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THE CHEMISTRY OF TRIFLUOROSULFINIC ACID AND ITS DERIVATIVES

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To Professor George H. Cady on his 70th birthday

SUMMARY

The preparation of NaSO₂CF₃, KSO₂CF₃ and AgSO₂CF₃ from HSO₂CF₃ and the corresponding carbonates is described. CF₃S(O)N $[Si(CH_3)_3]_2$ or CF₃S(O)NHSi(CH₃)₃ react with SOCl₂ to form CF₃S(O)N=S=O. A compound with two sulfur atoms in oxidation state +4. The reaction products of CF₃S(O)NCO with CH₃OH, CH₃COOH, (CH₃)₂NH, (C₂H₅)₂NH, CF₃S(O)NH₂ and CF₃SO₂NH₂ are reported. In contrast to N $[Si(CH_3)_3]_3$ the tin analog reacted with CF₃S(O)Cl to CF₃S(O)OSn(CH₃)₃. CF₃S(O)NHC(O)OCH₃ and PCl₅ gave CF₃S(O)NHC(O)CH₃ and not the substituted iso-cyanidemonochloride CF₃S(O)-N=C OCH₂.

In 1971 we developed an easy synthetic route for the preparation of perfluoroalkane sulfinic acids. We used perfluoroalkane sulfonicfluorides as starting materials and they were reduced to the corresponding sulfur (IV) compounds with hydrazine.

$$2CF_{3}SO_{2}F + 5N_{2}H_{4} \rightarrow 2CF_{3}S(0)O[N_{2}H_{5}] + 2N_{2} + 2[N_{2}H_{5}]F^{1}$$

The free acid is formed from the hydrazonium salt with concentrated sulfuric acid.

The trifluoromethane sulfinic acid reacts with the carbonates of sodium potassium and silver to yield CF_3SO_2Na ,

 $\begin{array}{l} {\rm CF_3SO_2K} \mbox{ and } {\rm CF_3SO_2Ag} \mbox{ respectively}^2. \mbox{ The silver salt is sensitive to light. Carbonates of Ba}^{2+} \mbox{ and Ca}^{2+} \mbox{ reacted as well} \\ \mbox{with } {\rm HSO_2CF_3} \mbox{ but no salts of the composition } {\rm Ba(SO_2CF_3)_2 \ or } {\rm Ca(SO_2CF_3)_2 \ could be \ isolated. \ Iminosulfur \ oxides \ are \ usually \ prepared \ from \ amides \ and \ thionyldichloride. \ By \ using \\ {\rm CH_3S(0)NH_2 \ as \ a \ starting \ material \ we \ were \ only \ able \ to \ isolate \ the \ acid \ chloride \ {\rm CF_3S(0)Cl}^{3,4}. \ {\rm CF_3S(0)N=S=0 \ was \ obtained \ by \ reacting \ {\rm CF_3S(0)N[Si(CH_3)_3]_2 \ or \ {\rm CF_3S(0)N=S=0 \ was \ obtained \ by \ reacting \ {\rm CF_3S(0)N[Si(CH_3)_3]_2 \ or \ {\rm CF_3S(0)N=S=0 \ with \ S(0)Cl_2. \end{array}} \end{array}$

$$CF_{3}S(0)N[Si(CH_{3})_{3}]_{2} + SOCl_{2} \rightarrow CF_{3}S(0)N=S=0 + 2(CH_{3})_{3}SiCl$$

$$CF_{3}S(0)N-Si(CH_{3})_{3} + SOCl_{2} \rightarrow CF_{3}S(0)N=S=0 + (CH_{3})_{3}SiCl + HCl$$

 ${\rm CF}_3{\rm S}({\rm O}){\rm N=S=0}$ is a distillable yellow liquid with boiling point of $48^{\rm O}{\rm C}/15$ Torr.

The silicon containing compounds were formed by the reaction of $CF_3S(O)Cl$ and $N[Si(CH_3)_3]_3$ or $HN[Si(CH_3)_3]_2$. In comparison to the protonated molecules they are much more stable and therefore they can be isolated without decomposition.

 $CF_3S(0)N[Si(CH_3)_3]_2$ is a colourless liquid which was not obtained in pure state. In contrast to $N[Si(CH_3)_3]_3$, $N[Sn(CH_3)_3]_3$ and excess of $CF_2S(0)Cl$ gave $CF_3S(0)OSn(CH_3)_3$, which can be better prepared from the free acid and $(CH_3)_3SnCl^4$.

Recently we described the synthesis of $CF_3S(O)NCO$. We were interested in the trifluoromethane substituted urethanes. We had shown that the fluorosulfonylcompounds gave the following reaction products⁵:

$$FSO_2^{N-C-OR + PCl_5} \rightarrow FSO_2^{N=C} + POCl_3 + HCl_3$$

By fluorination of FSO₂N= C^{C1} with sodium fluoride, the migration of the R-group to the nitrogen atom under formation of a carbo-nylfluoride unit was observed. This work was extended to include the reactions of CF₃S(0)NCO.

$$CF_3S(0)NCO + CH_3OH \rightarrow CF_3-S(0)-N-C(0)OCH_3$$

$$CF_{3}S(0)NCO + R_{2}NH \longrightarrow CF_{3}-S(0)-N-C(0)NR_{2}$$

$$R = CH_{3} \text{ and } C_{2}H_{5}$$

$$CF_{3}S(0)NCO + CH_{3}COOH \longrightarrow CF_{3}-S(0)-N-C(0)CH_{3} + CO_{2}$$

When the same procedure is used to study the reaction of PCl_5 with $CF_3-S(0)-N-C(0)OCH_3$, the following reaction products were isolated:

$$CF_3S(0) - N - C(0)CH_3$$
, HC1, POCl₃

There was no evidence that the desired compound $CF_3S(0)N=C_{OCH_3}^{C1}$ was among the products.

The reaction of $CF_3S(O)NCO$ and $CF_3S(O)NH_2$ as well as $CF_3SO_2NH_2$ has been studied.

In both cases the symmetric bisubstituted urea was obtained. We were not able to prepare the bisubstituted urea from $CF_3S(0)NCO$ and $CF_3SO_2NH_2$. Both compounds were refluxed in benzene but under these conditions no reaction was observed.

The new compounds described in this article are summarized in the table.

TABLE

Compounds with a trifluoromethanesulfinic group

		% yield	m.p/(b.p) ⁰ C
<u></u>	<u>,</u>		
1	CF ₃ S(0)ONa	98	350
2	CF3S(0)OK	96	350
3	CF ₃ S(0)OAg	81	140 (dec.)
4	CF ₃ S (O) NSO	52	(48/15 Torr)
5	CF3S (0) NHC (0) OCH3	96	(51/0.1 Torr)
6	$CF_{3}S(0)$ NHC(0) N(CH ₃) ₂	94	(113/0.1 Torr)
7	$CF_3S(0)$ NHC(0) N(C_2H_5)	95	93
8	CF ₃ S(0)NHC(0)CH ₃	90	50
9	CF ₃ S(0)NHCONH(0)SCF ₃	95	152
10	$CF_{3}^{s}S(0)$ NHCONHO ₂ SCF ₃	93	155

EXPERIMENTAL

General

All reactions were carried out in well dried Pyrex flasks under an atmosphere of nitrogen.

Infrared spectra were recorded using a Perkin-Elmer infrared spectrophotometer model No. 157. Liquids as capillary films with sodium chloride windows, solids in nujol mull or as potassium bromide pellets.

Nuclear magnetic resonance spectra were recorded using a Varian XL-100 spectrometer. Tetramethylsilane and trichloro-fluormethane were used as external standards.

Preparation of the compounds 1, 2 and 3

To a mixture of 0.1 mole of Na_2CO_3 (1), K_2CO_3 (2) or Ag_2CO_3 (3) and 50 ml of dry ethanol was added 0.2 mole CF_3SO_2H using a dropping funnel. The solvent was removed under vacuum and the product was dried under vacuum.

$CF_3S(0)NSO 4:$

To 0.05 mole $CF_3S(0)NHSi(CH_3)_3$ at $15^{\circ}C$ was added dropwise 0.05 mole $SOCl_2$. The addition was carried out over a period of 5 hrs. The product was purified by distillation under water pump vacuum.

¹⁹F-NMR: $\delta_{CF_3} = 76.35$ ppm. IR: 1243 sh, 1200 vs, 1160 s, 1110 vs, 1093 sh, 755 cm⁻¹ w. calcd. % C 6.7 F 31.8 N 7.8 S 35.7 found % 6.7 32 7.8 35.6

CF₃S(O)NHCOOCH₃ 5:

To 0.1 mole $CF_3S(0)NCO$ was added 0.1 mole CH_3OH using a dropping funnel. The flask was maintained at O^OC . The product was purified by distillation under vacuum.

¹⁹F-NMR: $\delta_{CF_3} = 77.43 \text{ ppm}$ ¹H-NMR: $\delta_{NH} = -9.0 \text{ ppm}$, $\delta_{CH_3} = -3.99 \text{ ppm}$. IR: 3180 s, 2950 w, 1740 vs, 1453 vs, 1410 s, 1300 s, 1242 s, 1200 vs, 1160 vs, 1120 vs, 1067 m, 942 m, 850 m, 770 m, 750 cm⁻¹ w. calcd. % C 18.8 H 2.1 F 29.8 N 7.3 S 16.7 found % 18.9 2.1 30.0 7.3 16.7

$CF_3S(0)$ NHCON (CH₃) 2 6:

To a solution of 0.05 mole $CF_3S(0)NC0$ in 50 ml benzene at O^OC was condensed 0.05 mole $HN(CH_3)_2$. Then the mixture was allowed to warm up to room temperature. The solvent was removed under vacuum and the product was purified by distillation under vacuum.

> ¹⁹F-NMR: $\delta_{CF_3} = 76.52$ ppm. ¹H-NMR: $\delta_{NH} = -9.0$ ppm, $\delta_{CH_3} = -3.05$ ppm.

IR: 3150m, 2950 m, 2800 w, 1748 w, 1670 vs, 1600 m, 1500 s, 1438 s, 1270 w, 1195 vs, 1147 vs, 1118 vs, 1018 947 s, 904 m, 830 m, 755 cm⁻¹ m. calcd. % C 23.5 H 3.4 F 27.9 N 13.7 S 15.7

found % 25.3 3.9 25.9 14.8 14.6

CF₃S(0)NHCON(C₂H₅)₂7:

To a solution of 0.05 mole $CF_3S(0)NC0$ in 30 ml benzene at O^OC was added 0.05 mole $HN(C_2H_5)_2$ in 10 ml benzene. A white solid was formed which was filtered, washed with benzene and dried under vacuum.

¹⁹F-NMR:
$$\delta_{CF_3} = 75.49 \text{ ppm}.$$

¹H-NMR: $\delta_{\rm NH} = -7.53 \text{ ppm}, \ \delta_{\rm CH_3} = -1.17 \text{ ppm t},$ $\delta_{\rm CH_2} = -3.36 \text{ ppm q}.$ IR (KBr): 3100 s, 2980 m, 1645 vs, 1490 sh, 1463 s, 1450 s, 1390 m, 1186 m, 1195 vs, 1150 vs, 1122 s, 1090 m, 973 m, 940 m, 888 m, 780 m, 750 cm⁻¹ m. calcd. % C 31.0 H 4.7 F 24.5 N 12.1 S 13.8 found % 31.1 4.7 24.5 12.1 13.8

CF3S(O)NHCOCH38:

To 0.1 mole $CF_3S(0)NCO$ was added 0.1 mole CH_3COOH . The flask was maintained at $50^{\circ}C$. After 1 h a white solid was formed. The solid was purified by sublimation under vacuum.

¹⁹F-NMR: $\delta_{CF_3} = 76.83 \text{ ppm}.$ ¹H-NMR: $\delta_{NH} = -7.42 \text{ ppm}, \delta_{CH_3} = -3.78 \text{ ppm}.$ IR (KBr): 3220 m, 2800 w, 1720 s, 1440 s, 1190 vs, 1150 vs, 1085 vs, 980 m, 917 m, 840 s, 740 cm⁻¹ w. calcd. % C 20.5 H 2.3 F 32.5 N 8.0 S 18.3 found % 20.3 2.4 32.4 8.1 18.3

(CF₃S(O)NH)₂CO 9:

0.05 mole $CF_3S(0)NH_2$ and 0.05 mole $CF_3S(0)NC0$ in 30 ml benzene were heated under reflux. After a short time a white solid is formed which was filtered, washed with benzene and dried under vacuum.

¹⁹F-NMR: $\delta_{CF_3} = 76.63$ ppm.

¹H-NMR: $\delta_{NH} = -9.94$ ppm.

IR (nujol mull): 3200 s, 1720 m, 1672 s, 1198 vs, 1140 sh, 1110 s, 1090 sh, 800 m, 738 s, 700 cm⁻¹m. calcd. % C 12.3 H 0.7 F 39.1 N 9.6 S 21.9 found % 12.2 0.8 39.3 9.7 21.7 CF₃S(O)NHCONHSO₂CF₃ 10:

To a solution of 0.07 mole $CF_3S(0)NH_2$ in 20 ml benzene at O^OC was added 0.07 mole CF_3SO_2NCO . A white solid was formed which was filtered, washed with benzene and dried under vacuum.

> ¹⁹F-NMR: $\delta_{CF_3SO} = 76.48 \text{ ppm}, \ \delta_{CF_3SO_2} = 79.67 \text{ ppm}.$ ¹H-NMR: $\delta_{NH} = -10.78 \text{ ppm}.$ IR (nujol mull): 3200 s, 1700 s, 1380 s, 1200 vs, 1120 vs, 1042 m, 1022 s, 818 m, 735 m. calcd. % C 11.7 H 0.7 F 37.0 N 9.1 S 20.8 found % 11.7 0.8 36.7 9.1 20.7

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