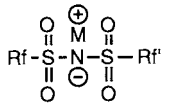
A New One-Pot Synthesis of Bisperfluoroalkanesulfonylamides and Bispentafluorobenzenesulfonylamide as Potassium Salts

Kensaku Sogabe,[†] Yasuchika Hasegawa,[†,††] Yuji Wada,[††] Takayuki Kitamura,[††] and Shozo Yanagida[††]
[†]*New Development Division, New Japan Chemical Co., Ltd., 13 Yoshijima, Yagura-cho, Fushimi-ku, Kyoto 612-8224*
[††]*Material and Life Science, Graduate School of Engineering, Osaka University, Yamada-oka, Suita, Osaka 565-0871*

(Received May 8, 2000; CL-000431)

Bisperfluoroalkanesulfonylamides were synthesized as potassium salts by one-pot reaction of perfluoroalkanesulfonyl halides with acetamide derivatives in the presence of K_2CO_3 in THF.

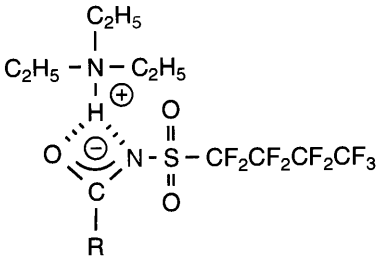
There has been significant recent interest in bisperfluoroalkanesulfonylamides as intermediates of agricultural chemicals,[1] fluorination reagents of aromatic compounds,[2] electrolytes of electrochemical fuel cell,[3] and Lewis acid catalysts.[4] Furthermore, we recently found that the use of bisperfluoroalkanesulfonylamides as ligand leads to the enhanced luminescence of the lanthanide complexes.[5] The synthetic processes of perfluorinated sulfonylamides are much different from those used in general organic syntheses because of the presence of perfluorinated groups.[6] DesMarteau et al. reported the multistep reactions using liquid NH_3 and trimethyldisilazane for synthesis of the sulfonylamides in 1984.[7] Asahi Chemical Industry Co. Ltd. patented a similar but modified method using $LiN(SiMe_3)_2$.[8] Central Glass Co. Ltd. succeeded in industrial one-pot synthesis by reaction of perfluoroalkanesulfonyl fluoride with liquid NH_3 in the presence of triethylamine (TEA) as a base under –40 °C in 1996.[9] More recently, 3M Co. patented a preparation method by reaction of perfluoroalkanesulfonylamide and perfluoroalkanesulfonyl halides in the presence of a non-nucleophilic base such as lithium carbonate.[10] We report here a new one-pot synthesis of bisperfluoroalkanesulfonylamides through the reaction of perfluoroalkanesulfonyl halides with acetamide derivatives in the presence of K_2CO_3 as a base.



perfluoroalkane-sulfonylamide salt

A 100 mL three neck flask, equipped with a thermometer and a reflux condenser was purged with dry nitrogen gas, and anhydrous THF (30 mL), K_2CO_3 (10.0 g, 72 mmol) and trifluoroacetamide (CF_3CONH_2, 3.3 g, 28 mmol) were introduced into the flask. The reaction mixture was warmed up to 65 °C under magnetic stirring. Perfluorooctanesulfonyl fluoride ($C_8F_{17}SO_2F$, 14.1 g, 28 mmol) was added dropwise over 30 min and the mixture was kept at 65 °C. After 3 h reaction, another $C_8F_{17}SO_2F$ (14.1 g, 28 mmol) was added dropwise over 30 min and stirred for 3 h. After the mixture was cooled to ambient temperature, the solvent was evaporated to dryness under reduced pressure. Acetone (50 mL) was added to the solid residue, and the resulting solution was filtered to remove K_2CO_3 and KF. The filtrate was evaporated under a reduced pressure and the residure was washed with diethyl ether (100 mL) to remove unreacted CF_3CONH_2 and $C_8F_{17}SO_2F$. The white residue was recrystallized with ethanol (50 mL), giving bisperfluorooctanesulfonylamide potassium salt as colorless needles (20.5 g, 72% yield) (Table 1, run 1). This salt was identified by means of ^1H-, ^{19}F-NMR (Nihon Electron NMR EX-270, 270MHz), IR (Perkin Elmer 1720-X), UV absorption (Shimadzu UV-2100), and elemental analysis (Perkin-Elmer 240C).[11]

Instead of using CF_3CONH_2, acetamide can be used as a source of the amide group for the synthesis (Table 1, run 2). Furthermore, we carried out the several reactions using other substrates and amides. Bispentafluorobenzenesulfonylamide potassium salt was also synthesized by the reaction of



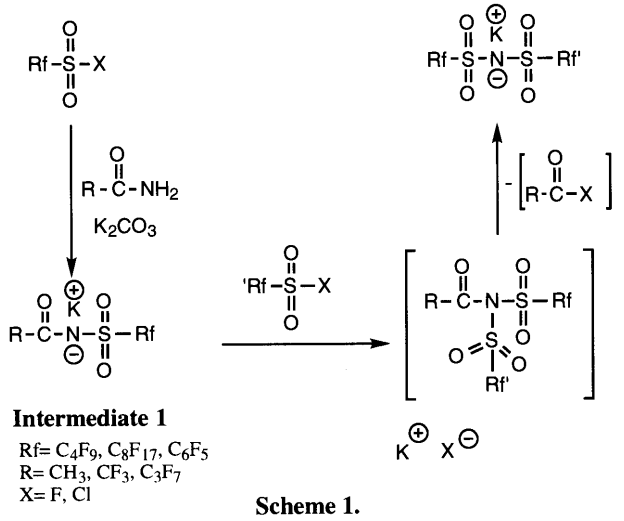
4: R = CF_3
5: R = C_3F_7

Figure 1. Postulated structure of triethlamine salt of intermediate 1.

Table 1. One-pot synthesis of bisperfluoroalkanesulfonylamides and bispentafluorobenzenesulfonylamide using acetamides and bases

Run	substrate	Amine	Base	Product	Yield / %
1	$C_8F_{17}SO_2F$	CF_3CONH_2	K_2CO_3	**1:** $K^+[C_8F_{17}SO_2NSO_2C_8F_{17}]^-$	72
2	$C_8F_{17}SO_2F$	CH_3CONH_2	K_2CO_3	**1:** $K^+[C_8F_{17}SO_2NSO_2C_8F_{17}]^-$	75
3	$C_6F_5SO_2Cl$	CH_3CONH_2	K_2CO_3	**2:** $K^+[C_6F_5SO_2NSO_2C_6F_5]^-$	54
4	$C_4F_9SO_2F$	CF_3CONH_2	K_2CO_3	**3:** $K^+[C_4F_9SO_2NSO_2C_4F_9]^-$	77
5	$C_4F_9SO_2F$	CF_3CONH_2	$N(C_2H_5)_3$	**4:** $[NH(C_2H_5)_3)]^+[C_4F_9SO_2NCOCF_3]^-$	82
6	$C_4F_9SO_2F$	$C_3F_7CONH_2$	$N(C_2H_5)_3$	**5:** $[NH(C_2H_5)_3]^+[C_4F_9SO_2NCOC_3F_7]^-$	87

acetamide with $C_6F_5SO_2Cl$ (Table 1, run 3). In the synthesis of bisperfluorobutanesulfonylamide potassium salts using $C_4F_9SO_2F$, we found that K_2CO_3 is indispensable as a base (Table 1, run 4). The use of TEA resulted in the production of half-sulfonylated intermediates without giving the objective bisperfluorobutanesulfonylamide potassium salts (Table 1, runs 5 and 6). The ammonium cation $[TEA]^+H$ might stabilize the intermediates as depicted in Figure 1, preventing the intermediate from reacting with another sulfonyl fluoride. The salt was identified by ^1H-, ^{19}F-NMR, IR, UV absorption and elemental analysis.[11] We proposed Scheme 1 as a plausible pathway giving bisperfluoroalkanesulfonylamides. Acysulfonylamide potassium salt (Intermediate 1) formed from sulfonyl halides and acetamides would undergo further reaction with sulfonyl halide, giving bisperfluoroalkanesulfonylamides through elimination of acetyl group as a good leaving group in an S_N2-type reaction.



Intermediate 1

Rf= C_4F_9, C_8F_{17}, C_6F_5
R= CH_3, CF_3, C_3F_7
X= F, Cl

Scheme 1.

We developed a new one-pot synthetic route of bisperfluoroalkanefulfonylamides and bispentafluorobenzenesulfonylamide using acetamide derivatives instead liq. NH_3 under much mild conditions.

References and Notes

1 Central Glass Co. Ltd., J. P. Patent, 070246338 (1995).

2 A. Vij, R. L. Kirchmeier, J. M. Shreeve and R. D. Verma, *Coord. Chem. Rev.*, **158**, 413 (1997).

3 a) K. Sung and D. D. DesMarteau, *Polym. Prepr., Am. Chem. Soc., Div. Polym. Chem.*, **33** (**2**), 168 (1992); b) D. D. DesMarteau, Report (1992), GRI-92/0385 Order No. PB93-132710.

4 H. Kobayashi, Z. Nie and T. Sonoda, *Chem.Lett.*, **1955**, 30.

5 Y. Hasegawa, T. Ohkubo, K. Sogabe, Y. Kawamura, Y. Wada, N. Nakashima and S. Yanagida, *Angew. Chem., Int. Ed. Engl.*, **39**, 357 (2000).

6 a) I. A. Koppel, R. W. Taft, F. Anvia, S. Zhu, L. Hu, K. Sung, D. D. DesMarteau, L. M. Yagupolskii, Y. L. Yagupolskii, N. V. Ignat'ev, N. V. Kondratenko, A. Y. Volkonskii, V. M. Vlasov, R. Notalio and P. Maria, *J. Am. Chem. Soc.*, **116**, 3047 (1994). b) S. Singh, D. D. DesMarteau, S. S. Zuberi, M. Witz and H. N. Huang, *J. Am. Chem. Soc.*, **109**, 7194 (1987). c) T. Gramstad and Haszeldine, *J. Chem. Soc.*, **56**, 173 (1973). d) Asahikasei Co.Ltd., J. P. Patent, 57164991 (1982). e) H. M. Scholberg and H. G. Bryce, U. S. Patent, 2717871 (1955). f) M. Shmeisser and P. Sartori, *Chemie-Ing-Techn.*, **36**, 9 (1964). g) F. G. Drakesmith and D. A. Hughes; *J. Appl. Electrochem.*, **6**, 23 (1976).

7 J. Foropoulos, and D. D. DesMarteau, *Inorg. Chem.*, **23**, 3720 (1984).

8 Asahi Chemical Industry co. Lid., J. P. Patent, 09173856 (1997).

9 Central Glass Co. Ltd., J. P. Patent, 0881436 (1996).

10 R. D. Howells, W. M. Lamanna, A. D. Fanta and J. E. Waddell, PCT Int. Appl., WO 97 23,448 (1997).

11 **1**: ^{19}F-NMR (CD_3OD, C_6F_6): δ –79.20 (t, 6F, CF_3), –112.57 (t, 4F, CF_2), –118.27 (br, 4F, CF_2), –119.39 (br, 12F, CF_2), –120.61 (br, 4F, CF_2), –124.17 (br, 4F, CF_2); IR (KBr): 1354 (S=O), 1249 (C–F), 1202 (C–F), 1152 (S–O). Found: C, 17.30; H, 0.09; N, 2.17%. Calcd for $C_{16}O_4N_1F_{34}S_2K_1$: C, 18.85; H, 0; N, 1.37%. **2**: ^{19}F-NMR (CD_3OD, C_6F_6): δ –137.13 (o-, 4F, CF_2), –153.00 (p-, 2F, CF), –161.66 (m-, 4F, CF_2); IR: 1489 (C_6F_5), 1306 (S=O), 1252 (C–F), 1226 (C–F), 1116 (S–O); UV (CH_3OH): 227 nm (K absorption-band), 268 nm (B absorption-band). Found: C, 24.54; H, 0.22; N, 0.09%. Calcd for $C_{12}O_4N_1F_{10}S_2K_1$: C, 27.97; H, 0; N, 2.72%. **3**: ^{19}F-NMR (CD_3OD, C_6F_6): δ –79.37 (t, 6F, CF_3), –111.57 (t, 4F, CF_2), –119.29 (br, 4F, CF_2), –124.35 (br, 4F, CF_2); IR (KBr): 1347 (S=O), 1235 (C–F), 1201 (C–F), 1126 (S–O) cm^{-1} Found: C, 14.16; H, 0.17; N, 0.83%. Calcd for $C_8O_4N_1F_{18}S_2K_1$: C, 15.51; H, 0; N, 2.26%. **4**: ^{19}F-NMR (acetone-d_6, C_6F_6): δ –74.20 (m, 3F, CF_3), –79.37 (t, 3F, CF_3), –112.42 (t, 2F, CF_2), –119.23 (p, 2F, CF_2), –124.19 (h, 2F, CF_2); ^1H-NMR (Acetoned_6, TMS): δ 1.4 (t, 9H, CH_3), 3.5 (q, 6H, CH_2), 8.0(br, 1H, NH); ^{13}C-NMR (acetone-d_6, TMS): δ –108 to –124 (C_3F_8), 141.26 (CF_2), 137.46 (CF_2), 162.78 (C=O). Found: C, 28.89; H, 3.35; N, 5.8%. Calcd for $C_{12}H_{16}O_3N_2F_{12}S$: C, 29.03; H, 3.26; N, 5.64%. **5**: ^{19}F-NMR (acetone-d_6, C_6F_6): δ –79.29 (t, 6F, CF_3), –112.50 (br, 2F, CF_2), –115.75 (br, 2F, CF_2), –119.10 (br, 2F, CF_2), –124.15 (t, 2F, CF_2), –124.73 (t, 2F, CF_2); ^1H-NMR (acetone-d_6, TMS): δ 1.4 (t, 9H, CH_3), 3.4 (q, 6H, CH_2), 7.8 (br, H, NH); IR (Neat): 3102 (N–H), 2821 (C–H), 1667 (C=O), 1325 (S=O), 1217 (C–F), 1139 (C–F), 1121 (S–O). Found: C, 27.49; H, 2.53; N, 4.80%. Calcd for $C_{14}H_{18}O_4N_2F_{16}S$: C, 27.37; H, 2.95; N, 4.56 %. The compound **5** has one H_2O molecule. In case of the bisperfluoroalkanesulfonylamide potassium salts, measured values by elemental analysis did not coincident with calculated values, because these were unflammable metal salts containing many fluorine atoms.