DEHYDROHALOGENATION OF FLUORINATED SULFENYL CHLORIDES. SYNTHESIS AND PROPERTIES OF PERFLUOROISOBUTYLENE SULFIDE*

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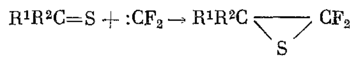
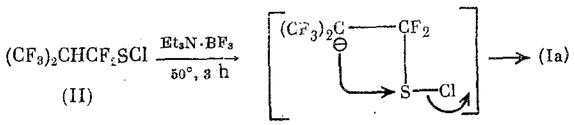
Perfluorothiiranes are a difficultly accessible and practically unstudied class of organic fluorine compounds. The method known for their synthesis, the reaction of perfluorothiocarbonyl compounds with difluorocarbene generated from perfluoropropylene, yields the compounds mixed with other products, and they must be purified by preparative GLC [2, 3, 4]:



(I)

$R^1=R^2=CF_3$ (a); $R^1=F$, $R^2=Cl$ (b); $R^1=CF_3$, $R^2=F$ (c); $R^1=R^2=F$ (d).

In the present work the dehydrochlorination of fluorinated sulfenyl chlorides (SC) has been investigated for the synthesis of fluorothiiranes. We find that 2-hydroperfluoroisobutanesulfenyl chloride (II) is smoothly dehydrochlorinated when heated with the $Et_3N \cdot BF_3$ complex in a sealed ampul, to form thiirane (Ia):



(II)

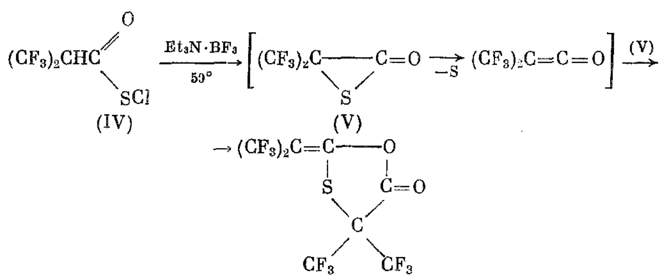
Compound (II) is obtained by chlorination of the adduct of perfluoroisobutylene and diethyldithiophosphoric acid (IIIa), or benzyl mercaptan (IIIb):

$$(CF_3)_2CHCF_2S{-}R \xrightarrow{Cl_2} (II)$$

(III)

$R=(EtO)_2P(S)$ (a), $PhCH_2$ (b)

2-Hydrohexafluorosiobutyrylsulfenyl chloride (IV) is dehydrochlorinated under similar conditions. However, the compound bis(trifluoromethyl)-α-thiolactone (V), that is apparently formed is unstable and partly loses S to form bis(trifluoromethyl)ketene. The latter forms, by cycloaddition to (V), an oxathiolanone.



(IV) (V) (VI)

When bis(trifluoromethyl)ketene is added to the reaction mixture, the yield of the oxathiolanone (VI) increases; this confirms the proposed reaction scheme. The structure of (VI) was demonstrated by IR, ^{19}F NMR, and mass spectra, and by conversion to the ester (VII)

* Previous communication, see [1].

† Deceased.

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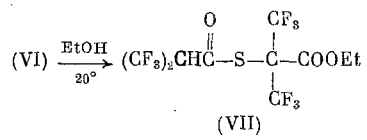
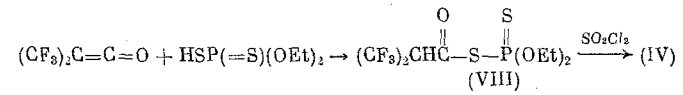


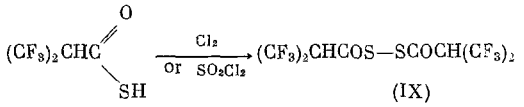
(VII)

The starting SC (IV) was obtained by the addition of diethyldithiophosphoric acid to bis(trifluoromethyl)ketene and chlorination of the adduct (VIII):



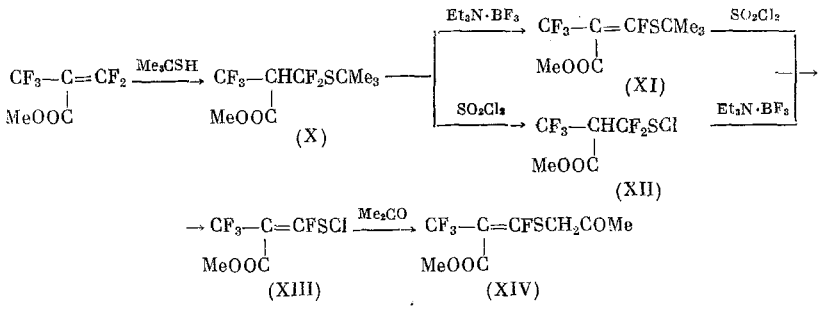
(VIII)

An attempt to obtain (IV) by the procedure for synthesizing trifluoroacetylsulfenyl chloride [5] yielded the disulfide (IX):



(IX)

In contrast to (II) and (IX), compound XII under the influence of $Et_3N \cdot BF_3$ underwent not dehydrochlorination, but dehydrofluorination to form the unsaturated SC, compound (XIII). The latter was obtained by a countersynthesis, by chlorination of the unsaturated ester (XI); for further confirmation of its structure it was converted to the sulfide (XIV) by reaction with acetone:

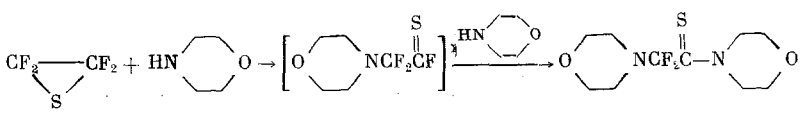


(X) (XI) (XII) (XIII) (XIV)

Compounds (XI) and (XII) were obtained by addition of tert-butyl mercaptan to methyl perfluoromethacrylate and treatment of adduct (X) with $Et_3N \cdot BF_3$ and sulfuryl chloride, respectively.

These results permit us to conclude that the course of the dehydrohalogenation of fluorinated SC depends very strongly on SC structure. In some cases 1,3-dehydrohalogenation yields a three-membered heterocycle containing sulfur; in others there is exclusively 1,2-dehydrohalogenation to form α, β-unsaturated SC.* 1,3-Dehydrohalogenation is an intramolecular sulfenylation of the carbanion generated by the deprotonation of the fluorocarbanion of sulfenyl chlorides is known [7, 8]. It should be noted that cyclization of sulfenyl chlorides to thiirane is a new reaction for this class of compounds that is so thoroughly known [9].

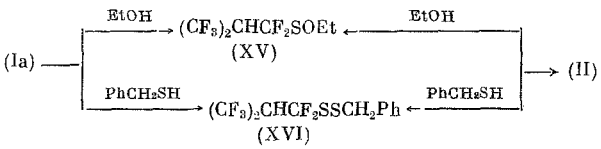
Of the perfluorothiiranes, only perfluoroethylene sulfide has been studied previously (Id). Using the reaction of (Id) with morpholine it was shown [2] that this compound is attacked by nucleophiles at the C atom, i.e., like the unfluorinated analogs [10]:



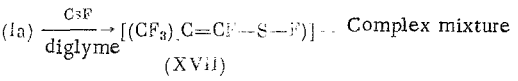
(Id)

As has been shown, perfluoroisobutylene sulfide (Ia) is attacked by nucleophiles at the S atom, not the C atom. Thus Ia reacts with ethanol and benzyl mercaptan to yield the ethyl ester of the sulfenic acid (XV), and the disulfide (XVI), respectively. The structures of the products were confirmed by spectral data and by the countersynthesis from SC (II):

* For the synthesis and properties of the fluorinated unsaturated SC, see [6].

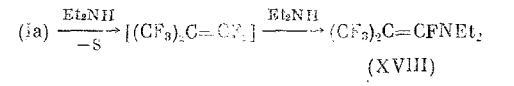


In the presence of CsF, (Ia) is converted to a complex mixture of products, probably by disproportionation of the intermediate sulfenyl fluoride (XVII):

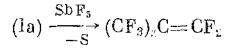


Data are available concerning the low stability of sulfenyl fluorides [11].

Like the thioglycidic ester CH_2——$CHCOOMe$ [12], perfluoroisobutylene sulfide (Ia) loses sulfur by the action of diethylamine, and the resulting perfluoroisobutylene reacts with Et_2NH to give the substituted vinyl product (XVIII):



Desulfurization of (Ia) also occurs by the action of SbF_5:



EXPERIMENTAL

^{19}F NMR spectra (84.6 MHz) and ^1H spectra (60 MHz) (δ, ppm) were obtained on Perkin Elmer R-32 and Perkin Elmer R-12 spectrometers with CF_3COOH and TMS internal standards. IR spectra were obtained on a UR-20 spectrometer. Purity of materials was monitored by GLC on a LKhM-8MD apparatus, model 3, column of 20% QF on Chromatone. Mass spectra were obtained on a Varian MAT CH-8 apparatus (70 eV); m/z and the proposed assignment are given.

Perfluoroisobutylene Sulfide (Ia). A mixture, 17.4 g, of 80% (II) and 20% 1,3,3,3-tetrafluoro-2-trifluoromethylpropenesulfenyl chloride was heated with 17.4 g of $Et_3N \cdot BF_3$ in a glass ampul for 3 h at 50°C. The volatile products were separated in vacuum (3 mm) and distilled. There was obtained 8.9 g (60%) of Ia, bp 44-46°C (cf. [4]). Found: F 65.44; S 13.75%; mol.wt. 231.976. C_4F_8S. Calculated: F 65.49; S 13.82%; mol. wt. 231.959. Mass spectrum (ions with > 15% intensity): 232 (M^+), 213 ($M^+ - F$), 181 ($M^+ - SF$), 163 ($M^+ - CF_3$), 144 ($M^+ - CF_4$), 113 ($M^+ - C_2F_5$), 69 (CF_3^+), 63 (SCF^+). ^{19}F NMR spectrum: −11.6 t $(CF_3)_2$, 27.7 hept (CF_2), $J_{FF} = 9.4$ Hz.

2-Hydroperfluoroisobutanesulfenyl Chloride (II). (a) To 13.3 g (38 mmoles) of (IIIa) (obtained by the method of [13]) was added 10.2 g (76 mmoles) of SO_2Cl_2 dropwise with stirring and cooling to ~ 10°C. The mixture was held for 30 min until gas evolution finished. The products were vacuum distilled (110 mm) with heating to 100°C, into a trap at −78°C. Distillation yielded 6.3 g (62%) of II, bp 93-95°C. Found: C 18.35; H 0.47; F 56.80; S 11.92%. C_4HF_8SCl. Calculated: C 17.85; H 0.37; F 56.60; S 11.91%. PMR spectrum: 3.9 t hept (CH). ^{19}F NMR spectrum: 2.0 oct (CF_2), −15.3 t.d (CF_3), $J_{CF_2-H} = J_{CF_2CF_3} = 11.3$, $J_{CF_3-H} = 7.5$ Hz.

(b) A mixture, 27.4 g, containing 80% of (IIIb) and 20% of 1-benzylthioperfluoro-2-methyl-1-propene (obtained according to [6]), was treated at 20°C with a stream of Cl_2 until the exothermic reaction was finished. The reaction products were separated in vacuum (4 mm) at 50°C. Redistillation yielded 17.4 g of a mixture with bp 85-95°C; it consisted of 80% of (II), which was identified by ^{19}F NMR of (II) obtained by method (a), and 20% of 1,3,3,3-tetrafluoro-2-trifluoromethylpropenesulfenyl chloride, which was identical by ^{19}F NMR with that obtained according to [6].

2-Bis(trifluoromethyl)methylene-4,4-bis(trifluoromethyl)-1,3-oxathiolan-5-one (VI). (a) A mixture of 3.0 g (12 mmoles) of (IV) and 2.1 g (12 mmoles) of $Et_3N \cdot BF_3$ was heated under reflux for 2 h at 50°C. The reaction products were removed in vacuum at 2 mm at 100°C into a trap at −78°C. Redistillation yielded 1.2 g (51%) of (VI), bp 55-56°C (50 mm). Found: C 24.78; F 58.87; S 8.63%. $C_8F_{12}O_2$. Calculated: C 24.74; F 58.76;

S 8.25%. Mass spectrum: 388 (M^+), 369 ($M^+ - F$), 325 ($M^+ - FCO_3$), 182 ($C_3F_6S^+$), 178 ($C_4F_6O^+$), 159 ($C_4F_5O^+$), 113 ($C_2F_3S^+$), 69 (CF_3^+). IR spectrum (ν, cm^{-1}): 1650 (C=C), 1860 (C=O). ^{19}F NMR spectrum: −8.6 s $(CF_3)_2$, −17.8 q (CF^1_3), −8.7 q (CF^2_3), ratio of intensities 2:1:1; $J_{CF^1_3-CF^2_3} = 7.5$ Hz.

(b) A mixture of 6.7 g (27 mmoles) of (IV), 6.8 g (40 mmoles) of $Et_3N \cdot BF_3$, and 7.8 g (40 mmoles) of bis(trifluoromethyl)ketene was heated in a glass ampul for 2 h at 50°C. The reaction products were removed in vacuum (2 mm) at 100°C into a trap at −78°C. Redistillation yielded 3.8 g of (VI), bp 55-56°C (50 mm), identical by GLC and ^{19}F NMR with that obtained by method (a).

Ethyl Ester of 2-Trifluoromethyl-2-[bis(trifluoromethyl)-thioacetoxy]-3,3,3-trifluoropropionic Acid (VII). A mixture of 3.2 g (8 mmoles) of (VI) and 4 ml of abs. EtOH was kept for 24 h at ~ 20°C, washed with water, and extracted with ether. The ether extract was dried with $MgSO_4$ and distilled. There was obtained 2.6 g (72%) of the ester (VII), bp 95-96°C (25 mm), which crystallized on standing. Found: C 27.65; H 1.41; F 52.42; S 7.57%. $C_{10}H_6F_{12}SO_3$. Calculated: C 27.66; H 1.39; F 52.51; S 7.37%. IR spectrum (ν, cm^{-1}): 1740, 1770 (C=O). PMR spectrum (in CCl_4): 1.5 t (Me), 4.3 m (CH_2, CH), $J_{CH_3-CH_2} = 6.7$ Hz. Ratio of intensities 1:1. ^{19}F NMR spectrum (in CCl_4): −12.7 s (CF_3), −4.0 d (CF_3), $J_{FH} = 7.5$ Hz.

S-(2-Hydrohexafluoroisobutyryl)-O,O'-diethyldithiophosphate (VIII). To a solution of 18.0 g (96 mmoles) of diethyldithiophosphoric acid in 30 ml of abs. ether was added 18.3 g (102 mmoles) of bis(trifluoromethyl)-ketene with stirring and cooling to ~ 10°C. The mixture was kept for 1 h at 20°C, the solvent and low-boiling products were removed in vacuum (20 mm), and the residue was distilled. There was obtained 29.8 g (85%) of phosphate (VIII), bp 96-98°C (2 mm). Found: C 26.39; H 3.16; F 31.55; S 17.15; P 8.91%. $C_8H_{11}F_6PS_2O_3$. Calculated: C 26.37; H 3.02; F 31.31; S 17.58; P 8.51%. IR spectrum (ν, cm^{-1}): 1730 (C=O). PMR spectrum: 1.4 t (Me), 4.3 m (CH_3, CH), $J_{CH_3-CH_2} = 6.7$ Hz. Ratio of intensities 1:1. ^{19}F NMR spectrum: −14.2 d (CF_3) $J_{FH} = 7.5$ Hz.

2-Hydrohexafluoroisobutyrylsulfenyl Chloride (IV). To 19.2 g (52 mmoles) of (VIII) was added 7.1 g (52 mmoles) of SO_2Cl_2 dropwise with stirring and cooling to 0°C. The mixture was kept at ~ 20°C until gas evolution finished. The low-boiling products were removed in vacuum (30 mm). The reaction flask was then connected through a reflux condenser to a U-tube cooled to −78°C, wherein the products boiling at 50°C (2 mm) were collected. Redistillation yielded 2.6 g (20%) of (IV), bp 62-64°C (80 mm), which crystallized on standing. Found: C 19.40; H 0.36; F 46.10; S 13.33%. C_4HF_6SOCl. Calculated: C 19.47; H 0.41; F 46.24; S 12.98%. IR spectrum (ν, cm^{-1}): 1730 (C=O). PMR spectrum: 4.3 h (CH). ^{19}F NMR spectrum: −13.3 d, $J_{FH} = 7.5$ Hz.

2-Hydrohexafluoroisobutyryl Disulfide (IX). To 2.6 g (19 mmoles) of SO_2Cl_2 was added 2.1 g (9 mmoles) of α-hydrohexafluorothiolisobutyric acid (obtained according to [14]) dropwise at ~ 10°C. After the exothermic reaction had cooled, the mixture was heated at 80°C until gas evolution finished, and the low-boiling products were removed in vacuum. There was obtained 1.1 g (53%) of the disulfide (IX), mp 65-66°C (in sealed capillary). Found: C 22.81; H 0.48; F 54.05; S 15.26%. $C_8H_2F_{12}S_2O_2$. Calculated: C 22.74; H 0.47; F 54.02; S 15.16%. IR spectrum (ν, cm^{-1}), broad band with maximum at 1740 (C=O). PMR spectrum (in ether): 4.9 hept (CH). ^{19}F NMR spectrum (in ether): −13.8 d (CF_3), $J_{FH} = 7.5$ Hz. (IX) was also obtained by the reaction of α-hydrohexafluorothioisobutyric acid with Cl_2 at −78°C.

1-tert-Butylthio-1,1,3,3,3-pentafluoro-2-carbomethoxypropane (X). A mixture of 11.3 g (60 mmoles) of methyl perfluoromethacrylate, 5.7 g (60 mmoles) of tert-butyl mercaptan, and 10 ml of N-methylpyrrolidone was heated under a reflux condenser for 10 min at 50°C. Low boiling materials were removed in vacuum (20 mm). The residue was washed with water, and the organic layer was dried with $MgSO_4$ and distilled. There was obtained 10.1 g (61%) of (X), bp 62-64°C (3 mm). Found: C 39.14; H 4.69; S 11.17%. $C_9H_{13}F_5SO_2$. Calculated: C 38.57; H 4.66; S 11.44%. PMR spectrum: 1.45 s (Me_3C), 3.8 m (CH, MeO), ratio of intensities 9:4. ^{19}F NMR spectrum: −5.3 (F_A), −8.4 (F_B), −15.1 t.d (CF_2), $J_{F_A-F_B} = 218.0$, $J_{F_A-CF_3} = J_{F_B-CF_3} = J_{F_A-H} = 11.0$, $J_{F_B-H} = 9.1$, $J_{CF_3-H} = 7.5$ Hz.

1-tert-Butylthio-1,3,3,3-tetrafluoro-2-carbomethoxypropene (XI). A mixture of 12.2 g (44 mmoles) of (X) and 11.4 g (68 mmoles) of $Et_3N \cdot BF_3$ was heated under a reflux condenser for 1 h at 70°C. Distillation yielded 6.4 g (57%) of (XI), bp 71-73°C (2 mm) as a mixture of 85% cis and 15% trans isomers. Found: C41.19; H 4.61; F 28.81; S 11.95%. $C_9H_{12}F_4SO_2$. Calculated: C 41.53; H 4.61; F 29.23; S 12.30%. IR spectrum (ν, cm^{-1}): broad band with maximum at 1720 (C=O). PMR spectrum: 1.45 s (Me_3C), 3.65 s (MeO), ratio of intensities 3:1. ^{19}F NMR spectrum: cis isomer: −13.3 q (CF), −20.2 d (CF_3), $J_{FF} = 24.4$ Hz; trans isomer: −16.9 q (CF), −21.3 d (CF_3), $J_{FF} = 14.0$ Hz.

1,1,3,3,3-Pentafluoro-2-carbomethoxypropanesulfenyl Chloride (XII). To 4.3 g (15 mmoles) of (X) was added 6.2 g (45 mmoles) of SO_2Cl_2 dropwise with stirring and cooling to ~ 10°C. The mixture was kept for 30 min until gas evolution had finished. The low-boiling materials were driven off in vacuum (20 mm) and the residue was distilled. The fraction with bp 38-52°C (4 mm) (3.2 g) was practically pure (XII). Redistillation yielded pure (XII), bp 41-43°C (4 mm). Found: C 23.85; H 1.80%. $C_5H_4F_5SO_2Cl$. Calculated: C 23.22; H 1.56%. PMR spectrum: 3.8 s (MeO), 4.2 m (CH), ratio of intensities 3:1. ^{19}F NMR spectrum: 2.8 (F_A), −2.2 (F_B), −14.7 t.d (CF_3), $J_{F_A-F_B} = 218.0$, $J_{F_A-CF_3} = 13.2$, $J_{F_B-CF_3} = J_{F_B-H} = 9.4$, $J_{CF_3-H} = 7.5$, $J_{F_A-H} = 11.3$ Hz.

1,3,3,3-Tetrafluoro-2-carbomethoxypropenesulfenyl Chloride (XIII). (a) To 2.0 g (7.6 mmole) of (XI) was added 3.0 g (22 mmoles) of SO_2Cl_2 dropwise with stirring and cooling to ~ 10°C. The mixture was kept for 30 min until gas evolution had finished. The low-boiling materials were driven off in vacuum (20 mm), and the residue was distilled. There was obtained 1.3 g (71%) of (XIII), bp 52-54°C (1 mm). Found: C 25.45; H 1.57%. $C_5H_3F_4SO_2Cl$. Calculated: C 25.17; H 1.26%. IR spectrum (ν, cm^{-1}): 1660, 1730 (C=C, C=O). PMR spectrum: 3.7 s (MeO). ^{19}F NMR spectrum: −19.1 m, −21.6 m.

(b) A mixture of 2.2 g (8.5 mmoles) of (XII) and 2.2 g (13 mmoles) of $Et_3N \cdot BF_3$ was heated for 2 h under a reflux condenser; then the temperature was raised from 50 to 80°C. Distillation yielded 1.5 g (74%) of product with bp 52-54°C (1 mm), which by GLC and ^{19}F NMR was identical with (XIII) obtained by method (a).

1,3,3,3-Tetrafluoro-2-carbomethoxypropenyl-2'-oxopropyl Sulfide (XIV). A mixture of 1.6 g (6.7 mmoles) of (XIII) and 4 ml of abs. acetone was held for 30 min at ~ 20°C. The low-boiling materials were driven off in vacuum (20 mm) and the residue was distilled. There was obtained 1.5 g (86%) of (XIV), bp 122-124°C (2 mm), mp 57-58°C. Found: C 36.50; H 2.85; F 28.75; S 11.71%. $C_8H_8F_4SO_3$. Calculated: C 36.92; H 3.08; F 29.23; S 12.31%. IR spectrum (ν, cm^{-1}): broad band with maxima at 1690, 1710, 1730 (C=C, C=O). PMR spectrum (in C_6H_6): 1.3 s (Me), 2.7 d (CH_2), 3.0 s (MeO), $J_{HF} = 2.7$ Hz. ^{19}F NMR spectrum (in C_6H_6): −14.9 q.d (CF), −21.1 d (CF_3), $J_{FF} = 30.0$ Hz.

Ethyl-1,1,3,3,3-Pentafluoro-2-trifluoromethylpropyl Sulfenate (XV). (a) A mixture of 5.2 g (22 mmoles) of (Ia) and 1.0 g (22 mmoles) of abs. ethanol was kept at ~ 20°C for 7 days. Distillation yielded 3.8 g (61%) of (XV), bp 55-58°C (65 mm). Found: C 26.03; H 2.14; F 54.28%. $C_6H_6F_8SO$. Calculated: C 25.91; H 2.17; F 54.65%. PMR spectrum: 1.1 t (Me), 3.9 m (CH_2, CH), $J_{CH_3-CH_2} = 7.3$ Hz, ratio of intensities 1:1. ^{19}F NMR spectrum: 8.0 (CF_2), oct, −5.1 t.d (CF_3), $J_{CF_2-H} = J_{FF} = 11.3$, $J_{CF_3-H} = 8.5$ Hz.

(b) A mixture of 1.3 g (5 mmoles) of (II) and 1 ml of abs. ethanol was heated under reflux for 6 h at 70°C. The mixture was poured into water and the organic layer was dried with $MgSO_4$. Distillation yielded 0.8 g (57%) of (XV), bp 55-58°C (65 mm), which by GLC and NMR was identical with XV obtained by method (a).

Benzyl 1,1,3,3,3-Pentafluoro-2-trifluoromethylpropyl Disulfide (XVI). (a) A mixture of 3.0 g (13 mmoles) of (Ia), 1.5 g (12 mmoles) of benzyl mercaptan, and 10 ml of abs. ether was kept at ~ 20°C for 6 days. After the solvent was removed, distillation yielded 1.4 g (30%) of (XVI), bp 90-92°C (2 mm). Found: F 42.30%. $C_{11}H_8F_8S_2$. Calculated: F 42.67%. PMR spectrum: 3.7 m (CH_2, CH), 7.1 s (Ph), ratio of intensities 3:5. ^{19}F NMR spectrum: −1.1 oct (CF_2), −16.0 t.d (CF_3), $J_{CF_2-H} = J_{FF} = 11.3$, $J_{CF_3-H} = 7.5$ Hz.

(b) To 3.0 g (11 mmoles) of (II) was added 1.2 g (9.6 mmoles) of benzyl mercaptan dropwise at ~ 20°C. The mixture was kept until gas evolution had finished (4 h), then heated at 60°C for 2 h. Distillation yielded 1.2 g (31%) of XVI, bp 90-92°C (2 mm), which by GLC and NMR was identical with the sample obtained by method (a).

Reaction of (Ia) with Diethylamine. To an excess of $HNEt_2$ (5 ml) at −78°C was added 2.2 g (9 mmoles) of (Ia) dropwise. After exothermic reaction had finished the reaction mixture was poured into water and extracted with ether, and the ether extract was dried with $MgSO_4$. After the ether was removed, distillation yielded 1.5 g (29%) of (XVIII), bp 52-54°C (3 mm), which by GLC and NMR was identical with a known sample [15].

Reaction of (Ia) with SbF_5. To 7.0 g of SbF_5 at ~ 20°C was added 0.9 g (4 mmoles) of (Ia) dropwise. The mixture was kept for 20 min and the reaction products were removed in vacuum (100 mm). There was obtained 0.4 g (52%) of perfluoroisobutylene, which by NMR was identical with a known sample.

CONCLUSIONS

1. A new synthesis of perfluoroisobutylene sulfide by dehydrochlorination of 2-hydroperfluoroisobutanesulfenyl chloride has been developed.

2. Dehydrochlorination of 2-hydrohexafluoroisobutyrylsulfenyl chloride yields 2-bis(trifluoromethyl)-methylene-4,4-bis(trifluoromethyl)-1,3-oxathiolan-5-one.

3. Nucleophilic reagents (ethanol, benzyl mercaptan) attack perfluoroisobutylene sulfide at the S atom.

4. By the action of amines and SbF_5, perfluoroisobutylene sulfide loses sulfur to form perfluoroisobutylene.

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REACTIONS OF N-, P-, S-, AND As-NUCLEOPHILES WITH CYANOACETYLENE

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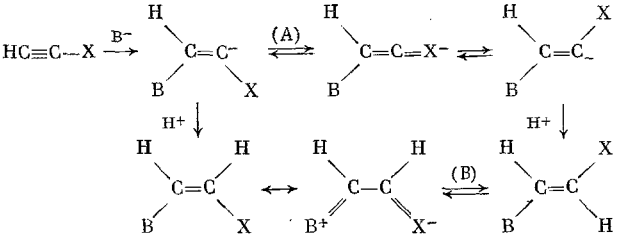
Nucleophilic reactions with activated acetylenes take place by trans(anti)-addition, according to the empirical Truce-Miller rule, which has been given a theoretical basis [1]. However, experimental findings with respect to the stereochemistry of the reaction are extremely contradictory (with different nucleophiles, activating groups, and conditions), and numerous exceptions to the rule have been studied [1]. This is particularly so with N-nucleophiles, and for secondary amines the reverse rule has been proposed involving cis-addition [2], although this was later refuted [3]. The main reasons for the ambiguous results are inversion of the vinyl carbanion (A), and the postisomerization of the initially formed trans-addition product (B)



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