POLYFLUORO-TERT-ALKYLSULFENYL CHLORIDES

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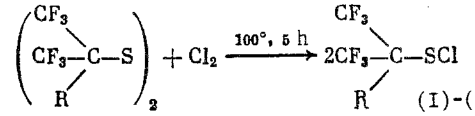
Primary polyfluoroalkylsulfenyl chlorides have been rather extensively studied [1]. Only α-chlorocarbonylhexafluoroisopropylsulfenyl chloride has been described among sulfenyl chlorides with a branched polyfluoroalkyl group at the sulfur atom. This chloride was prepared by the reaction of hexafluorodimethylketene with sulfur monochloride [2]. In the present work, syntheses are given for other sulfenyl chlorides with branched groups and several of their properties are reported.

Bis-polyfluoroalkyl disulfides with nonafluoro-tert-butyl, chlorooctafluoro-tert-butyl, α-methoxycarbonylhexafluoroisopropyl, and α-methoxycarbonyl-α-cyanotrifluoroethyl groups [2-5] were used as the starting compounds. The chlorination of the first three disulfides proceeds smoothly to give sulfenyl chlorides (I)-(III) with yields above 70%.

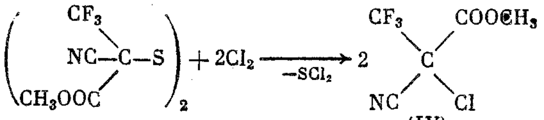


(I)-(III)

$R = CF_3$(I), $ClCF_2$(II), $COOCH_3$(III).

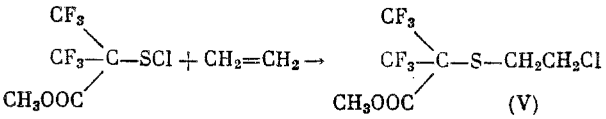
Products (I)-(III) are liquids with the light yellow color characteristic for polyfluoroalkylsulfenyl chlorides, which are resistant to heating and hydrolysis. These compounds have a sharp, irritating odor.

Bis(α-methoxycarbonyl-α-cyanotrifluoroethyl) disulfide is desulfurated under the conditions for the preparation of (I)-(III) and gives methyl ester (IV) in high yield.



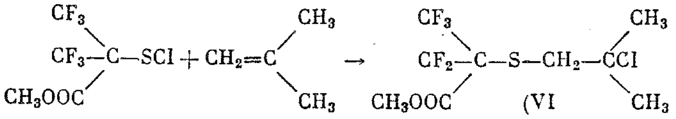
(IV)

Sulfenyl chlorides (I)-(III) have much lower reactivity than primary polyfluoroalkylsulfenyl chlorides [1]. Thus, sulfenyl chloride (III) does not react with ethylene in the absence of solvent although it slowly forms sulfide (V) in acetonitrile.



(V)

The reaction of sulfenyl chloride (III) with 2-methylpropene proceeds with the same difficulty and sulfide (VI) is obtained in high yield only upon heating to 120°C.



(VI

Sulfenyl chloride (III) reacts much more readily with cycloalkenes, especially with cyclopentene and cycloheptene. The addition in this case proceeds at 20°C and is markedly accelerated in the presence of CF_3CO_2H and leads to sulfides (VII)-(IX) in 70-85% yield. Sulfide (X) is formed as readily from sulfenyl chloride (I).

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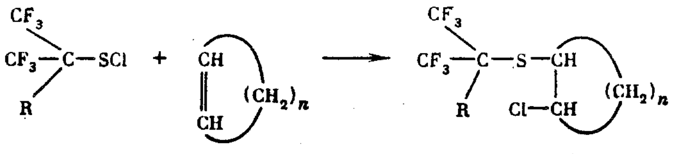
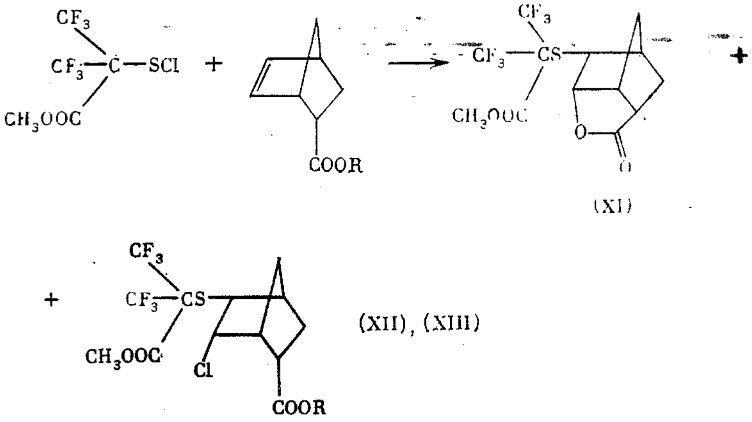


(VII) - (X)

R = CH_3OOC, $n = 3$(VII); $n = 4$(VIII); $n = 5$(IX); R = CF_3, $n = 3$(X).

At 20°C, (III) reacts at a significant rate with norbornene-2-carboxylic acid and its methyl ester. Lactone (XI) is formed in these reactions along with addition products (XII) and (XIII). In contrast to norbornene-2-carboxylic acid, vinylacetic acid does not react with (III) even at 150°C.

These results indicate that the differences in the reactivity of primary and branched polyfluoroalkylsulfenyl chlorides relative to alkenes are only quantitative in nature.



(XI)

(XII), (XIII)

R = CH_3(XII), H(XIII).

EXPERIMENTAL

The ^1H and ^{19}F NMR spectra were taken on a Bruker WP-200 spectrometer at 200 and 188 MHz, respectively. The chemical shifts (δ, ppm) are given relative to HMDS (internal standard) and CF_3CO_2H (external standard) for pure compounds or their 50% solutions in CCl_4. The IR spectra (ν, cm^{-1}) were taken on a UR-20 spectrometer.

Nonafluoro-tert-butylsulfenyl Chloride (I). A sample of 10.0 g bis(nonafluoro-tert-butyl) disulfide was added to a glass ampul and 2.8 g chlorine was added at −78°C. The ampul was sealed, slowly warmed to 20°C and then to 100°C. The mixture was maintained at this temperature for 5 h and cooled. The ampul was opened and the contents were fractionated to give 8.6 g (75.4%) sulfenyl chloride (I), bp 78°C, n_D^{25} 1.3335. ^{19}F NMR spectrum: −12.7 s (CF_3). Found, %: C 16.46; Cl 12.15; F 59.51; S 11.53. C_4ClF_9S. Calculated, %: C 16.75; Cl 12.39; F 59.68; S 11.17.

Chlorooctafluoro-tert-butylsulfenyl chloride (II) was obtained by analogy to (I) from 10.7 g bis(chlorooctafluoro-tert-butyl) disulfide and 2.85 g chlorine. The product yield was 8.75 g (72%), bp 115°C, n_D^{20} 1.3870 ^{19}F NMR spectrum (J, Hz): −26.95 sept (2F, $J_{F-F} = 12.0$), −14.65 t (6F, $J_{F-F} = 12.0$). Found, %: C 15.71; Cl 23.16; F 50.22; S 10.68. $C_4Cl_2F_8S$. Calculated, %: C 15.84; Cl 23.43; F 50.16; S 10.56.

α-Methyoxycarbonylhexafluoroisopropylsulfenyl chloride (III) was obtained by analogy to (I) from 40.35 g bis(α-methoxycarbonylhexafluoroisopropyl) disulfide and 11.9 g chlorine. The product yield was 34.72 g (75%), bp 75°C (50 mm), n_D^{25}1.3872. ^{19}F NMR spectrum: −13.6 s (CF_3). PMR spectrum: 3.95 s (CH_3). IR spectrum: 1760 (C=O) Found, %: C 21.59; H 1.12; F 41.09; S 11.66. $C_5H_3ClF_6O_2S$. Calculated, %: C 21.70; H 1.08; F 41.23; S 11.57.

Methyl ester of 2-cyano-2-chloro-3,3,3-trifluoropropionic acid (IV) was obtained analogously to (I) from 10.0 g bis(α-methoxycarbonyl-α-cyanotrifluoroethyl) disulfide and 3.6 g chlorine by maintaining the ampul at 100°C for only 1 h. The product yield was 9.0 g (88.5%), bp 56°C (32 mm), n_D^{25} 1.3695. ^{19}F NMR spectrum: −5.33 s (CF_3). PMR spectrum:

4.06 s (CH_3). IR spectrum: 2265 (C=N), 1785 (C=O). Found, %: C 29.51; H 1.41; Cl 18.09; F 28.47. $C_5H_3ClF_3NO_2$. Calculated, %: C 29.77; H 1.49; Cl 17.62; F 28.29.

α-Methoxycarbonylhexafluoroisopropyl-2-chloroethyl Sulfide (V). A sample of 7.7 g sulfenyl chloride (III) in 5 ml acetonitrile was placed in a steel test tube equipped with a needle valve. The test tube was cooled with liquid nitrogen and evacuated. A sample of 1.2 g ethylene was condensed and the test tube was left for five days at 20°C. The unreacted ethylene was removed and the residue was fractionated to give 2.3 g (27.1%) sulfide (V), bp 93-94°C (9 mm), n_D^{20} 1.4202. ^{19}F NMR spectrum: −12.31 s (CF_3). PMR spectrum: 3.95 s (CH_3), 3.68 m (CH_2Cl), 3.20 m (CH_2S). IR spectrum: 1770 (C=O). Found, %: C 27.21; H 2.27; F 37.28; S 10.66. $C_7H_7ClF_6O_2S$. Calculated, %: C 27.59; H 2.30; F 37.44; S 10.51.

α-Methoxycarbonylhexafluoroisopropyl-2-chloroisobutyl Sulfide (VI). A mixture of 6.0 g sulfenyl chloride (III) and 1.8 g isobutylene was heated in a glass ampul at 120°C for 1 h and cooled. The ampul was opened and the contents were fractionated to give 5.1 g (70.8%) sulfide (VI), bp 58°C (1 mm), n_D^{22} 1.4123. ^{19}F NMR spectrum: −12.99 s (CF_3). PMR spectrum: 3.86 s (3H), 3.15 s (2H), 1.65 s (6H). IR spectrum: 1775 (C=O). Found, %: C 32.17; H 3.21; F 34.40; S 9.78. $C_9H_{11}ClF_6O_2S$. Calculated, %: C 32.48; H 3.31; F 34.29; S 9.62.

α-Methoxycarbonylhexafluoroisopropyl-2-chlorocyclopentyl Sulfide (VII). A sample of 2.0 g cyclopentene was added with stirring and cooling to 7.5 g sulfenyl chloride (III). The mixture was maintained at 20°C for 30 h and fractionated to give 7.95 g (85.5%) sulfide (VII), bp 72°C (1 mm), n_D^{25} 1.4309. ^{19}F NMR spectrum: −12.4 s (CF_3). PMR spectrum: 4.16 m (1H), 3.9 s (3H), 3.56 m (1H), 1.50-2.6 m (6H). IR spectrum: 1750 (C=O). Found, %: C 34.58; H 3.23; F 33.21; S 9.12. $C_{10}H_{11}ClF_6O_2S$. Calculated, %: C 34.83; H 3.19; F 33.09; S 9.29.

α-Methoxycarbonylhexafluoroisopropyl-2-chlorocyclohexyl Sulfide (VIII). a) A sample of 0.34 g CF_3CO_2H was added with stirring and cooling to a mixture of 8.2 g sulfenyl chloride (III) and 5.0 g cyclohexene. The mixture was maintained at 20°C for 15 h and fractionated to give 9.1 g (85.6%) sulfide (VIII), bp 84°C (1 mm), n_D^{20} 1.4386. ^{19}F NMR spectrum (CCl_4, J, Hz): −12.64 q (CF_3, J_{F-F} = 11.4), −12.04 q (CF_3, J_{F-F} = 11.4). PMR spectrum (CCl_4): 4.15 m (1H), 3.85 s (3H), 3.28 m (1H), 1.2-2.38 m (8H). IR spectrum: 1760 (C=O). Found, %: C 36.72; H 3.65; F 32.69; S 8.98. $C_{11}H_{13}ClF_6O_2S$ Calculated, %: C 36.82; H 3.63; F 31.80; S 8.93.

b) A sample of 2.5 g cyclohexene was added to a solution of 5.7 g sulfenyl chloride (III) in 2 ml ether. The mixture was maintained for six days at 20°C and fractionated to give 4.74 g (64.1%) sulfide (VIII).

α-Methoxycarbonylhexafluoroisopropyl-2-chlorocycloheptyl sulfide (IX) was obtained from 5.5 g sulfenyl chloride (III) and 2.0 g cyclopentene analogously to sulfide (VII). The product yield was 5.28 g (71.3%), bp 105°C (1 mm), n_D^{22} 1.4471. ^{19}F NMR spectrum (CCl_4): −12.43 m (CF_3). PMR spectrum (CCl_4): 4.32 m (1H), 3.88 s (3H), 3.47 m (1H), 1.30-2.30 m (10H). IR spectrum: 1760 (C=O). Found, %: C 38.50; H 3.95; F 30.42; S 8.67. $C_{12}H_{15}ClF_6 \cdot O_2S$. Calculated, %: C 38.66; H 4.03; F 30.60; S 8.59.

Nonafluoro-tert-butyl-2-chlorocyclopentyl sulfide (X) was obtained from 3.8 g sulfenyl chloride (I) and 0.9 g cyclopentene analogously to (VII) with maintenance of the mixture for 40 h at 20°C. The product yield was 2.72 g (58.0%), bp 69°C (10 mm), n_D^{20} 1.3982. ^{19}F NMR spectrum: −12.96 s (CF_3). PMR spectrum: 4.34 m (1H), 3.83 m (1H), 1.55-2.33 m (6H). Found, %: C 30.12; H 2.19; F 48.38; S 9.21. $C_9H_8ClF_9S$. Calculated, %: C 30.47; H 2.26; F 48.24; S 9.03.

Methyl Ester of 5-(α-Methoxycarbonylhexafluoroisopropylthio)-6-chlorobicyclo[2.2.1]heptane-2-carboxylic Acid (XII) and 4(α-Methoxycarbonylhexafluoroisopropylthio)-6-oxatricyclo[3.2.1.1^{3,8}]nonan-7-one (XI). A solution of 5.8 g sulfenyl chloride (III) and 3.2 g methyl ester of bicyclo[2.2.1]hept-5-ene-2-carboxylic acid in 2 ml ether was maintained for 72 h at 20°C and fractionated to give 7.2 g (85%) of an 8:7 mixture of bicycloheptane (XII) and tricyclononanone (XI), bp 125-130°C (1 mm), n_D^{25} 1.4551. ^{19}F NMR spectrum of (XII): −12.4 m (CF_3). PMR spectrum of (XII): 4.10-4.20 m (4H), 3.9 s (3H), 3.6 s (3H), 2.70-3.30 m (2H), 2.30-2.60 m (2H), 1.30-2.20 m (4H). ^{19}F NMR spectrum of (XI) (J, Hz): −12.9 q (CF_3, J_{F-F} = 12), −11.98 q (CF_3, J_{F-F} = 12). PMR spectrum of (XI): 4.68 m (1H), 3.99 s (3H), 3.23 m (1H), 2.95 m (1H), 2.35-2.63 m (2H), 1.55-2.18 m (4H). The crystals precipitated upon standing, were washed with pentane and dried to give 1.35 g (17%) tricyclononanone (XI), mp 66°C. Found, %: C 41.31; H 3.13; S 8.46. $C_{13}H_{12}F_6O_4S$. Calculated, %: C 41.27; H 4.17; S 8.47.

5-(α-Methoxycarbonylhexafluoroisopropylthio)-6-chlorobicyclo[2.2.1]heptane-2-carboxylic Acid (XIII) and (XI). A solution of 10.4 g sulfenyl chloride (III) and 5.2 g bicyclo[2.2.1]-hept-5-ene-2-carboxylic acid in 5 ml ether was maintained for 48 h at 20°C and fractionated to give 9.22 g (61.4%) of a 7:5 mixture of acid (XIII) and tricyclononanone (XI), bp 160-165°C (1 mm), n_D^{25} 1.4593. ^{19}F NMR spectrum of (XIII): −12.5 m (CF_3). PMR spectrum of (XIII): 11.79 br s (1H), 4.14-4.50 m (1H), 3.89 s (3H), 1.24-3.34 m (8H). The precipitated crystals were washed with pentane and dried to give 1.56 g (11%) tricyclonanone (XI), mp 66°C.

CONCLUSIONS

Polyfluoroalkylsulfenyl chlorides with tert-alkyl groups were obtained and these compounds were found to be similar to sulfenyl chlorides with primary polyfluoroalkyl groups in electrophilic addition at the C=C bond and are distinguished only in somewhat reduced reactivity.

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