2,4-pentanedione ($pK_a = 9$) and cyclopentadiene ($pK_a = 15$), it seems likely that the reaction proceeds by protonation as the first step:

$$\overset{\delta+}{M}=\overset{\delta-}{O} + \text{Hacac} \rightarrow [M^+\text{—}O\text{—}\text{Hacac}^-]$$

Other acidic materials reacted similarly, such as alcohols and carboxylic acids.

The small yields of $OM(acac)_2$ compounds produced (Table III) from the sesquioxide vaporization studies are probably due to reaction with MO_2 vapor species in similar oxo-protonation reactions:

$$MO_2 + 2\text{acacH} \rightarrow OM(acac)_2 + H_2O$$

To our disappointment, TiO and VO vapors did not yield stable low-valent adducts with amines, phosphines, or other similar ligands. Apparently complexes such as $(bpy)_2TiO$ or $[(EtO)_3P]_4VO$ are not stable under our experimental conditions.

Experimental Section

A. General Procedures. All of the cocondensation reactions were carried out by using a standard resistive heating metal atom apparatus.[34] Metal oxides were vaporized from 0.005 in. thick tungsten boat sources available from R. D. Mathis Co. The TiO and VO solids were obtained from Cerac Chemical Co. and were 99.9% and 99.5% pure, respectively. The Ti_2O_3 solid used was 99+% from Alfa, and the V_2O_3 was 99% from Aldrich Chemicals. Metals were vaporized from 0.010 in. thick tungsten boats as follows: Granular vanadium (Alfa Chemicals) was heated to its softening point and held there during evaporation. Titanium ($^1/_8$-in. rod (Materials Research Corp., Marz grade)) was heated to just below its melting point to avoid alloying with the boat (alloying causes the boat to melt). Manipulations of the compounds were all carried out under anaerobic conditions using standard Schlenkware and a Vacuum Atmospheres drybox.

Chlorine from Matheson was frozen in a liquid-nitrogen trap (evacuated to <1 μm) and then expanded into a 3.5-L glass bulb monitoring the pressure via an oil-covered Hg manometer. The bulb was filled to about 500 mmHg prior to reactions, providing a 100-mmol sample that was inlet to the reactor by using a Teflon needle valve and an oil filled bubbler to control the rate. The 2,4-pentanedione (reagent grade) was dried over sodium 2,4-pentanedionate for 24 h and then distilled in vacuo. All solvents (reagent grade) were refluxed under nitrogen and distilled immediately prior to use from appropriate drying agents.

B. Reaction of Metal Oxide Vapors with Chlorine: V_2O_3 Evaporation as a Typical Example. Chlorine (102 mmol) was cocondensed at liquid-nitrogen temperature with 0.089 g (1.31 mmol) of vapor from solid V_2O_3 during a 1-h reaction, forming a yellow-green matrix. As the reactor warmed, the excess chlorine was pumped out through a −78 °C trap, to collect any volatile vanadium-containing compounds, and condensed in a liquid nitrogen trap. After the system was warmed to room temperature, there was a small amount of yellow liquid in the −78 °C trap and a light green solid remained in the reactor. The reactor was flushed with N_2, and the green solid was washed twice with 40 mL of THF and filtered through a fine-porosity fritted-glass disk. The THF solution was reduced to the white solid $OVCl_2(THF)_2$ in vacuo, and characterized by its mass spectrum and infrared spectrum. The liquid recovered from the −78 °C trap was shown to be $OVCl_3$ by its infrared spectrum and mass spectrum.

C. Reaction of Metal Oxide Vapors and 2,4-Pentanedione: TiO Evaporation as a Typical Example. During a 2-h reaction about 30 mL of 2,4-pentanedione was codeposited with 0.293 g (4.57 mmol, 42% of the sample) of vapor from TiO. The matrix varied in color from light brown to brown-black immediately after the Dewar flask was removed. The matrix turned blue upon warming. Excess 2,4-pentanedione was recovered, leaving a dark blue solid. The reactor was flushed with N_2, the contents were washed out with 50 mL of toluene, and the mixture was filtered. The toluene was evaporated, leaving 0.498 g (31.6% yield) of $Ti(acac)_3$, identified by comparison of its mass spectrum and infrared spectrum with those of a sample from Aldrich. The recovered excess 2,4-pentanedione contained a few drops of immiscible liquid identified as water by GC/MS.

D. Analysis of $OV(acac)_2$ and $V(acac)_3$ Mixtures. Quantitative Mass Spectral Analysis. Three standard samples of $OV(acac)_2$ and $V(acac)_3$ containing 41.5, 8.46, and 4.44 mol % $V(acac)_3$ were prepared in a N_2-filled glovebox and intimately ground. Approximately 1-mg samples of the standards were quantitatively vaporized in the mass spectrometer by slowly heating the probe to 250 °C at 15 °C/min while one scan/3 s was acquired for 20 min at 15 eV. Individual mass chromatograms were generated for the 265- and 348-amu ion intensity. These showed that $V(acac)_3$ vaporized at a slightly lower temperature range of 50–150 °C, while $OV(acac)_2$ vaporized from 100 to 200 °C. At 225 °C the intensity of both ions had reduced and leveled off. Integration of the parent ion peak intensity of the $OV(acac)_2$ (265 amu) and the $V(acac)_3$ compound (348 amu) versus time gave 40.2, 7.87, and 4.72 mol % $V(acac)_3$. The method was therefore shown to be valid to within ±1.5 mol % and was used to calculate the percent composition of the compound mixture obtained from the reaction of 2,4-pentanedione with metal oxides and the metal chloride compounds.

Qualitative Infrared Spectral Analysis. The infrared spectra of pure samples obtained from Aldrich Chemical Co. were recorded for the purpose of comparison with product mixtures obtained. All sample spectra were obtained as Nujol mulls prepared in a nitrogen-filled glovebox and placed between two KBr plates.

For the titanium compounds the most obvious difference in the spectra is the appearance of a band at 590 cm^{-1}, which can be attributed to the bridging oxo group.

Acknowledgment. The support of the National Science Foundation and partial support of the Army Research Office are acknowledged with gratitude.

---

[34] Klabunde, K. J.; Timms, P. L.; Skell, P. S.; Ittel, S. *Inorg. Synth.* **1979**, *19*, 59.

Contribution from the Howard L. Hunter Chemistry Laboratory,
Clemson University, Clemson, South Carolina 29634-1905

Chemistry of Perfluoromethylsulfonyl Perfluorobutylsulfonyl Imide

Sukhjinder Singh and Darryl D. DesMarteau*

Received October 25, 1989

Selected chemistry of the unsymmetrical imide perfluoromethylsulfonyl perfluorobutylsulfonylimide, $CF_3SO_2N(H)SO_2C_4F_9$, is described. The potassium, cesium, and silver derivatives were prepared by reaction of the respective carbonates with the imide. The silver compound is a useful reagent for synthesis of both organic and inorganic derivatives. Reaction with methyl iodide or ethyl iodide resulted in high yields of the alkyl imides. Chlorine reacts with the silver derivative to give the chloroimide in excellent yield. Reaction of $CF_3SO_2N(Cl)SO_2C_4F_9$ with NO and NO_2 formed the corresponding nitroso and nitro derivatives, and CO and ethylene react at 22 °C to give addition compounds. UV photolysis of the chloroimide resulted in the quantitative formation of C_4F_9Cl and the cyclic dimer of the resultant $CF_3SO_2NSO_2$.

Introduction

The (trifluoromethyl)sulfonyl group, CF_3SO_2–, has been reported to be one of the strongest neutral electron-withdrawing groups.[1,2] Furthermore, the CF_3SO_2– group has the added synthetic value of having high stability under a wide variety of reaction conditions.[3-5] In disubstituted amines, the presence of

---

[1] Gramstad, T.; Hazeldine, R. N. *J. Chem. Soc.* **1957**, 4069.

[2] Bordwell, F. G.; Vanier, N. R.; Mathews, W. S.; Hendrickson, J. B.; Skipper, P. L. *J. Am. Chem. Soc.* **1975**, *97*, 7160.

[3] Senning, A. *Chem. Rev.* **1965**, *65*, 385.

0020-1669/90/1329-2982$02.50/0

two sulfonyl groups on nitrogen drastically increases the acidity of the remaining proton, as shown by $(FSO_2)_2NH$,[6] $(CF_3SO_2)_2NH$,[7] and certain $(R_fSO_2)_2NH$[8] derivatives.

The chemistry of $(FSO_2)_2NH$[6,9-11] and $(CF_3SO_2)_2NH$[7,12,13] has led to a variety of interesting compounds, including examples of xenon-nitrogen bonds.[11-13] Several homologous perfluoroalkylsulfonyl imides of the type $R_fSO_2N(H)SO_2R_f'$ have been known since 1972,[8] but the only derivatives reported other than the sodium salts utilized in the synthesis of the imides were $CH_3N(SO_2C_4F_9)_2$[8] and several $R_fSO_2N(F)SO_2R_f'$ compounds.[14] In view of the increased interest in these compounds for electrochemical applications,[15] their unusual reactivity as shown by the *N*-fluoro derivatives,[14] and limited evidence that showed that the chemistry of $(C_4F_9SO_2)_2NH$ only partially paralleled that of $(CF_3SO_2)_2NH$, we chose to investigate the chemistry of $CF_3SO_2N(H)SO_2C_4F_9$ in more detail. The latter was chosen over other available imides for its obvious relationship to $(CF_3SO_2)_2NH$ and $(C_4F_9SO_9)_2NH$ and a relatively low molecular weight, which would provide reasonable volatility of covalent derivatives, thereby facilitating handling by vacuum-line techniques.

Experimental Section

All manipulations of volatile compounds were carried out in Pyrex and stainless-steel vacuum systems equipped with glass-Teflon and Teflon-packed stainless-steel valves, respectively. Pressures were measured with a Wallace and Tiernan differential pressure gauge, Series 1500. Amounts of reactants and products were measured by *PVT* measurements or by direct weighing. Temperatures were measured by using a digital-indicating iron-constantan thermocouple. Melting points were taken on a standard capillary tube apparatus or by a modified Stock technique. Molecular weights were determined by vapor density measurements using a calibrated 0.25-L Pyrex bulb fitted with a glass-Teflon valve.

Infrared spectra were obtained on a Perkin-Elmer 1430 IR spectrometer employing a 3600 or 7500 data station and a 10-cm gas cell fitted with AgCl or KCl windows. Solids were sampled as Nujol mulls or thin films between AgCl or KCl windows. Raman spectra were obtained on a Spex 1403 Ramalog double monochromator with a Scamp data system. Mass spectra were obtained on a HP 5985B GC/MS system by direct inlet of gas and solid samples.

^{19}F and ^1H NMR spectra were recorded on a JEOL FX-90Q spectrometer at 84.25 and 89.55 MHz, with $CFCl_3$ or $(CH_3)_4Si$ as the internal reference and an appropriate deuterated lock solvent.

Materials. $CF_3SO_2N(H)SO_2C_4F_9$ was prepared by a modified (see Discussion) literature method.[8] $C_4F_9SO_2F$ and hexamethyldisilazane used in the preparation of the above imide were purchased from PCR, Inc., and distilled before use. Trifluoromethanesulfonyl fluoride, CF_3SO_2F, was supplied by 3M Co. All other reagents were readily available from commercial sources and were appropriately purified as needed.

Preparation of $CF_3SO_2N(M)SO_2C_4F_9$, M = Ag, K, or Cs. In a typical reaction, 7.0 g (16.2 mmol) of $CF_3SO_2N(H)SO_2C_4F_9$ was dissolved in 30 mL of distilled water in a 100-mL round-bottom flask. A slight excess of Ag_2CO_3 (2.5 g, 9.06 mmol) was slowly added to the above solution with stirring. The contents were heated at ~60 °C for 1 h, and excess Ag_2CO_3 was filtered out. Excess water was removed under vacuum, and the resulting solid was dissolved in 30 mL of diethyl ether; the solution was filtered, and the ether was removed under vacuum. Final drying under vacuum at 25 °C gave the white solid $CF_3SO_2N(Ag)SO_2C_4F_9$ (7.6 g, 14.1 mmol) in 87% yield: mp 209-210 °C; IR (Nujol, AgCl) 1358 (s), 1329 (s), 1289 (vw), 1209 (vs, br), 1166 (w), 1140 (s), 1121 (s), 1064 (ms), 846 (vw), 817 (ms), 776 (vw), 750 (ms), 696 (m), 644 (m), 595 (s), 511 (m) cm^{-1}; ^{19}F NMR (δ; acetone-d_6) $CF_3{}^ASO_2N(Ag)SO_2CF_2{}^ECF_2{}^DCF_2{}^CCF_3{}^B$ A = −78.4 (s), B = −80.8 (tt), C = −125.7 (m), D = 120.6 (m), E = −112.2 (br t) ppm ($J_{BC} = 9.7$, $J_{BD} = 2.4$, $J_{DE} = 15.3$ Hz).

The potassium and cesium derivatives were prepared similarly in an aqueous medium with a 10% excess of M_2CO_3. A white crystalline solid separated upon cooling to 20 °C, which was filtered out and washed three times (5 mL each) with cold (~15 °C) distilled water to remove traces of K_2CO_3. The white crystalline solid was dissolved in acetone, and the solution was filtered. Excess solvent was removed under vacuum, and the product was dried as above.

$CF_3{}^ASO_2N(K)SO_2CF_2{}^ECF_2{}^DCF_2{}^CCF_3{}^B$: yield 90%; mp 213-214 °C; IR (solid, KCl) 1372 (s, sh), 1344 (s), 1291 (vw), 1204 (vs), 1145 (s), 1068 (s), 872 (m), 808 (w), 785 (ms), 746 (s), 734 (sh), 696 (m), 656 (ms), 633 (w), 601 (s), 514 (ms) cm^{-1}; ^{19}F NMR (δ; acetone-d_6) A = −79.3 (s), B = −81.0 (tt), C = −125.9 (m), D = −120.8 (m), E = −113.2 (br t) ppm ($J_{BC} = 10$, $J_{BD} = 2.5$, $J_{DE} = 14$ Hz).

$CF_3{}^ASO_2N(Cs)SO_2CF_2{}^ECF_2{}^DCF_2{}^CCF_3{}^B$: yield 80%; mp ~148 °C; IR (solid, KCl) 1336 (s), 1241 (w), 1199 (s), 1170 (m), 1141 (ms), 1074 (s), 1026 (w), 842 (vw), 806 (w), 785 (m), 750 (sh), 734 (m), 699 (w), 646 (s), 573 (ms), 519 (ms) cm^{-1}; ^{19}F NMR (δ; acetone-d_6) A = −79.2 (s), B = 80.8 (tt), C = −125.7 (m), D = −120.8 (m), E = −113.1 (br t) ppm (*J* values essentially identical with those of the K salt above).

Preparation of $CF_3SO_2N(Cl)SO_2C_4F_9$. $CF_3SO_2N(Ag)SO_2C_4F_9$ (4.96 g, 9.2 mmol) was loaded into a 100-mL Pyrex reactor, which was then evacuated to remove traces of water, if any. Chlorine (18.5 mmol) was then condensed onto the silver derivative cooled to −196 °C. The reactor was allowed to warm slowly to 22 °C in an empty, cold Dewar flask over 4 h and then left at 22 °C for 24 h in the absence of light. The volatile materials were then transferred to the vacuum line and passed through −38 and −196 °C traps. Essentially pure $CF_3SO_2N(Cl)SO_2C_4F_9$ (4.2 g, 9.0 mmol, 97% yield) was collected in the −38 °C trap. *Caution!* Many *N*-halo compounds are known to be powerful explosives. We have not encountered any difficulties in the course of this research for the quantities indicated, but due caution must be exercised when working with these materials on a large scale.

$CF_3SO_2N(Cl)SO_2C_4F_9$ is a low-volatility colorless liquid at 22 °C: mp −32 to −30 °C; IR (vapor in equilibrium with liquid, AgCl) 1463 (s), 1446 (sh), 1351 (m), 1289 (vw), 1246 (vs), 1205 (sh), 1146 (m), 1132 (ms), 1027 (w), 843 (ms), 802 (w), 769 (vw), 741 (m), 700 (w), 631 (vw), 583 (ms), 498 (m) cm^{-1}; ^{19}F NMR (δ) $CF_3{}^ASO_2N(Cl)SO_2CF_2{}^ECF_2{}^DCF_2{}^CCF_3{}^B$ A = −71.3 (s), B = −81.1 (tt), C = −126.1 (m), D = −120.8 (m), E = −104.5 (br t) ppm ($J_{BC} = 9.8$, $J_{BD} = 2.0$, $J_{DE} = 13.7$ Hz).

Attempts to obtain a mass spectrum by direct insertion gave major ions for the acid $CF_3SO_2N(H)SO_2C_4F_9$, [CI] *m/z* 432 [M + 1] (100%), with only a small parent ion for the *N*-chloro derivative, [CI] *m/z* 467/469 [MH^+] (10/3%).

In routine handling, the *N*-chloro derivative was found to be very moisture sensitive and readily hydrolyzed to $CF_3SO_2N(H)SO_2C_4F_9$.

Photolysis of $CF_3SO_2N(Cl)SO_2C_4F_9$. $CF_3SO_2N(Cl)SO_2C_4F_9$ (1.04 g, 2.2 mmol) was added by vacuum transfer to a 50-mL Pyrex vessel fitted with an insert containing a medium-pressure, 250-W Hg lamp. The sample was irradiated for 2 h, and volatiles were passed through a series of cold traps. The −90 and −140 °C traps contained C_4F_9Cl (2.0 mmol), identified by IR spectroscopy and molecular weight (found 257, calcd 254.5). The −196 °C trap contained a very small amount of COF_2 and CF_3Cl. A white solid was obtained in a −30 °C trap, which slowly transferred under dynamic vacuum and proved to be identical with the previously reported $(CF_3SO_2NSO_2)_2$[7,16] (~1.0 mmol): mp ~54 °C; IR (gas in equilibrium with solid, 27 °C) 1454 (s), 1240 (vs), 1207 (s, sh), 1128 (ms), 1054 (vw), 906 (s), 741 (vw), 658 (ms), 600 (m), 515 (w), 473 (w) cm^{-1}.

Preparation of $CF_3SO_2N(CH_3)SO_2C_4F_9$. Methyl iodide (9.0 mmol) was condensed onto $CF_3SO_2N(Ag)SO_2C_4F_9$ (1.6 g, 3.0 mmol) in a 50-mL Pyrex reactor. An immediate formation of AgI was seen as the reactor warmed to room temperature. After 1 h the volatile materials were pumped through a −20 °C trap for a long time, where pure $CF_3SO_2N(CH_3)SO_2C_4F_9$ (1.14 g, 2.6 mmol), a low-volatility colorless liquid, was collected in 86% yield: IR (vapor in equilibrium with liquid) 2978 (vw), 1451 (ms), 1423 (ms), 1351 (m), 1241 (vs), 1210 (s, sh), 1140 (ms), 1047 (w), 1028 (vw), 844 (ms), 805 (w), 743 (m), 701 (vw), 668 (vw), 647 (vw), 598 (ms), 504 (m) cm^{-1}; IR (liquid) 2978 (w), 1449 (s), 1421 (s), 1348 (s), 1286 (sh), 1211 (vs, br), 1142 (s), 1074 (sh), 1048 (ms), 1028 (sh), 843 (s), 805 (w), 744 (ms), 700 (w), 667 (w), 648 (w),

---

(4) Howells, R. D.; McCown, J. D. *Chem. Rev.* **1977**, *77*, 69.

(5) Hendrickson, J. B.; Sternback, D. D.; Bain, K. W. *Acc. Chem. Res.* **1977**, *10*, 306.

(6) Ruff, J. K. *Inorg. Chem.* **1965**, *4*, 1446.

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

(8) Meussdorffer, J. N.; Niederprum, H. *Chem.-Ztg.* **1972**, *96*, 582.

(9) Ruff, J. K. *Inorg. Chem.* **1966**, *5*, 732.

(10) Lustig, M.; Bumgardner, C. L.; Johnson, F. A.; Ruff, J. K. *Inorg. Chem.* **1964**, *3*, 1165.

(11) DesMarteau, D. D.; LeBlond, R. D.; Hossain, S. F.; Nothe, D. *J. Am. Chem. Soc.* **1981**, *103*, 7734.

(12) Singh, S.; DesMarteau, D. D. To be submitted for publication.

(13) Foropoulos, J., Jr.; DesMarteau, D. D. *J. Am. Chem. Soc.* **1982**, *104*, 4260.

(14) Singh, S.; DesMarteau, D. D.; Zuberi, S. S.; Witz, M.; Huang, H.-N. *J. Am. Chem. Soc.* **1987**, *109*, 7194.

(15) Razaq, M.; Razaq, A.; Yeager, E.; DesMarteau, D. D.; Singh, S. *J. Appl. Electrochem.* **1987**, *17*, 1064.

(16) Roesky, H. W.; Amarki, M.; Schonfelder, L. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1978**, *33B*, 1072.

595 (s), 506 (ms) cm^{-1}; ^{19}F NMR (δ) $CF_3{}^ASO_2N(CH_3)SO_2CF_2{}^ECF_2{}^DCF_2{}^CCF_3{}^B$ A = –73.7 (s), B = –81.2 (tt), C = –126.2 (m), D = 121.1 (m), E = –107.2 (br t) ppm (J_{BC} = 9.5, J_{BD} = 2.0, J_{DE} = 14 Hz); ^{1}H NMR (δ) 3.6 (s) ppm; major *m/z* [CI] (relative intensity) 446 $[MH]^+$ (100), 382 $[MH - SO_2]^+$ (24), 312 $[M - CF_3SO_2]^+$ (6), 296 $[M - CF_3SO_3]^+$ (23), 226 $[M - C_4F_9]^+$ (6), 210 $[M - OC_4F_9]^+$ (9), 146 $[CF_3SONCH_3]^+$ (7), 131 $[CF_3SON]^+$ (2).

Preparation of $CF_3SO_2N(C_2H_5)SO_2C_4F_9$. Ethyl iodide (1.0 g, 6.4 mmol) and $CF_3SO_2N(Ag)SO_2C_4F_9$ (1.02 g, 1.9 mmol) were allowed to react under the same conditions given for the preparation of the *N*-methyl derivative. After 1 h, the volatile products were removed as above by heating the reactor to ~60 °C. The product $CF_3SO_2N(C_2H_5)SO_2C_4F_9$ (0.74 g, 1.6 mmol) was isolated as a clear, colorless, low-volatility liquid in 85% yield: IR (liquid, AgCl) 2998 (w), 2950 (vw), 1432 (vs), 1349 (s), 1323 (w), 1221 (vs, br), 1140 (s), 1122 (s), 1030 (s), 941 (mw), 878 (s), 805 (mw), 755 (s), 742 (sh), 700 (w), 665 (m), 601 (s), 506 (ms) cm^{-1}; ^{19}F NMR (δ) $CF_3{}^ASO_2N(C_2H_5)SO_2CF_2{}^ECF_2{}^DCF_2{}^CCF_3{}^B$ A = –72.7 (s), B = –81.1 (tt), C = –126.2 (m), D = –121.2 (m), E = –105.8 (br, t) ppm (J_{FF} values essentially identical with those of the CH_3 derivative above); ^{1}H NMR (δ) CH_3 = 1.46 (t), CH_2 = 4.09 (q) ppm ($^3J_{HH}$ = 7.0 Hz); major *m/z* [CI] (relative intensity) 460 $[MH]^+$ (100), 432 $[MH - C_2H_4]^+$ (13), 396 $[MH - SO_2]^+$ (8), 240 $[M - C_4F_9]^+$ (4), 224 $[M - OC_4F_9]^+$ (4).

Preparation of $CF_3SO_2N(NO)SO_2C_4F_9$. Excess NO (3×) was added to $CF_3SO_2N(Cl)SO_2C_4F_9$ (1.4 g, 3.0 mmol) in a 100-mL Pyrex reactor at –196 °C. The reactor was placed in a bath at –150 °C and allowed to warm to –20 °C overnight. Reaction began near –140 °C, at which point a deep orange color appeared, indicating the formation of NOCl. NOCl and excess NO were pumped away from the solid product through –150 and –196 °C traps. The –150 °C trap contained NOCl (3 mmol), identified by IR spectroscopy. $CF_3SO_2N(NO)SO_2C_4F_9$ (1.37 g, 3.0 mmol) remained in the reactor as a white crystalline solid in quantitative yield: mp 153–154 °C; IR (solid, AgCl) 2284 (w), 1352 (s), 1330 (s, sh), 1214 (s, br), 1145 (s), 1080 (s), 1033 (w), 1009 (vw), 874 (w), 861 (w), 822 (ms), 780 (m), 750 (ms), 729 (ms), 696 (m), 651 (w), 606 (s), 518 (m) cm^{-1}; Raman (solid, 22 °C) 2294 (s), 1322 (w), 1176 (w), 1123 (w), 1057 (vw), 826 (vw), 755 (sh), 739 (s), 563 (ms), 532 (vs), 409 (vw), 382 (m), 354 (vs), 294 (w, br) cm^{-1}; ^{19}F NMR (δ ; CD_3CN) $CF_3{}^ASO_2N(NO)SO_2CF_2{}^ECF_2{}^DCF_2{}^CCF_3{}^B$ A = –78.9 (s), B = –80.4 (tt), C = –125.3 (m), D = –120.5 (m), E = –112.6 (br t) ppm (J_{BC} = ~10, J_D = 2.4, J_{DE} = ~14.6 Hz).

Preparation of $CF_3SO_2N(NO_2)SO_2C_4F_9$. $CF_3SO_2N(Cl)SO_2C_4F_9$ (1.10 g, 2.4 mmol) and N_2O_4 (10 mmol) were condensed together in a 100-mL Pyrex reactor at –196 °C. The contents were allowed to warm directly to room temperature and stand for 24 h. The volatiles ($ClNO_2$ and excess N_2O_4) were pumped away at 22 °C, leaving the white crystalline solid $CF_3SO_2N(NO_2)SO_2C_4F_9$ (1.14 g, 2.4 mmol) in quantitative yield: mp 134–135 °C; IR (solid, KCl) 2385 (m), 1437 (w), 1348 (s), 1197 (s, br), 1157 (s), 1084 (s), 1034 (w), 1009 (vw), 869 (w), 826 (mw), 781 (w), 750 (mw), 728 (mw), 696 (w), 652 (sh), 628 (sh), 610 (m), 566 (m), 517 (m) cm^{-1}; Raman (solid, 22 °C) 2312 (m), 1408 (ms), 1327 (vw), 1241 (w), 1174 (vw), 1126 (vw), 1058 (vw), 739 (ms), 563 (ms), 532 (s), 406 (vw), 383 (ms), 353 (vs), 305 (w, br) cm^{-1}; ^{19}F NMR (δ; CD_3CN) $CF_3{}^ASO_2N(NO_2)SO_2CF_2{}^ECF_2{}^DCF_2{}^CCF_3{}^B$ A = –78.9 (s), B = –80.4 (tt), C = –125.3 (m), D = –120.5 (m), E = –112.6 (br t) ppm (J_{FF} values essentially identical with those of the NO derivative above).

Preparation of $CF_3SO_2N(COCl)SO_2C_4F_9$. Carbon monoxide (8.0 mmol) was added to $CF_3SO_2N(Cl)SO_2C_4F_9$ (1.0 g, 2.1 mmol) in a 50-mL Pyrex reactor at –196 °C. The reaction was allowed to proceed at room temperature for 20 h in the dark. Excess CO was pumped away by holding the reactor at –10 °C, giving $CF_3SO_2N(COCl)SO_2C_4F_9$ (1.0 g, 2.0 mmol) as a colorless low-volatility liquid in 94% yield: IR (vapor in equilibrium with liquid) 1793 (mw), 1459 (ms), 1351 (w), 1287 (sh), 1246 (s), 1200 (sh), 1149 (mw), 1125 (mw), 1022 (m), 936 (mw), 871 (sh), 846 (vw), 742 (w), 702 (vw), 624 (mw), 592 (vw), 499 (w) cm^{-1}; IR (liquid, AgCl) 1786 (s), 1454 (s), 1350 (ms), 1221 (vs, br), 1195 (s), 1145 (s), 1119 (s), 1020 (s), 934 (s), 868 (w), 843 (sh), 800 (vw), 742 (m), 699 (w), 624 (s), 590 (ms), 500 (ms) cm^{-1}; ^{19}F NMR (δ; $CDCl_3$) $CF_3{}^ASO_2N(COCl)SO_2CF_2{}^ECF_2{}^DCF_2{}^CCF_3{}^B$ A = –68.9 (s), B = –81.1 (tt), C = –125.9 (m), D = –120.8 (m), E = –100.6 (br t) ppm (J_{FF} values essentially identical with those of the CH_3 derivative); major *m/z* [CI] (relative intensity) 432 $[CF_3SO_2N(H_2)SO_2C_4F_9]^+$ (40), 430 $[M - COCl]^+$ (96), 394 $[M - SO_2Cl]^+$ (100), 344 $[M - CF_2SO_2Cl]^+$ (8), 283 $[C_4F_9SO_2]^+$ (7), 219 $[C_4F_9]^+$ (23), 131 $[CF_3SON]^+$ (16). A peak in CI (direct insertion) at 432 is due to hydrolysis of $CF_3SO_2N(COCl)SO_2C_4F_9$ giving rise to an M + 1 ion for $CF_3SO_2N(H)SO_2C_4F_9$.

Preparation of $CF_3SO_2N(C_2H_4Cl)SO_2C_4F_9$. Ethylene (5.0 mmol) and $CF_3SO_2N(Cl)SO_2C_4F_9$ (0.63 g, 1.35 mmol) were condensed together in a 50-mL Pyrex reactor at –196 °C. The reactor was allowed to warm slowly to room temperature over 12 h. Excess C_2H_4 was pumped away by holding the reactor at –10 °C. The product $CF_3SO_2N(C_2H_4Cl)SO_2C_4F_9$ (0.64 g, 1.3 mmol) was obtained as a nearly involatile colorless liquid in 96% yield: IR (liquid, AgCl) 3040 (vw), 2983 (vw), 1451 (s), 1426 (vs), 1349 (ms), 1319 (vw), 1224 (vs, br), 1142 (s), 1123 (s), 1066 (m), 1021 (ms), 961 (w), 854 (s), 804 (w), 741 (s), 702 (vw), 678 (mw), 651 (mw), 602 (s), 507 (s) cm^{-1}; ^{19}F NMR (δ; $CDCl_3$) $CF_3{}^ASO_2N(CH_2CH_2Cl)SO_2CF_2{}^ECF_2{}^DCF_2{}^CCF_3{}^B$ A = –72.1 (s), B = –81.1 (tt), C = –126.0 (m), D = –121.0 (m), E = –105.1 (br t) ppm (J_{FF} values identical with those of the CH_3 derivative); ^{1}H NMR (δ CH_2 = 4.22 (t), CH_2Cl = 3.71 (t) ppm ($^3J_{HH}$ = 7.6 Hz); major *m/z* [CI] (relative intensity) 496/494 $[MH]^+$ (25/58), 458 $[M - Cl]^+$ (99), 432/430 $[MH - SO_2]^+$ (39/100), 394 $[M - SO_2Cl]^+$ (36), 380 $[M - CH_2SO_2Cl]^+$ (90), 344 $[M - CF_2SO_2Cl]^+$ (14), 131 $[CF_3SON]^+$ (14).

Results and Discussion

Initially, the synthesis of $CF_3SO_2N(H)SO_2C_4F_9$ was carried out by the literature method.[8] We found that the compound could be prepared equally well by starting with either sulfonyl fluoride in the first step. However in larger scale preparations, we found that the next-to-the-last step proceeded at a faster rate by using $C_4F_9SO_2N(Na)SiMe_3/CF_3SO_2F$ rather than $CF_3SO_2N(Na)SiMe_3/C_4F_9SO_2F$. The larger perfluoroalkyl group decreases the solubility of R_fSO_2F in dioxane, whereas the sodium salt is still of reasonable solubility.

$$R_fSO_2F \xrightarrow{NH_3} R_fSO_2NHNH_4 \xrightarrow{HCl} R_fSO_2NH_2 \xrightarrow{NaOMe} R_fSO_2NHNa$$

$$\xrightarrow{(Me_3Si)_2NH} R_fSO_2NNaSiMe_3 \xrightarrow{R_f'SO_2F} R_fSO_2N(Na)SO_2R_f' \xrightarrow{H_2SO_4} R_fSO_2N(H)SO_2R_f'$$

$$R_f \neq R_f' = CF_3, C_4F_9$$

In the formation of $R_fSO_2N(Na)SO_2R_f'$, dioxane is strongly complexed to the sodium, and prolonged heating under vacuum is necessary to remove it completely. If the dioxane is not completely removed, the yield and purity of the anhydrous imide on treatment with sulfuric acid will be lowered. The melting point and ^{1}H and ^{19}F NMR data agreed with the literature values.[8] The infrared spectrum of the imide was not previously reported and was obtained for a solid film on AgCl.[17]

The imide dissolves in water exothermically to give a stable acidic solution with pK_a ≃ 1. Neutralization of aqueous perfluoromethylsulfonyl perfluorobutylsulfonyl imide with either potassium carbonate, cesium carbonate or silver carbonate led to the isolation of the corresponding salts according to

$$2\ CF_3SO_2N(H)SO_2C_4F_9 + M_2CO_3 \xrightarrow[1\ h]{\sim 60°C} CF_3SO_2N(M)SO_2C_4F_9 + CO_2 + H_2O$$

M = K, Cs or Ag

The potassium and cesium salts are white crystalline solids soluble in acetone, acetonitrile, and hot water. The melting point of the cesium salt (~148 °C) is lower as compared to those of the potassium (213–214 °C) and silver (209–210 °C) salts. This observation is in agreement with the findings on $(CF_3SO_2)_2NM$, M = K,[12] Ag,[12] or Cs[7] derivatives.

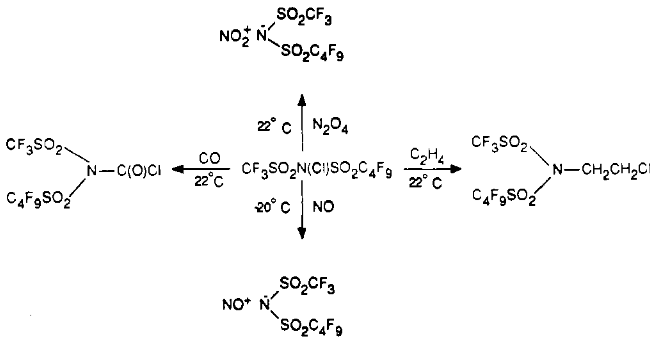
The infrared spectra of the potassium, cesium, and silver salts are similar and suggest the presence of the $CF_3SO_2NSO_2C_4F_9$ anions, as shown by the large decrease in the antisymmetric $\nu(SO_2)$ to 1330–1350 cm^{-1} from 1431 cm^{-1} in the parent imide. However, on the basis of crystal structures of metal derivatives for related imides,[18] these salts probably contain extensive oxygen–metal bonding, giving rise to novel layered structures wherein the formal negative charge on nitrogen is delocalized over the $-O_2SNSO_2-$ framework. The two-dimensional layers will be composed of an extensive network of oxygen–metal and nitrogen–metal interactions with the fluorocarbon groups positioned above and below this network. These layers then stack together to give a graphite-like solid.

---

(17) IR (solid): 3237 (m), 1431 (s, br), 1353 (m), 1309 (ms), 1214 (s), 1193 (s), 1141 (s), 1034 (m), 864 (s), 827 (m), 789 (w), 741 (m), 703 (w), 654 (m), 631 (w), 615 (w), 590 (ms), 532 (mw), 494 (ms) cm^{-1}.

(18) DesMarteau, D. D. To be published.

Scheme I



The silver derivative exhibits a remarkably high solubility in a variety of solvents including water, ethanol, diethyl ether, acetone, and acetonitrile and has reasonable solubility in dichloromethane. It is a very useful ligand-transfer reagent as shown by its reaction with alkyl iodides.

$$CF_3SO_2N(Ag)SO_2C_4F_9 + RI \xrightarrow{22^\circ C} CF_3SO_2N(R)SO_2C_4F_9 + AgI$$

$(R = CH_3, C_2H_5)$

It is clear from this that a large variety of related reactions would be possible.

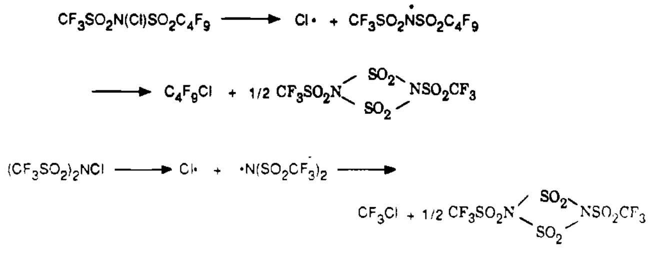
The chemical shift of the methyl protons ($\delta = 3.60$ ppm) in $CF_3SO_2N(CH_3)SO_2C_4F_9$ is comparale to those in $(FSO_2)_2NCH_3$[6] ($\delta = 3.64$ ppm) and $(CF_3SO_2)_2NCH_3$[12] ($\delta = 3.60$ ppm) and can be correlated with the electronegativity of the ligands.[19-21] The electronegativitiy of the $(FSO_2)_2N$[6] group (3.6) determined by the method of Cavanaugh and Bailey[22] has been found to be larger than that of either the nitrogen atom or the SO_2F group (3.1) and is probably the result of delocalization of electrons through sulfur-nitrogen π bonding.

Chlorine was found to react with $CF_3SO_2N(Ag)SO_2C_4F_9$ in the absence of light to produce $CF_3SO_2N(Cl)SO_2C_4F_9$ in high yield.

$$CF_3SO_2N(Ag)SO_2C_4F_9 + Cl_2 \xrightarrow[22^\circ C]{dark} CF_3SO_2N(Cl)SO_2C_4F_9 + AgCl$$

It was found on different-scale preparations that if the pressure of chlorine falls below ~1.5 atm during the reaction, then the yield of the *N*-chloro derivative decreases. The *N*-chloro derivative is stable indefinitely at 22 °C in the dark. As expected, the chlorine derivative was very useful for further synthetic reactions as shown in Scheme I. The ease of addition of CO and C_2H_4 is similar to that of perfluoroalkyl hypochlorites,[23] and reflects the pronounced positive halogen character of the chlorine atom. Similarly, the reactions with NO and N_2O_4 demonstrate the strong oxidizing ability of the compound and the ability of the resultant anion to stabilize the NO^+ and NO_2^+ cations. The vibrational spectra for the products show strong bands at 2284 (IR) and 2294 (Raman) cm^{-1}, indicative of NO^+, and 1408 (Raman) cm^{-1}, for NO_2^+,[24,25] and are very similar to the related $(CF_3SO_2)_2N^-$ derivatives.[7]

The photolysis of $CF_3SO_2N(Cl)SO_2C_4F_9$ was carried out to see if the $CF_3SO_2\dot{N}SO_2C_4F_9$ radical might be stable enough to provide a route to the hydrazine. However, the photolysis reactions of $CF_3SO_2N(Cl)SO_2C_4F_9$ and $(CF_3SO_2)_2NCl$[7] are quite analogous excepting that the former loses C_4F_9Cl exclusively.



The formation of C_4F_9Cl rather than CF_3Cl clearly indicates that the larger R_f group is preferentially eliminated from the intermediate radical. This is consistent with the generally observed lower thermal stability of such compounds with increasing size of R_f. However, other factors are also important since we have previously failed to isolate $(C_4F_9SO_2)_2NX$ (X = Cl, F)[14,27] under conditions that give excellent yields of $CF_3SO_2N(X)SO_2C_4F_9$, $CF_3SO_2N(F)SO_2C_6F_{13}$, and $C_4F_9SO_2N(F)SO_2C_6F_{13}$.[14]

Summary

An improved synthesis of the imide $CF_3SO_2N(H)SO_2C_4F_9$ was developed in order to investigate its reaction chemistry. Metal derivatives of the imide are readily obtained by reaction with carbonates in water, and the novel Ag(I) derivative, with a remarkably high solubility in solvents of different polarity, was shown to be an effective reagent for the synthesis of derivatives of the imide. This work, along with that previously reported for $(CF_3SO_2)_2NH$, indicates that perfluoroalkylsulfonylimides, $R_fSO_2N(H)SO_2R_f'$, can have an extensive and varied chemistry rivaling that of the more common fluorinated acids such as R_fSO_3H and R_fCO_2H.

Acknowledgment. The financial support of this research by the Gas Research Institute and the National Science Foundation is gratefully acknowledged. We also thank 3M Co. and Dr. Fred Behr for generous samples of CF_3SO_2F.

---

(19) Allred, A. L.; Rochow, E. G. *J. Inorg. Nucl. Chem.* **1958**, *5*, 269.

(20) Gasteiger, J. *Nachr. Chem., Tech. Lab.* **1980**, *28*, 17.

(21) Kloter, G.; Pritzkow, H.; Seppelt, K. *Angew. Chem.* **1980**, *92*, 954.

(22) Cavanaugh, J. R.; Bailey, P. B. *J. Chem. Phys.* **1961**, *34*, 1099.

(23) Gould, D. E.; Anderson, L. R.; Young, D. E.; Fox, W. B. *J. Am. Chem. Soc.* **1969**, *91*, 1310. Schack, C. J.; Moya, W. J. *J. Am. Chem. Soc.* **1969**, *91*, 2902. Young, D. E.; Anderson, L. R.; Gould, D. E.; Fox, W. B. *Tetrahedron Lett.* **1969**, 723; *J. Am. Chem. Soc.* **1970**, *92*, 2313.

(24) Gerding, H.; Hontgraff, H. *Recl. Trav. Chim. Pays-Bas* **1953**, *72*, 21.

(25) Qureshi, A. M.; Carter, H. A.; Aubke, F. *Can. J. Chem.* **1971**, *49*, 35.

(26) See ref 7 for other examples.

(27) Foropoulos, J., Jr. Ph.D. Dissertation, Kansas State University, 1982.