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N-Substituted (*F*-Tetramethylene)sulfoxyimides

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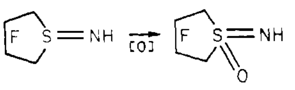
(*F*-Tetramethylene)sulfoxyimide, $CF_2CF_2CF_2CF_2S(O){=}NH$, is a useful precursor to a new family of compounds, $CF_2CF_2CF_2CF_2S(O){=}NR$ (R = $CF_3C(O)$, $(CH_3)_3Si$, CN, Cl, Ag, Li). The latter compound forms $CF_2CF_2CF_2CF_2S(O){=}NC(O)N{=}S(O)CF_2CF_2CF_2CF_2$ with $OCCl_2$.

Introduction

Earlier we reported that (*F*-tetramethylene)sulfoxyimide, $CF_2CF_2CF_2CF_2S(O){=}NH$, was synthesized in high yield by the oxidation of the corresponding imide $CF_2CF_2CF_2CF_2S{=}NH$ with *m*-chloroperbenzoic acid, MCPBA[2] (eq 1). As



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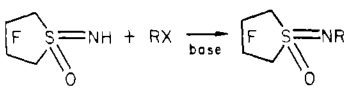
one of a series of studies on the preparation of the derivatives from $CF_2CF_2CF_2CF_2SF_2$, we now report the results of the experiments which were conducted to obtain compounds that contain the $CF_2CF_2CF_2CF_2S(O){=}N$ group. Although $(CF_3)_2S(O){=}NH$ has been shown to be useful as a precursor to sulfoxyimides,[3-5] these compounds are first examples of fluorinated monocyclic sulfoxyimides. The present investigation includes the reactions of $CF_2CF_2CF_2CF_2S(O){=}NH$ with compounds such as $CF_3C(O)F$, $ClSi(CH_3)_3$, ClCN, $COCl_2$, F_2, and AgF_2 and with Ag_2O and *n*-BuLi to produce the silver and lithium salts, respectively. The photolysis of $CF_2CF_2CF_2CF_2S(O){=}NCl$, which was produced either by the reaction of $CF_2CF_2CF_2CF_2S(O){=}NAg$ with Cl_2 or by the reaction of $CF_2CF_2CF_2CF_2S(O){=}NH$ with Cl_2 in the presence of CsF, has been examined.

Results and Discussion

Reactions of (*F*-tetramethylene)sulfoxyimide, $CF_2CF_2CF_2CF_2S(O){=}NH$, and compounds, which have a labile halogen such as $ClSi(CH_3)_3$, $CF_3C(O)F$, and ClCN, result in new N-substituted fluorinated monocyclic sulfoxyimides (eq 2).



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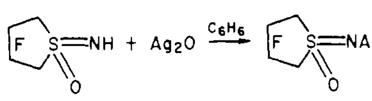
R = $Si(CH_3)_3$ (71%), $C(O)CF_3$ (51%), CN (64%)

The presence of a base was required for these reactions. These new compounds are transparent liquids at 25 °C and, with the exception of $CF_2CF_2CF_2CF_2S(O){=}NCN$, are stable at least to their boiling points. Above 25 °C, $CF_2CF_2CF_2CF_2S(O){=}NCN$ decomposes to form a yellow viscous compound.

With Ag_2O in benzene, the white silver salt $CF_2CF_2CF_2CF_2S(O)NAg$ is formed (eq 3). It darkens slowly on exposure to light. When $CF_2CF_2CF_2CF_2S(O){=}NAg$ was treated with CH_3I and Cl_2, $CF_2CF_2CF_2CF_2S(O){=}NCH_3$[2] (16.8%) and $CF_2CF_2CF_2CF_2S(O){=}NCl$ (71.1%) result, respectively. Direct chlorination of $CF_2CF_2CF_2CF_2S(O){=}NH$ in the presence of CsF also produces the *N*-chloro compound (eq 4).



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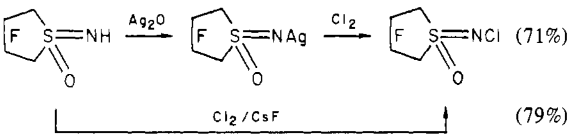

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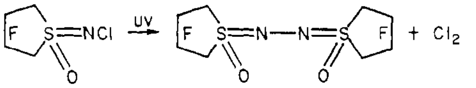
This new $CF_2CF_2CF_2CF_2S(O){=}NCl$ is a transparent colorless liquid at 25 °C which solidifies below −40 °C. When $CF_2CF_2CF_2CF_2S(O){=}NCl$ was photolyzed by using a low-pressure Hg lamp at 25 °C for 12 h, a pale yellow involatile liquid was formed together with Cl_2, SOF_2, and small quantities of $ClCF_2CF_2CF_2CF_2Cl$ (eq 5). The elemental analysis



(5)

of this compound favored the expected bis(sulfoxyimide) structure. Mass spectra did not exhibit a molecular ion at *m/e* 524, but showed *m/e* 486 $[C_8F_{14}S_2O_2N_2]^+$ $(M - 2F)^+$ as the highest peak. The ^{19}F NMR spectrum contained complicated resonances rather than the number of peaks expected for such a structure. More work needs to be completed before the existence of a bis(sulfoxyimide) can be confirmed.

While Ruff[6] has reported the preparation of $F_2S(O){=}NF$ by the reaction of $F_2S(O){=}NC(O)F$ with elemental fluorine, no derivatives of *F*-alkyl compounds such as $(R_f)_2S(O){=}NF$ have been synthesized. Therefore, we attempted the fluorination of $CF_2CF_2CF_2CF_2S(O){=}NH$ with elemental fluorine in the presence of KF to obtain the corresponding *N*-fluorosulfoxyimide. However, only cleaved products such as NF_3 and CF_4 and $CF_2CF_2CF_2CF_2SO_2$ were obtained. Some unreacted starting material was recovered.

The formation of $CF_2CF_2CF_2CF_2O_2$ can result from the hydrolysis of $CF_2CF_2CF_2CF_2S(O)F_2$, which was prepared earlier by the oxidative fluorination of $CF_2CF_2CF_2CF_2S{=}O$ with ClF.[7] $CF_2CF_2CF_2CF_2S(O)F_2$ is unstable in the pres-

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(1) Visiting Research Scholar on leave from the Government Industrial Research Institute, Nagoya, Japan, 1979–1980.

(2) Abe, T.; Shreeve, J. M. *J. Chem. Soc., Chem. Commun.* **1981**, 242.

(3) Sauer, D. T.; Shreeve, J. M. *Inorg. Chem.* **1972**, *11*, 238.

(4) Sauer, D. T.; Shreeve, J. M. *Z. Anorg. Allg. Chem.* **1971**, *385*, 113.

(5) Morse, S. D.; Shreeve, J. M. *Inorg. Chem.* **1977**, *16*, 33.

(6) Ruff, J. K. *Inorg. Chem.* **1966**, *5*, 1787.

(7) Abe, T.; Shreeve, J. M. *J. Fluorine Chem.* **1973/74**, *3*, 17.

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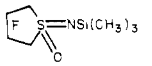
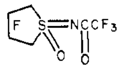
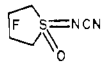
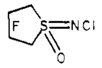
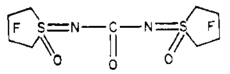
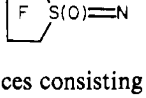
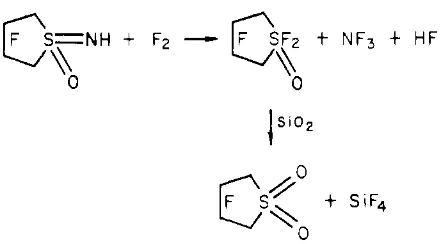
Table I. ^{19}F and ^1H NMR Spectral Data for Some (*F*-Tetramethylene)sulfoxyimides

compd	α-CF_2	β-CF_2	others
	−116.9, −119.7 (1, J_{AB} = 210.9)[a]	−132.8 (complex, 1)	δ(CH_3) 0.28
	−111.2, −112.9 (4, J_{AB} = 203.9)	−131.8 (complex, s, 4)	φ(CF_3) −76.5 (s, 3)
	−111.5 (complex)	−131.5 (complex, s)	
	−109.1, −113.8 (J_{AB} = 202.6)	−132.2 (complex, s)	
	−111.1, −113.3 (J_{AB} = 203.1)	−132.1 (complex, s)	

[a] All *J* values are in Hz.

ence of Pyrex glass, giving the sulfone. This suggests that the fluorination reaction of $CF_2CF_2CF_2CF_2S(O){=}NH$ with fluorine proceeds as in eq 6. When $CF_2CF_2CF_2CF_2S(O){=}NH$ was reacted with *n*-BuLi, the stable white solid $CF_2CF_2CF_2CF_2S(O){=}NLi$ was formed. When this lithium salt was reacted with $COCl_2$, the disubstituted compound carbonylbis(*F*-tetramethylene)sulfoxyimide was produced, viz. eq 7. This compound is a colorless solid at 25 °C. Its infrared spectrum shows a strong absorption band at 1676 cm^{-1} due to $\nu_{C=O}$. Generally, with the exception of $CF_2CF_2CF_2CF_2S(O){=}NCN$, the ^{19}F NMR spectra of the compounds which contain the  moiety showed resonances consisting of an AB pattern at φ −109 to −116 and φ = −112 to −120 with J_{AB} = 203–211 Hz and a resonance at φ = −132 to −133. The former resonances (AB pattern) were assigned to the coupling due to geminal fluorines at α-CF_2 and the latter to those of β-CF_2, respectively. For $CF_2CF_2CF_2CF_2S(O){=}NCN$, however, only two resonances at φ = −131.5 (α-CF_2) and φ = −111.5 (β-CF_2) were observed.



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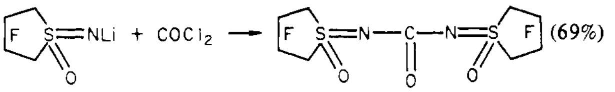

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Experimental Section

Materials. $CF_2CF_2CF_2CF_2S(O){=}NH$ was prepared by the oxidation of $CF_2CF_2CF_2CF_2S{=}NH^2$ with MCPBA. The remainder of the starting materials were obtained from commercial suppliers and used without further purification.

General Procedures. Most gases and volatile liquids were handled in a conventional Pyrex glass vacuum apparatus equipped with a Heise-Bourdon tube guage. All starting materials and products were purified by trap-to-trap distillation and gas chromatography. Infrared spectra were recorded with a Perkin-Elmer 599B spectrometer using a 10-cell equipped with KBr windows. ^{19}F NMR spectra were run on a Varian HA-100 spectrometer and JEOL FX-90Q spectrometer by using CCl_3F as an internal standard. ^1H NMR spectra were obtained on a Varian EM 360 spectrometer with tetramethylsilane as an internal standard. Mass spectra were determined with a Perkin-Elmer Hitachi RMU-6E spectrometer operating at an ionization potential of 17 eV. Elemental analyses were performed by Beller Laboratories, Göttingen, Germany, or at the University of Idaho.

Preparation of $CF_2CF_2CF_2CF_2S(O){=}NSi(CH_3)_3$. Into a 100-mL reaction vessel were condensed 2.23 mmol of $CF_2CF_2CF_2CF_2S(O){=}NH$, 8 mmol of $(CH_3)_3SiCl$, and 3 mmol of $(CH_3)_3N$ at −196 °C. The reaction mixture was gradually raised to 25 °C for 1 h. Purification by means of trap-to-trap distillation and subsequent gas chromatographic separation afforded $CF_2CF_2CF_2CF_2S(O){=}NSi(CH_3)_3$ in a yield of 70.9%. It is a colorless liquid with a boiling point of 99.6 °C from the equation $\log P_{torr} = 7.27 - 1636.3/T$. The molar heat of vaporization is 7.5 kcal, and the Trouton constant is 20.1 eu.

The ^{19}F NMR and ^1H spectral data are given in Table I. The mass spectrum shows a molecular ion and appropriate fragment ions. The infrared spectrum (capillary film) is as follows: 2965 (w), 1410–1490 (m, br), 1336 (m), 1300 (m), 1260 (m), 1234 (s), 1200 (m, sh), 1182 (vs), 1056 (w), 985 (s), 954 (s), 883 (w, sh), 856 (vs), 770 (w), 685 (w), 662 (w), 612 (w), 515–555 (w) cm^{-1}.

Anal. Calcd for $C_7F_8SNSiH_6$: C, 25.08; N, 4.18; H, 2.69. Found: C, 24.73; N, 4.28; H, 2.66.

Preparation of $CF_2CF_2CF_2CF_2S(O){=}NC(O)CF_3$. Into a 100-mL flask which contained 1 g of dry powdered NaF were condensed 2.06 mmol of $CF_2CF_2CF_2CF_2S(O){=}NH$ and 6 mmol of $CF_3C(O)F$ at −196 °C. After 8 h, the product was initially separated by trap-to-trap distillation. Subsequent gas chromatographic separation yielded pure $CF_2CF_2CF_2CF_2S(O){=}NC(O)CF_3$ in a yield of 50.5%. This compound is a colorless liquid having a boiling point of 100.1 °C from the equation $\log P_{torr} = 7.64 - 1776.4/T$. The molar heat of vaporization is 8.1 kcal, and the Trouton constant is 21.8 eu.

The ^{19}F NMR spectral data are given in Table I. The mass spectrum has no molecular ion, but shows *m/e* 290 $[M - CF_3]^+$ as the largest ion and other appropriate fragment ions. The infrared spectrum (capillary film) is as follows: 1650–1680 (br, s), 1347 (s), 1300 (s), 1150–1255 (vs), 1060 (m), 990 (vs), 955 (vs), 892 (w), 846 (m, sh), 830 (m), 772 (m), 739 (m), 676 (w), 642 (w), 612 (m), 536 (w), 502 (w) cm^{-1}.

Anal. Calcd for $C_6F_{11}SNO_2$: C, 20.06; N, 3.90. Found: C, 19.58; N, 4.13.

Preparation of $CF_2CF_2CF_2CF_2S(O){=}NCN$. Into a 100-mL reaction vessel were condensed 1.88 mmol of $CF_2CF_2CF_2CF_2S(O){=}NH$, 8 mmol of ClCN, and 4 mmol of $(CH_3)_3N$ at −196 °C. The reaction mixture was warmed gradually to 25 °C. The purification was conducted by trap-to-trap distillation using traps at −40 and −196 °C. The product was a colorless liquid which was mixed with small quantities of white sublimable solid. Purification by gas chromatography was unsuccessful due to its thermal instability above 25 °C. Therefore, the product was purified only by means of repeated trap-to-trap distillation to remove the white sublimable solid until the transparent colorless liquid $CF_2CF_2CF_2CF_2S(O){=}NCN$ was left (64.4%). It has a vapor pressure of ~1 torr at 25 °C.

The ^{19}F NMR spectral data are in Table I. The mass spectrum shows a molecular ion and appropriate fragment ions. The infrared spectrum (capillary film) is as follows: 2255 (vs), 2230 (vs) ($\nu_{C\equiv N}$), 1475 (w), 1456 (w), 1340 (vs) 1304 (s), 1255 (vs), 1230 (m, sh), 1215 (m, sh), 1186 (vs), 1058 (m), 987 (vs), 960 (ms), 873 (w), 818 (m), 795 (m, sh), 770 (w), 665 (w), 612 (w), 598 (w), 545 (m, sh), 532 (m), 482 (w), 450 (m) cm^{-1}.

Anal. Calcd for $C_5F_8SN_2O$: C, 20.83; N, 9.72. Found: C, 21.15; 10.00.

Preparation of $CF_2CF_2CF_2CF_2S(O){=}NAg$. Into a 100-mL reaction vessel which contained a 1.0 mmol of Ag_2O and 20 mL of benzene was condensed $CF_2CF_2CF_2CF_2S(O){=}NH$ (2.05 mmol) at −196 °C. The reaction vessel was shielded from light with aluminum foil, warmed to 25 °C, and agitated by using a magnetic stirrer for 8 h. A white gelatinous compound formed. The solvent and the unreacted imide were removed under dynamic vacuum, yielding a white solid of the silver salt.

(1) **Reaction with CH_3I.** Into a 100-mL reaction vessel which contained 1.3 mmol of $CF_2CF_2CF_2CF_2S(O){=}NAg$ was condensed 1.3 mmol of CH_3I at −196 °C. The reaction mixture was warmed gradually to 25 °C. The color of the reaction mixture changed to yellow-green. After 5 h, the product was separated by trap-to-trap distillation through a trap at −98 °C which retained the unreacted CH_3I (1.09 mmol) and a trap at −40 °C which retained $CF_2CF_2CF_2CF_2S(O){=}NCH_3$[2] (0.22 mmol, yield 16.8%).

(2) **Reaction with Cl_2.** Into a reaction vessel which contained 2.5 mmol of $CF_2CF_2CF_2CF_2S(O){=}NAg$ was condensed 3.4 mmol of Cl_2 at −196 °C. The reaction mixture was warmed gradually to 25 °C. After 1 h, the product was purified by trap-to-trap distillation through a trap at −40 °C which retained $CF_2CF_2CF_2CF_2S(O){=}NCl$ (1.77 mmol, 71.1%). This compound is a colorless liquid which solidifies at −40 °C.

The ^{19}F NMR spectral data are in Table I. The mass spectrum of this compound shows no molecular ion but shows *m/e* 262 $[M - Cl]^+$ as the largest ion and other appropriate fragment ions. The infrared spectrum (capillary film) is as follows: 1338 (ms), 1313 (vs), 1252 (s), 1186 (vs), 1074 (m), 1047(m), 987 (vs), 934 (s), 673 (w), 652 (w), 614 (w), 570 (w), 540 (w), 507 (m), 458 (w).

Anal. Calcd for C_4F_8SNOCl: C, 16.13; N, 4.71, Cl, 11.93. Found: C, 16.00; N, 4.92; Cl, 11.52.

Reaction of $CF_2CF_2CF_2CF_2S(O){=}NH$ with Cl_2 in the Presence of CsF. Into a 75-mL Hoke cylinder which contained 5 g of CsF were condensed 1.98 mmol of $CF_2CF_2CF_2CF_2S(O){=}NH$ and 2.5 mmol of Cl_2. The reaction mixture was warmed gradually to 25 °C. After 8 h, the product was separated by trap-to-trap distillation to give $CF_2CF_2CF_2CF_2S(O){=}NCl$ (78.8%).

Reaction of $CF_2CF_2CF_2CF_2S(O){=}NH$ with Elemental F_2. Into a 150-mL Hoke cylinder which contained 7 g of powdered KF were condensed 2.34 mmol of $CF_2CF_2CF_2CF_2S(O){=}NH$ and 2.4 mmol of F_2 at −196 °C. The reaction mixture was warmed to −78 °C over 2 h and then to 25 °C over an additional 2.5 h. The product was separated by trap-to-trap distillation. The first trap (−196 °C) contained mainly CF_4 and small amounts of SiF_4 and NF_3 (0.25 mmol). In the second trap (−98 °C), mainly $CF_2CF_2CF_2CF_2SO_2$ (0.36 mmol) was found. The third trap (−40 °C) was empty. In the last trap (−23 °C), a colorless solid (0.14 g) was obtained. The infrared spectrum of the solid showed the presence of $CF_2CF_2CF_2CF_2SO_2$ and $CF_2CF_2CF_2CF_2S(O){=}NH$. No evidence was found for the formation of $CF_2CF_2CF_2CF_2S(O){=}NF$.

Preparation of $CF_2CF_2CF_2CF_2S(O){=}NC(O)N{=}S(O)CF_2CF_2CF_2CF_2$. Into a 100-mL reaction vessel which contained 0.91 mL of 2.2 M *n*-BuLi–*n*-hexane solution (equivalent to 2.0 mmol of BuLi) and 2.0 mL ether was condensed 2.06 mmol of $CF_2CF_2CF_2CF_2S(O){=}NH$ at −196 °C. The reaction mixture was warmed slowly to 25 °C. After 30 min, the volatile compounds were removed under dynamic pumping, leaving a white solid of $CF_2CF_2CF_2CF_2S(O){=}NLi$. Onto this was condensed 1.0 mmol of $COCl_2$ at −196 °C, and the solution was warmed gradually to 25 °C. After 7.5 h, volatile compounds (unreacted $COCl_2$ and $CF_2CF_2CF_2CF_2S(O)NH$ formed as a result of the hydrolysis of the Li salt) were removed under dynamic vacuum, leaving a brown solid. This solid was rinsed with small aliquots of CH_2Cl_2, and the solution was evaporated to dryness to leave a brown solid. Under sublimation, a colorless solid, $CF_2CF_2CF_2CF_2S(O){=}NC(O)N{=}S(O)CF_2CF_2CF_2CF_2$, was obtained in a yield of 68.6%.

The ^{19}F NMR spectral data are in Table I. The mass spectrum shows a molecular ion and appropriate fragment ions. The infrared spectrum (KBr disk) is as follows: 1676 (ms) ($\nu_{C=O}$), 1300–1320 (s), 1255 (s), 1186 (vs), 1140 (m), 1098 (w), 1060 (w), 988 (s), 958 (m), 924 (m), 911 (m), 615 (w), 545 (w), 495 (w) cm^{-1}. Anal. Calcd for $C_9F_8S_2O_3N_2$: C, 19.57. Found: C, 19.35.

Photolysis of $CF_2CF_2CF_2CF_2S(O){=}NCl$. Into a 95-mL quartz vessel was condensed 1.77 mmol of $CF_2CF_2CF_2CF_2S(O){=}NCl$, and the solution was photolyzed by using a Hanovia utility UV lamp for 12 h at 25 °C. The volatile products were separated by trap-to-trap distillation using traps cooled at −196 and −98 °C. In the first trap, SOF_2 and Cl_2 were obtained (0.5 mmol). In the second trap, $ClCF_2CF_2CF_2CF_2Cl$ was found (0.6 mmol). The yellow material which remained in the bottom of the quartz vessel was rinsed out with small aliquots of CH_2Cl_2, and the solvent was removed to give a transparent yellow liquid (0.18 g). This compound had an irritating odor. No further purification was attempted.

The ^{19}F NMR spectrum contained four major resonance bands at $\phi = -132.3, -131.8, -117.2$, and -113.4. Among them, the bands at $\phi = -132.3$ and -117.2 are considered to be those of β-CF_2 and α-CF_2, respectively. The mass spectrum did not exhibit a molecular ion, but a peak at *m/e* 486 which may be $[M - 2F]^+$ is found. Other peaks have not been identified. The infrared spectrum (capillary film) is as follows: 1612 (m), 1405 (m), 1295–1340 (vs), 1235–1258 (s), 1170–1195 (vs), 1145 (ms, sh), 1090 (s), 1056 (ms), 985–992 (vs), 930 (s), 893 (w), 670 (w), 612 (w), 505–545 (w). The band at 1612 cm^{-1} does not support a bis(sulfoxyamide).

Anal. Calcd for $C_8F_{16}S_2O_2N_2$: C, 18.32; N, 5.34. Found: C, 18.19; N, 5.92.

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Registry No. $CF_2CF_2CF_2CF_2S(O){=}NSi(CH_3)_3$, 77589-40-3; $CF_2CF_2CF_2CF_2S(O){=}NC(O)CF_3$, 77589-41-4; $CF_2CF_2CF_2CF_2S(O){=}NCN$, 77589-42-5; $CF_2CF_2CF_2CF_2S(O){=}NCl$, 77589-43-6; $CF_2CF_2CF_2CF_2S(O){=}NC(O)N{=}S(O)CF_2CF_2CF_2CF_2$, 77589-44-7; $CF_2CF_2CF_2CF_2S(O){=}NAg$, 77589-45-8; $CF_2CF_2CF_2CF_2S{=}NLi$, 77589-46-9; $CF_2CF_2CF_2CF_2S(O){=}NH$, 77589-47-0; $CF_2CF_2CF_2CF_2S(O){=}NCH_3$, 77589-48-1; $(CH_3)_3SiCl$, 75-77-4; $CF_3C(O)F$, 354-34-7; ClCN, 506-77-4; Ag_2O, 20667-12-3; CH_3I, 74-88-4; Cl_2, 7782-50-5; $COCl_2$, 75-44-5.