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SOME FLUORINATED HETEROCYCLIC AND ACYCLIC DERIVATIVES OF CHLOROCARBONYLSULFENYL CHLORIDE

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SUMMARY

For the first time, fluorinated oxathialones, polyfluoroalkylchlorothioformates, chlorocarbonylpolyfluoroalkylsulfenate esters, a chlorocarbonylhexafluoroisopropylidenimino sulfenate, and a 5-trifluoromethyl-2-oxo-1,3,4-oxathiazole were synthesized by reacting chlorocarbonylsulfenyl chloride with $R_fC(O)CH_2C(O)R'$ (R_f = CF_3; R' = CF_3, OC_2H_5), R_fOH, $R_fO^-Li^+$ (R_f = CF_3CH_2, $(CF_3)_2CH$), $(CF_3)_2C{=}N^-Li^+$ and $CF_3C(O)NH_2$. Perfluorosuccinic acid and mercury(II) trifluoroacetate with ClC(O)SCl gave their respective anhydrides.

INTRODUCTION

Many derivatives of chlorocarbonylsulfenyl chloride (ClC(O)SCl) [1] have found practical applications as insecticides, soil softening agents and as protective agents against herbicide damage to plants [2-4]. Not surprisingly, hard nucleophiles, such as ROH [5] and R_2NH [5,6], attack at the harder carbon center, and softer nucleophiles, such as RSH [5,7] and $>C{=}C\overset{-}{-}$, react at the softer sulfur center. Chlorocarbonylsulfenyl chloride is a useful reagent for ring closure reactions. A number of substituted 1,3-oxathiol-2-ones [8] and 5-substituted-2-oxo-1,3,4-oxathiazoles [5,9] were synthesized by this route.

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In this paper are reported the first fluoro-substituted oxathiolones and oxathiazole-2-ones as well as a number of other fluorine-containing derivatives of chlorocarbonylsulfenyl chloride.

RESULTS AND DISCUSSION

Chlorocarbonylsulfenyl chloride is a bifunctional molecule with two electrophilic centers at sulfur and at carbon. Therefore, nucleophilic attack may occur at either center to give rise to linkage isomers.

Several types of nucleophiles and reaction conditions were selected for this study.

Reaction with R_fOH (R_f = CF_3CH_2, $(CF_3)_2CH$)

$$R_fOH + ClC(O)SCl \xrightarrow{B} \underset{(1,\ 3)}{R_fOSC(O)Cl} + \underset{(2,\ 4)}{R_fOC(O)SCl}$$

B = py, Et_3N

$$R_fO^-Li^+ + ClC(O)SCl \longrightarrow \underset{(1,\ 3)}{R_fOSC(O)Cl}$$

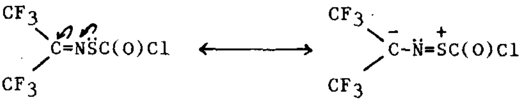
R_f = CF_3CH_2 (1, 2), $(CF_3)_2CH$ (3, 4)

The base plays an important role in these reactions since it activates both the sulfur and carbon centers and facilitates the formation of both carboxylic and sulfenate esters [10].

On the other hand, $R_fO^-Li^+$ selectively attacked at the sulfur at low temperature and gave only a single isomer for each lithiated alcohol, 1 and 3 [11]. While 3 is moderately stable at 25 °C, it does decompose to sulfur, chloro(hexafluoroisopropyl)carbonate and other unidentified materials. The two compounds, 1 and 3, were characterized in the usual manner, i.e., infrared, NMR and mass spectral analysis as well as elemental analyses for stable compounds. Sulfenate esters lacked a band that could be assigned to ν_{S-Cl} in the 600 cm^{-1} region but retained a band attributed to ν_{C-Cl} at ~ 820-830 cm^{-1}. The reverse was the case for the carboxylic esters. Mass spectra contained molecular ions at m/e 194 for 1 and 2 and at 262 for 3 and 4.

Reaction with hexafluoroisopropylidenimine, $(CF_3)_2C{=}N^-Li^+$

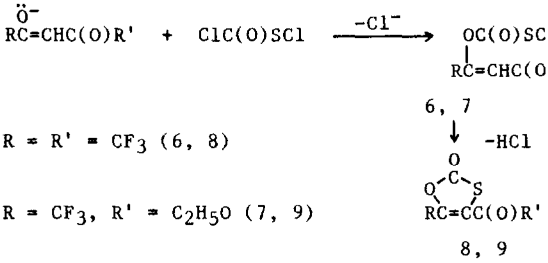
Hexafluoroisopropylidenimine lithium, $(CF_3)_2C{=}\bar{N}\overset{+}{Li}$, reacted selectively at the sulfur atom in the temperature range between -135 to 0 °C in ether and gave only chlorocarbonylhexafluoroisopropylidenimino sulfenate, $(CF_3)_2NSC(O)Cl$, 5. The carbonyl stretching frequency at 1815 cm^{-1} is in essential agreement with the SC(O)Cl functional group. $\nu_{C=N}$ at 1335 cm^{-1} has shifted by 45 cm^{-1} to lower energy than its precursor which suggests that the following resonance occurs.



Additionally, the C-Cl stretching frequency is observed at 807 cm^{-1}. The mass spectral fragmentation pattern also supports the formation of 5 only.

Reactions with $RC(O)CH_2C(O)R'$ (R = R' = CF_3; R = CF_3, R' = C_2H_5O)

Trifluoroacetylacetates exhibit a keto-enol equilibrium, and in the presence of a base the enolate is the predominant form. Both the carbon and the sulfur centers of ClSC(O)Cl are attacked by the enolate in a stepwise fashion, viz.,



R = R' = CF_3 (6, 8)

R = CF_3, R' = C_2H_5O (7, 9)

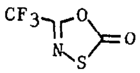
Compound 8 is a pale pink liquid, and it has uv absorption bands at 294 (t=3774), 221 (ε = 11020), and 218 (ε = 10977) nm. The first two result from n→π* and π→π* transitions in the enone system. Compound 6 was isolated as a yellow liquid which absorbs in the uv spectrum at 221 nm. It slowly changed to 8 on standing at 25 °C. In their infrared spectra, compounds 8 and 9 each have two carbonyl stretching frequencies at

1740 cm^{-1} due to -SC(O)O- and at 1794 cm^{-1} and 1722 cm^{-1}, that are assigned to $CF_3C(O)$- and $C_2H_5OC(O)$, respectively. In the ^{19}F NMR, 8 has two CF_3 resonances at ϕ -63 ($CF_3C=$) and ϕ -75 [$CF_3C(O)$], while 9 has one CF_3 resonance at ϕ -62.3. Mass spectral fragmentation patterns of 8 and 9 support the proposed structures. In the mass spectrum of compound 9, the base peak is m/e 142. This rearranged fragment, ($C_2H_5OC(O)CF_3^+$), resulted from a γ migration of the CF_3 group similar to a 1,3-sigmatropic shift [12,13].

Reaction with trifluoroacetamide

Trifluoroacetamide exists as a tautomeric mixture in the presence of a base where the reactive form is the enolimine. This species apparently attacked in a concerted fashion at both the carbon and sulfur centers with the imine attacking the latter center.

$ClC(O)SCl + CF_3C(=NH)OH \xrightarrow[-HCl]{py}$



Reactions with mercury(II) trifluoroacetate and tetrafluorosuccinic acids

The reactions of chlorocarbonylsulfenyl chloride with mercury(II) trifluoroacetate and tetrafluorosuccinic acid in the presence of pyridine gave sulfur, carbon dioxide and the respective acid anhydrides in essentially quantitative yield.

EXPERIMENTAL

Materials. Reagents were purchased as indicated: chlorocarbonylsulfenyl chloride (Fairfield), hexafluoroacetylacetone (Columbia Organic), perfluorosuccinic acid (Pierce), trifluoroacetamide and 2,2,2-trifluoroethanol (Aldrich), hexafluoroisopropanol and ethyl trifluoroacetoacetate (PCR). Hexafluoroisopropylidenimine [14] and mercury(II) trifluoroacetate [15] were prepared according to literature methods.

General Procedures

Varian 2290 uv, Perkin-Elmer 599B infrared, JEOL FX90Q Fourier transform NMR ($CFCl_3$ or $CDCl_3$) and VG 7070HS mass spectrometers were used for uv, infrared, NMR and mass spectral studies. Gases and volatile liquids were handled in Pyrex vacuum apparatus equipped with a Heise Bourdon tube gauge. Elemental analyses were performed by Beller Mikroanalytisches Laboratorium, Göttingen, F.R.G.

Reactions of chlorocarbonylsulfenyl chloride with a) 2,2,2-trifluoroethanol or hexafluoroisopropanol, and b) their lithium salts

a) Each alcohol (4 mmol) was condensed with pyridine (4 mmol) and methylene chloride (~ 10 mL) at -196 °C. An adduct was formed by stirring at 25 °C for 15 m. Chlorocarbonylsulfenyl chloride (4 mmol) was distilled into the mixture which was then stirred for 0.5 h at 35-40 °C. The products and some CH_2Cl_2 were retained at -60 °C. The latter was removed by fractional evaporation. Because attack occurs at either sulfur or carbon by each alcohol, two isomers that are not separable by bulb-to-bulb distillation techniques are formed. The yield of the ethanol derivative is ~ 35% of which 70% is $CF_3CH_2OC(O)SCl$, 2. The latter was separated from $CF_3CH_2OSC(O)Cl$, 1, by fractional evaporation. The isomeric mixture of products from $(CF_3)_2CHOH$ was not separated (45% yield).

b) Butyl lithium (4 mmol) was transferred to a 50 mL reaction vessel in an anhydrous N_2 atmosphere. Each alcohol (5 mmol) was added at -196 °C and the mixture was allowed to warm very slowly to 25 °C. After 0.5 h at 25 °C, the hexane and any excess alcohol were removed under dynamic vacuum. The lithium salt was dissolved in dry ether (5 mL) and $ClC(O)SCl$ (4 mmol) was added at -196 °C. The mixture was placed in a bath at -135 °C and the temperature allowed to rise very slowly to 0 °C. The mixture was stirred quickly and distilled at once. Each alcohol derivative stopped at -40 °C. The solvent was removed by fractional evaporation at 0 °C. $CF_3CH_2OSC(O)Cl$, 1, (74%) was stable at

25 °C; however, $(CF_3)_2CHOSC(O)Cl$, 3, (80%) decomposed to sulfur and other unidentified materials.

Spectral data for $CF_3CH_2OSC(O)Cl$, 1, are as follows: Infrared (cm^{-1}) -2960 (vw), 1787 (vs), 1282 (vs), 1180 (vs), 1130 (m), 1050 (s), 960 (m), 840 (vs), 810 (m), 600 (vw); NMR - ^{19}F ϕ -73.76 (tr) (J_{F-H} = 8 Hz); ^1H δ 4.3 (q); EI Mass - M^+, 194, 13.5%.

Spectral data for $CF_3CH_2OC(O)SCl$, 2, are as follows: Infrared (cm^{-1}) -2980 (vw), 1785 (m), 1420 (w), 1330 (ms), 1292 (vs), 1250 (s), 1185 (vs), 1130 (m), 850 (vw), 540 (vw,br), 410 (w); NMR - ^{19}F ϕ -72.85 (tr) (J_{F-H} = 8 Hz); ^1H δ 4.5 (q); EI Mass - M^+, (194, 0.5%); 127 ($CF_3CH_2OC(O))^+$, 21.9%); 83 ($CF_3CH_2O^+$, 100%).

Anal. Calcd. for $C_3ClF_3H_2O_2S$: C, 18.56; H, 1.03; S, 16.49. Found: C, 19.56; H, 1.40; S, 15.86.

Spectral data for $(CF_3)_2CHOSC(O)Cl$, 3, are as follows: Infrared (cm^{-1}) -2990 (vw), 2870 (vw), 1810 (s), 1790 (s), 1380 (ms), 1305 (s), 1270 (s), 1245 (s), 1215 (s), 1120 (vs), 1070 (vw), 820 (s); NMR - ^{19}F ϕ -72.74 (d) (J_{F-H} = 5.4 Hz); ^1H δ 5.54 (septet); EI Mass - M^+, (262, 6.8%); $(CF_3)_2CHOSCO^+$ (227, 0.4%); $CH(CF_3)_2{}^+$ (151, 35.7%); $ClC(O)S^+$ (95, 24.3%). The two isomers were not separated. The infrared spectrum of the mixture showed a carbonyl peak at 1784 cm^{-1}. For $(CF_3)_2CHOC(O)SCl$, 4, NMR - ^{19}F ϕ -72.33 (d) (J_{H-F} = 5.86 Hz); ^1H δ 5.8 (sept); EI Mass - 195 [$(CF_3)_2CHOCO^+$, 25%] plus other smaller fragments observed for $(CF_3)_2CHOSC(O)Cl$.

Reaction of chlorocarbonylsulfenyl chloride with hexafluoroisopropylidenimine

Four mmol each of $(CF_3)_2C{=}NH$ and butyllithium were condensed at -196 °C and allowed to warm very slowly to 25 °C. The hexane solvent was replaced by anhydrous ether (5 mL) that dissolved the white solid $(CF_3)_2C{=}NLi$. To the ether solution at -196 °C was added $ClC(O)SCl$ (4 mmol). The mixture was allowed to warm slowly to and remain at 20 °C for 20 m. The volatile materials were collected in a trap at -45 °C. The last traces of ether were removed by fractional evaporation. The yield of $(CF_3)_2C{=}NSC(O)Cl$, 5, was ~ 55%. Its vapor pressure at 25 °C is ~ 5 torr. Spectral data for $(CF_3)_2C{=}NSC(O)Cl$ are as follows:

Infrared (cm^{-1}) - 1815 (s), 1335 (s), 1260 (vs), 1200 (vs), 985 (m), 807 (vs); ^{19}F NMR - ϕ -67.7 (s); EI mass - M^+ (259, 0.5%); 196 ($(CF_3)_2CNS^+$, 38.3%); 69 (CF_3^+, 60.9%); 63 ($ClCO^+$, 100%).

Anal. Calcd. for C_4F_6ClNOS: C, 18.53; Cl, 13.51; N, 5.41; S, 12.36. Found: C, 19.11; Cl, 14.70; N, 5.38; S, 12.72.

Reaction of chlorocarbonylsulfenyl chloride with hexafluoroacetylacetone

Equimolar amounts (8 mmol) of hexafluoroacetylacetone and ClC(O)SCl were held at reflux (80 °C) for 2-3 h after which the temperature was raised to 100 °C for 2 h. The materials that were volatile at 25 °C under static vacuum (ClC(O)SCl, HCl, $CF_3C(O)CH_2C(O)CF_3$) were removed. A pale pink material was collected in a trap at -60 °C under dynamic vacuum (65% yield). (The pale yellow material that slowly converted to the pink liquid when it was allowed to stand for ~ two months also stopped in a trap at -60 °C.)

The pale yellow liquid, *O*-[4,4,4-trifluoro-3-oxo-1-(trifluoromethyl)-1-butenyl] (chlorothio)formate, 6, had infrared bands as follows (cm^{-1}): 1780 (s), 1740 (vs), 1600 (w), 1330 (s), 1165 (vs), 1030 (s), 900 (ms), 730 (ms), 635 (vw), 530 (vvw). The NMR spectra were: ^{19}F ϕ -63 (s) and ϕ -75 (s); ^1H δ 6.15 (s). The ultraviolet spectrum contained a band at 222 nm.

Anal. Calcd. for $C_6ClF_6O_3S$: C, 23.92; F, 37.87. Found: C, 25.12; F, 37.6.

The pale pink liquid, 4-(trifluoroacetyl)-5-(trifluoromethyl)-1,3-oxathiol-2-one, 8, has an infrared spectrum as follows (cm^{-1}): 1794 (vs), 1740 (s), 1600 (ms), 1330 (s), 1180 (vs,br), 1140 (s,br), 1000 (ms), 940 (ms), 880 (vw). The ^{19}F NMR spectrum contained bands at ϕ -63.01 (s) and ϕ -75.13 (s). The mass spectrum contained peaks at M^+ (266, 18.4%); 197 (M^+-69, 21.5%); 141 ($C_3F_3SO^+$, 79.3%); 113 (CF_3CS^+, 26.9%); 97 (CF_3CO^+, 13.6%); 69 (CF_3, 100%). The ultraviolet spectrum contained bands at 294, 221 and 218 nm.

Anal. Calcd. for $C_6F_6O_3S$: C, 27.07; F, 42.86; S, 12.03. Found: C, 27.43; F, 42.1; S, 12.03.

Reaction of chlorocarbonylsulfenyl chloride with ethyl trifluoroacetoacetate

Equimolar amounts (8 mmol) of $ClC(O)SCl$ and $CF_3C(O)CH_2(CO)OC_2H_5$ were mixed and slowly raised to 80 °C (3 h) and then to 110-120 °C where the mixture was held at reflux for 3.5 h. After cooling to 25 °C all the volatile materials ($ClC(O)SCl$, $CF_3C(O)CH_2C(O)OC_2H_5$, HCl) were removed under dynamic vacuum. The involatile materials were removed by heating the reaction vessel and collecting any materials at -60 °C in a "U" tube under dynamic vacuum. The last traces of impurities were removed under static vacuum while heating the "U" tube (~ 70 °C) and transferring the more volatile materials into a trap at -196 °C (yield ~ 65%).

The liquid infrared spectrum for ethyl 5-(trifluoromethyl)-2-oxo-1,3-oxathiole-4-carboxylate, 9, was as follows (cm^{-1}): 2990 (w), 1772 (vs), 1740 (vs), 1635 (ms), 1375 (ms), 1340 (vs), 1312 (s), 1270 (s), 1205 (vs), 1160 (vs), 1090 (s), 1010 (s), 860 (w), 840 (vw), 770 (w), 730 (w), 640 (w). The NMR spectra were: ^{19}F ϕ -62.26 (s); ^1H δ 1.9 (tr, J_{H-F} = 7.3 Hz), δ 4.9 (q); EI Mass - M^+ (242, 28.4%); 142 ($C_2H_5OC(O)CF_3^+$, 100%); 141 ($C_2H_4OC(O)CF_3^+$, 48.7%); 122 ($C_2H_4OC(O)CF_2^+$, 16.3%); 69 (CF_3^+, 63.9%).

Anal. Calcd. for $C_7H_5F_3O_4S$: C, 34.71; F, 23.55; H, 2.07. Found: C, 34.16; F, 25.5; H, 2.22.

Reaction of chlorocarbonylsulfenyl chloride with $Hg(OC(O)CF_3)_2$

To mercury(II) trifluoroacetate (4 mmol) that was dried under dynamic vacuum was added $ClC(O)SCl$ (6 mmol). The reaction mixture was stirred at 50-55 °C for 3 h. Using trap-to-trap distillation, $ClC(O)SCl$ was found in a trap at -45 °C, $CF_3C(O)OC(O)CF_3$ at -70 °C and CO_2 in -196 °C. The yield of pure anhydride was 30%.

Reaction of chlorocarbonylsulfenyl chloride with perfluorosuccinic acid

Perfluorosuccinic acid (2 mmol) was dissolved in 10 mL of ether to which 4.5 mmol of pyridine was then added. A white crystalline solid remained when the ether and pyridine were removed. To this was added ClC(O)SCl (2 mmol) and the mixture was warmed to 25 °C. Perfluorosuccinic anhydride and CO_2 were trapped at -70 °C and -196 °C, respectively. The anhydride was further purified by fractional evaporation under static vacuum (~ 100% yield based on CO_2 formed). The infrared spectrum of perfluorosuccinic anhydride was as follows (cm^{-1}): 1840 (vs), 1795 (s), 1370 (s), 1280 (w), 1190 (vs), 1050 (vs), 900 (vs), 800 (s), 740 (vw), 620 (w). The ^{19}F NMR spectrum has a band at ϕ -124.5 (s).

Reaction of chlorocarbonylsulfenyl chloride with trifluoroacetamide

Trifluoroacetamide (10 mmol) and ClC(O)SCl (10 mmol) were dissolved in 30 mL of ether. Pyridine (20 mmol) was added slowly with constant stirring under a N_2 atmosphere, and the mixture was stirred overnight. Pure white crystals of 5-trifluoromethyl-2-oxo-1,3,4-oxathiazole were obtained by sublimation under static vacuum at 25 °C (yield 15%). The gas phase infrared spectrum was as follows (cm^{-1}): 1823 (vs), 1813 (vs), 1698 (ms), 1633 (s), 1373 (vs), 1238 (vs), 1193 (vs), 1158 (vs), 978 (vs), 868 (vs), 800 (ms), 738 (s), 643 (ms), 588 (w), 543 (vw), 458 (vw). The ^{19}F NMR spectrum has a band at ϕ -69.6 (s). The mass spectrum (m/e): 171 (M^+, 39.8%), 143 (M^+-CO, 57.1%), 127 (M^+-CO_2, 8.5%), 115 (CF_3NS^+, 28.1%), 69 (CF_3^+, 100%), 46 (NS^+, 74.3%).

Anal. Calcd. for $C_3F_3NO_2S$: N, 8.19; S, 18.71. Found: N, 8.16; S, 18.47.

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