (m), 1601 (m), 1577 (m), 1481 (s), 1442 (s), 1399 (vs), 1343 (s), 1281 (s), 1224 (vs), 1209 (vs), 1193 (vs), 1160 (vs), 1139 (s), 1097 (vs), 1057 (vs), 1021 (s), 999 (s), 926 (s), 879 (s), 801 (s), 760 (s), 735 (m), 713 (m), 684 (m), 644 (m), 588 (m), 532 (s) cm^{-1}. ^{1}H NMR: δ 7.49–7.58 (m, C_6H_5). ^{19}F NMR: δ(A) −110.5, −112.3 (2F, AB type, $^2J = 238$ Hz); δ(B) −116.5, −117.8 (2F, AB type, $^2J = 256$ Hz); δ(C) −123.9 (2F, m). MS (CI): *m/e* 370 (MH^+, 100), 354 ($MH^+ - O$, 29). MS (EI): *m/e* 369 (M^+, 1.7), 135 (C_6H_5SNC, 35.7), 93 ($C_6H_5O^+$, 100), 65 ($C_5H_5^+$, 23.4).

The residue after distillation of **9** was sublimed to give **8** as white crystals, mp 155–157 °C. IR: 3051 (w), 1672 (m), 1646 (m), 1590 (m), 1539 (m), 1492 (w), 1367 (s), 1331 (s), 1277 (m), 1255 (m), 1224 (m), 1152 (vs), 1092 (m), 1013 (s), 903 (m), 803 (s), 751 (m), 689 (m), 611 (m), 533 (m) cm^{-1}. ^{1}H NMR: δ 7.40–7.61 (m, C_6H_5). ^{19}F NMR: δ(B) −119.3 (4F, t); δ(A) −125.7 (2F, m). MS (CI): *m/e* 370 (MH^+, 100). MS (EI): *m/e* 150 ($C_3F_5^+$, 17.5), 139 ($C_6H_5SON^+$, 5.4), 131 ($C_3F_4^+$, 6.6), 119 ($C_2F_5^+$, 6.6), 100 ($C_2F_4^+$, 100), 96 (CF_2SN^+, 5.7), 93 ($C_6H_5O^+$, 5.2), 65 ($C_5H_5^+$, 6.3), 64 (SO_2^+, 5.9), 48 (SO^+, 9.0).

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