Functionalization of alkenes by polyfluorinated α,β-unsaturated sulfenyl chlorides: reactions of 2-chloroperfluoro-1-cyclohexene-sulfenyl chloride-1 with activated olefins

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Abstract

A variety of β-chlorothioethers have been obtained by the reaction of 2-chloroperfluoro-1-cyclohexenesulfenyl chloride-1 (**I**) with t-butylethene, styrene, allylbenzene and *p*-methoxyallylbenzene in CH_2Cl_2 or CH_3NO_2. Skeletal rearrangement with 1,2-migration of the *p*-methoxyphenyl group occurs on reaction of **I** with *p*-methoxyallylbenzene along with the formation of addition products (Markovnikov and anti-Markovnikov adducts). A possible additive salt effect ($LiClO_4/CH_3NO_2$ system) has been examined for the reaction of **I** with t-butylethene, allylbenzene and *p*-methoxyallylbenzene; the effect is noted only in the case of t-butylethene, when intramolecular rearrangement with 1,2-migration of the methyl group takes place.

Introduction

The ability of sulfenyl chlorides to undergo addition reactions with unsaturated compounds is a well known and widely used method for the functionalization of alkenes [1]. In this context, it seemed interesting to investigate the reaction behaviour of the fluorine-containing α,β-unsaturated cyclic and linear sulfenyl chlorides previously obtained by us [2, 3]. These compounds contain an electron-deficient double bond capable of nucleophilic attack and mobile allylic (and in some cases vinylic) halogen atoms; this provides an opportunity to introduce versatile polyfunctional fluorinated building blocks into alkenes.

The highly electrophilic character of the polyfluorinated sulfenyl chlorides and the utilization of activated olefins, polar solvents and salt additives should lead, not only to addition reactions, but also to skeletal rearrangements.

The addition reaction of sulfenyl chlorides to olefins is commonly considered to be an electrophilic addition of the Ad_E2 type. The olefins act as nucleophiles and the sulfenyl chlorides as electrophiles, the positive charge being localized at the sulfur atom [4, 5]. On the other hand, we have shown previously that the polarization of the S–Cl bond in polyfluorinated α,β-unsaturated sulfenyl chlorides is not very pronounced. Depending on the reagent, nucleophilic attack takes place either at the sulfur atom (leading to elimination of the Cl^- anion) or at the chlorine atom, resulting in a transfer of a formally positive halogen [3]. Hence, studying the interaction of polyfluorinated α,β-unsaturated sulfenyl chlorides with activated olefins, which can be considered as nucleophiles, appears also to be interesting from the theoretical point of view.

Experimental

^1H NMR spectra were obtained on a Bruker WM-250 spectrometer (250 MHz), ^{13}C NMR spectra on a Bruker AM-300 (75 MHz) spectrometer in $CDCl_3$ with TMS as external reference. ^{19}F NMR spectra of compounds **II**, **IV**, **VII**, **IX**, **X**, **XIV** and **XV** were recorded on a Bruker AC-200 (188 MHz) spectrometer, while the spectra for compounds **VIII**, **XI–XIII** and **XVI** were recorded on a Perkin-Elmer R-32 (84.6 MHz) spectrometer, in both cases using CF_3COOH as external standard. IR spectra were undertaken on a UR-20 spectrometer. Mass spectra were measured on a VG 7070E instrument operating in the EI mode at 70 eV with a (25 m) capillary column OV-101; *m/z* values, proposed assignment and relative intensity (%) for the ^{32}S and ^{35}Cl isotopes are listed. The purity of the

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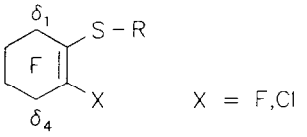
TABLE 1. ^{19}F NMR spectral data [($CDCl_3$) δ (ppm)] for compounds of the general formula:



X = F,Cl

Comp. No.	X	δ_1	δ_2	δ_3	δ_4	δ_X
IV	F	26.18(s)	53.74(s)	53.74(s)	28.69(s)	30.16(s)
VI	F	39.2(m)	54.2(m)	54.55(m)	39.2(m)	26.6(m)
VII	Cl	26.9(m)	55.9(m)	55.9(m)	31.7(m)	–
VIII[a]	F	29.6(m)	56.0(m)	56.7(m)	40.4(m)	39.8(m)
IX	Cl	27.0(m)	56.0(m)	56.0(m)	31.5(m)	–
X	Cl	27.0(m)	56.0(m)	56.0(m)	31.5(m)	–
XI	Cl	26.2(m)	55.6(m)	55.6(m)	31.1(m)	–
XII	Cl	26.2(m)	55.6(m)	55.6(m)	31.1(m)	–
XIII	Cl	26.2(m)	55.6(m)	55.6(m)	31.1(m)	–
XIV	F	30.8(m)	55.9(m)	56.7(m)	40.8(m)	33.7(m)
XV	Cl	27.6(s)	55.8(s)	55.8(s)	31.4(s)	–
XVI[a]	Cl	27.3(s)	56.2(s)	56.2(s)	31.3(s)	–

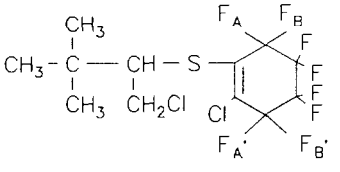
[a]Neat.

compounds was monitored by GLC methods on an LKhM-8 MD (model 3) chromatograph using a column (3 m×4 mm) packed with 20% QF on Chromaton and on a Zvet-530 chromatograph using a column (3 m×4 mm) packed with 10% SKFT-50 on Chromaton, and by TLC on 'Silufol' plates. Isolation of compound **XV** was performed by column chromatography on L5/40 SiO_2 (Chemapol) and of compounds **IX–XIV** on L40/100 SiO_2 (Chemapol). The ^{19}F NMR spectra of the compounds obtained (excluding **II**) are listed in Table 1.

1-Chloro-3,3-dimethylbut-2-yl-2'-chloroperfluoro-1'-cyclohexenyl sulfide (II)

Method a

A solution consisting of 0.71 g (1.08 ml) of t-butylethene in 1 ml of abs. CH_3NO_2 was added dropwise at 20 °C to a stirred solution consisting of 1.71 g of **I** [2] in 8 ml of abs. CH_3NO_2. The mixture was then stirred for 2 h at 20 °C, kept at the same temperature for 15 h and distilled to give 1.49 g (69.3%) of **II** (b.p. 80 °C/0.5 mmHg). Analysis: Found: C, 34.30; H, 2.66; F, 37.08; S, 8.04; Cl, 17.18%. Calc. for $C_{12}H_{12}Cl_2F_8S$: C, 35.05; H, 2.94; F, 36.97; S, 7.80; Cl, 17.25%. MS: 410 $[M^+]$ 7.0; 395 $[M-CH_3]^+$ 2.5; 318 $[M-C_4H_9Cl]^+$ 31.4; 163 $[C_4F_6H]^+$ 7.3; 83 $[C_6H_{11}]^+$ 59.7; 69 $[C_5H_9]^+$ 28.9; 57 $[C_4H_9]^+$ 100.0; 55 $[C_4H_7]^+$ 39.4; 43 $[C_3H_7]^+$ 48.1. IR (ν, cm^{-1}): 1590 (C=C). ^1H NMR δ: 1.1 (s, $(CH_3)_3$); 3.7 (m, CH_2Cl); 4.0 (m, CHS) ppm (intensity ratio: 9:2:1). ^{13}C NMR δ: 27.8 (q, CH_3); 36.4 (s, C); 46.9 (t, CH_2); 61.2 (d, CH) ppm. ^{19}F NMR ($CDCl_3$) δ: ($4CF_2$, four AB-systems); 24.8 (F_A); 26.93 (F_B); 30.7 ($F_{A'}$); 33.5 ($F_{B'}$); 54.9 ($F_{A''}$); 57.0 ($F_{B''}$); 55.5 ($F_{A'''}$); 57.3 ($F_{B'''}$) ppm; $J(F_A-F_B)=J(F_{A'}-F_{B'})=J(F_{A''}-F_{B''})=J(F_{A'''}-F_{B'''})=283.9$ Hz.



Method b

A solution consisting of 0.65 g (1 ml) of t-butylethene in 1 ml of abs. CH_2Cl_2 was added dropwise to a solution consisting of 1.46 g **I** in 6 ml of abs. CH_2Cl_2 at 20–25 °C with stirring. Stirring was continued for 1.5 h at 20 °C and the mixture was distilled; the fraction with b.p. 80 °C/5 mmHg was collected. The mixture (1.00 g) obtained contained 87% **II** (identical to a sample prepared by procedure a) and 13% di(2-chloroperfluoro-1-cyclohexenyl) disulfide (**III**) (according to GLC, ^{19}F NMR and GC–MS methods). ^{19}F NMR and IR spectra of **III** were identical to those reported previously [2]. MS for compound **III**: 582 $[M^+]$ 90.7; 563 $[M-F]^+$ 7.8; 291 $[C_6F_8ClS]^+$ 26.5; 272 $[C_6F_7ClS]^+$ 41.3; 237 $[C_6F_7S]^+$ 15.2; 172 $[C_4F_3ClS]^+$ 57.6.

3,3-Dimethyl-1-buten-2-yl-perfluoro-1'-cyclohexenyl sulfide (IV)

Compound **II** (3.3 g) and 8.0 g of well-dried CsF in 15 ml of abs. CH_3CN were shaken in a steel autoclave for 10 h at 150 °C. The mixture was then diluted with water, extracted with ether, the ether extract dried over $MgSO_4$ and distilled. The product mixture (0.86 g, b.p. 63–64 °C/3 mmHg) obtained consisted of 70% **IV** and

30% di(perfluoro-1-cyclohexenyl)disulfide (**VI**) (according to GLC, ^{19}F NMR and GC–MS data).

Compound **IV**: ^1H NMR δ: 1.25 (s, $(CH_3)_3$); 4.95 (br s, H^1); 5.4 (d, H^2) (intensity ratio: 9:1:1). MS: 358 $[M^+]$ 16.11; 343 $[M-CH_3]^+$ 7.01; 83 $[(CH_3)_3C_3H_2)]^+$ 21.09; 57 $[(CH_3)_3C]^+$ 100.00; 55 $[C_4H_7]^+$ 36.05.

Compound **VI**: $C_{12}F_{18}S_2$: MS: 550 $[M^+]$ 45.47; 531 $[M-F]^+$ 23.20; 381 $[M-C_3F_7]^+$ 5.95; 350 $[M-C_4F_8]^+$ 100.00; 131 $[C_3F_5]^+$ 5.97; 106 $[C_3F_2S]^+$ 9.48; 69 $[CF_3]^+$ 3.18.

2-Chloro-2-phenylethyl-2'-chloroperfluoro-1'-cyclohexenyl sulfide (VII)

A solution consisting of 1.15 g of styrene in 1 ml of abs. CH_3NO_2 was added dropwise to 3.31 g **I** in 10 ml of abs. CH_3NO_2 at 10–15 °C with stirring. The mixture was stirred for 1 h at 20 °C, then maintained at the same temperature for 15 h and distilled. Compound **VII** (2.65 g, 60.8%) (b.p. 135–137 °C/2 mmHg) was obtained. Analysis: Found: C, 38.89; H, 1.91; F, 35.15; S, 7.73%. Calc. for $C_{14}H_8Cl_2F_8S$: C, 38.99; H, 1.87; F, 36.25; S, 7.44%. IR (ν, cm^{-1}): 1500 (C_6H_5); 1590 (C=C). ^1H NMR δ: (CH_2, AB-system with additional doubling of each component); 3.73 (H_A); 3.77 (H_B); 5.05 (t, CHCl); 7.45 (s, C_6H_5) ppm; $J(H_A-H_B)=14.0$ Hz, $J(H_A-H)=J(H_B-H)=7.5$ Hz. ^{13}C NMR δ: 41.5 (t, *C*H_2); 61.0 (d, *C*H); 127.1 (d), 129.0 (d), 129.3 (d), 138.5 (s) (*C* arom.) ppm.

Styryl-perfluoro-1-cyclohexenyl sulfide (VIII)

Compound **VII** (3.32 g) and 3.0 g of well-dried CsF in 13 ml of abs. CH_3CN were refluxed with stirring for several hours; the progress of the reaction was monitored by GLC methods. The mixture was then poured into H_2O, extracted with ether, the ether extract dried with $MgSO_4$ an distilled to give 1.28 g (44.1%) of **VIII** (b.p. 110–112 °C/1 mmHg) (*trans*-isomer). Analysis: Found: C, 44.36; H, 1.82; F, 45.00; S, 8.53%. Calc. for $C_{14}H_7F_9S$: C, 44.45; H, 1.87; F, 45.21; S, 8.48%. MS: 378 $[M^+]$ 100.00; 377 $[M-H]^+$ 42.5; 359 $[M-F]^+$ 4.3; 135 $[C_6H_5C_2H_2S]^+$ 29.8; 134 $[C_6H_5CHCS]^+$ 13.9; 103 $[C_6H_5C_2H_2]^+$ 17.5; 102 $[C_6H_5CHC]^+$ 12.2; 91 $[C_6H_5CH_2]^+$ 48.7; 77 $[C_6H_5]^+$ 30.0; 69 $[CF_3]^+$ 3.2. IR (ν, cm^{-1}): 1500 (C_6H_5); 1580 (C=C cycl.); 1660 (C=C aliphatic). ^1H NMR δ: 6.81 (br.lines, H_A); 7.11 (H_B)(AB-system); 7.43 (s, C_6H_5) ppm; $J(H_A-H_B)=15.3$ Hz.

3-Phenyl-2-chloropropyl-2'-chloroperfluoro-1'-cyclohexenyl sulfide (IX) and 1-chloro-3-phenylprop-2-yl-2'-chloroperfluoro-1'-cyclohexenyl sulfide (X)

A solution consisting of 0.542 g of allylbenzene in 1 ml of abs. CH_3NO_2 was added dropwise at 20–25 °C with stirring to 1.5 g **I** in 4 ml of abs. CH_3NO_2. The mixture was then stirred for 1 h at 20 °C, maintained for 15 h at 20 °C and distilled. The product mixture (0.91 g, b.p. 116–120 °C/0.5 mmHg) obtained consisted of 76% **X**, 20% **IX** and 4% **III** (according to GLC, ^1H, ^{19}F NMR, GC–MS data). ^{19}F NMR and IR data for **III** were identical to literature data [2], the MS data being identical to that described in the experimental preparation of **II**. Product **X** (0.09 g) was isolated from the mixture by column chromatography on 60 g of SiO_2, eluent hexane.

Compound **IX**: MS: 444 $[M^+]$ 8.17; 117 $[C_6H_5CH_2CHCH]^+$ 100.00; 91 $[C_6H_5CH_2]^+$ 93.48. ^1H NMR δ: (CH_2S and CH_2, AB- and A'B'-systems, respectively, with additional doubling of each component); 3.19 (H_A); 3.21 (H_B); 3.40 ($H_{A'}$); 3.41 ($H_{B'}$); 4.25 (m, CH); 7.3 (m, C_6H_5) ppm; $J(H_A-H_B)=14.5$ Hz, $J(H_A-H)=7.5$ Hz, $J(H_B-H)=6.5$ Hz, $J(H_{A'}-H_{B'})=13.5$ Hz, $J(H_{A'}-H)=7.0$ Hz, $J(H_{B'}-H)=6.0$ Hz.

Compound **X**: Analysis: Found: C, 40.41; H, 2.22; F, 34.08; S, 7.24%. Calc. for $C_{15}H_{10}F_8SCl_2$: C, 40.47; H, 2.26; F, 34.14; S, 7.2%. MS: 444 $[M^+]$ 12.21; 318 $[M-C_6H_5CH_2Cl]^+$ 11.47; 153 $[M-C_6F_8ClS]^+$ 30.04; 117 $[C_6H_5CH_2CHCH]^+$ 23.92; 91 $[C_6H_5CH_2]^+$ 100.00. ^1H NMR δ: (CH_2Cl, AB-system with additional doubling of each component); 3.00 (H_A); 3.32 (H_B); 3.68 (m, CH_2); 3.98 (m, CHS); 7.33 (m, C_6H_5) ppm; $J(H_A-H_B)=14.5$ Hz, $J(H_A-H)=J(H_B-H)=7.2$ Hz.

2-Chloro-3-(p-methoxyphenyl)propyl-2'-chloroperfluoro-1'-cyclohexenyl sulfide (XI), 1-chloro-3-(p-methoxyphenyl)prop-2-yl-2'-chloroperfluoro-1'-cyclohexenyl sulfide (XII) and 2-(p-methoxyphenyl)-3-chloropropyl-2'-chloroperfluoro-1'-cyclohexenyl sulfide (XIII)

A solution consisting of 1.19 g of *p*-methoxyallylbenzene in 5 ml of abs. CH_2Cl_2 was added dropwise at 20 °C to a stirred solution consisting of 2.63 g of **I** in 10 ml of abs. CH_2Cl_2. The mixture was then stirred for 2 h at 20 °C, maintained for 15 h at the same temperature, and evaporated *in vacuo*. The residue (4.13 g) consisting of 44.1% **XII** and of 55.9% **XI** and **XIII** (GLC) was separated by column chromatography by portion {1 g per 60 g of SiO_2; eluent, hexane/chloroform (3:1)}. This resulted in 0.89 g (23.3%) of **XII** (b.p. 160 °C/1 mmHg) and 1.51 g (39.5%) of a mixture of **XI** and **XIII** (b.p. 160 °C/1 mmHg).

Compound **XII**: Analysis: Found: C, 40.19; H, 2.57; F, 32.04; S, 6.82%. Calc. for $C_{16}H_{11}OF_8Cl_2S$: C, 40.44; H, 2.55; F, 31.98; S, 6.75%. MS: 474 $[M^+]$ 5.0; 122 $[C_7H_9O]^+$ 8.8; 121 $[CH_3OC_6H_4CH_2]^+$ 100.0. ^1H NMR δ: (CH_2Cl, AB-system with additional doubling of each component); 2.95 (H_A); 3.25 (H_B); 3.66 (m, CH_2); 3.81 (s, OCH_3); 3.92 (m, CHS); 6.9 (m, 2H, Ar); 7.18 (m, 2H, Ar) ppm; $J(H_A-H_B)=14.5$ Hz, $J(H_A-H)=J(H_B-H)=7.0$ Hz.

Compound **XI**: MS: 474 $[M]^+$ 7.7; 147 $[CH_3OC_6H_4CH_2CHCH]^+$ 4.7; 122 $[C_7H_9O]^+$ 8.9; 121 $[CH_3OC_6H_4CH_2]^+$ 100.0. ^1H NMR δ: (CH_2S and CH_2, AB- and A'B'-systems, respectively, with additional doubling of each component); 3.10 (H_A); 3.16 (H_B); 3.37 ($H_{A'}$); 3.41 ($H_{B'}$); 3.81 (s, OCH_3); 4.20 (quin., CHCl); 6.89 (m, 2H, Ar); 7.15 (m, 2H, Ar) ppm; $J(H_A-H_B)=14.5$ Hz, $J(H_{A'}-H_{B'})=13.0$ Hz; $J(H_A-H)=J(H_B-H)=J(H_{A'}-H)=J(H_{B'}-H)=6.5$ Hz.

Compound **XIII**: MS: 474 $[M]^+$ 9.6; 183 $[CH_2ClCH(C_6H_4OCH_3)CH_2]^+$ 3.3; 169 $[CH_2Cl(CH_3OC_6H_4)CH]^+$ 100.0; 134 $[CH_2CHC_6H_4OCH_3]^+$ 27.7; 121 $[CH_3OC_6H_4CH_2]^+$ 13.2. ^1H NMR δ: 3.2 (m, CH); 3.55 (m, CH_2^1); 3.75 (m, CH_2^2); 3.81 (s, OCH_3); 6.9 (m, 2H, Ar); 7.15 (m, 2H, Ar) ppm; ^{13}C NMR δ: 36.0 (t, *C*H_2); 46.5 (d, *C*H); 47.5 (t, *C*H_2Cl); 55.0 (q, O*C*H_3); 114.0 (d), 128.0 (d), 130.5 (s), 159.5 (s) (*C* arom.) ppm.

3-(p-Methoxyphenyl)-1-propene-2-yl-perfluoro-1'-cyclohexenyl sulfide (XIV)

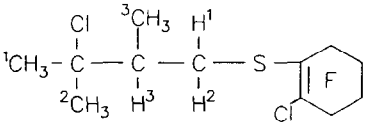
Well-dried CsF (1.1 g), 0.89 g **XII** and 15 ml of abs. CH_3CN were shaken in a steel autoclave for 11 h at 150 °C. The mixture was then poured into water, extracted with ether and the ether extract dried over $MgSO_4$. The solvent was removed and the residue was purified by column chromatography (SiO_2) using hexane as eluent. Compound **XIV** (0.2 g, 25.3%) was obtained. MS: 422 $[M]^+$ 43.74; 389 $[C_{15}H_9F_8OS]^+$ 6.21; 147 $[CH_3OC_6H_4CH_2CCH_2]$ 27.05; 146 $[C_{10}H_{10}O]^+$ 16.09; 122 $[C_7H_9O]^+$ 8.91; 121 $[CH_3OC_6H_4CH_2]^+$ 100.00; 77 $[C_6H_5]^+$ 9.56. ^1H NMR δ: 3.52 (s, CH_2); 3.83 (s, OCH_3); 5.38 (s, H^1); 5.45 (s, H^2); 6.9 (m, 2H, Ar); 7.11 (m, 2H, Ar) ppm.

2,3-Dimethyl-2-butenyl-2'-chloroperfluoro-1'-cyclohexenyl sulfide (XV)

Compound **I** (2.23 g, 0.0068 mol) was added to a solution consisting of 3.63 g (0.034 mol) of desiccated $LiClO_4$ in 23 ml of abs. CH_3NO_2. The mixture was stirred for 15 min when a solution consisting of 1.05 g (1.6 ml, 0.0125 mol) of t-butylethene in 2 ml of abs. CH_3NO_2 was added dropwise at 25 °C with stirring. Stirring was continued for 2 h at 20 °C, the solvent was evaporated *in vacuo*, the residue diluted with H_2O and extracted with CH_2Cl_2. The organic layer was separated and dried over $MgSO_4$; the solvent was evaporated *in vacuo* and the residue (2.14 g), consisting of 76% **XV** and 24% **II** (according to GLC, ^1H, GC–MS data), was purified by column chromatography on SiO_2 (35 g) (eluent, hexane) when 0.65 g (25.5%) of **XV** (b.p. 76 °C/0.5 mmHg) was obtained. Analysis: Found: C, 38.22; H, 2.93; F, 40.41; S, 8.66%. Calc. for $C_{12}H_{11}F_8ClS$: C, 38.49; H, 2.96; F, 40.59; S, 8.56%. IR (ν, cm^{-1}): 1590 (C=C cycl.); 1670 (C=C aliphatic). ^1H NMR δ: 1.72 (s, CH_3^1); 1.77 (s, CH_3^2); 1.80 (s, CH_3^3); 3.82 (s, CH_2) ppm.

3-Chloro-2,3-dimethylbutyl-2'-chloroperfluoro-1'-cyclohexenyl sulfide (XVI)

Dry HCl gas was passed through a mixture consisting of 1.34 g **XV** and 2.0 g of desiccated $LiClO_4$ in 15 ml of abs. CH_3NO_2 with stirring; the progress of the reaction was monitored by GLC methods. The solvent was then removed, the residue washed with water, extracted with CH_2Cl_2, the organic layer separated, dried over $MgSO_4$ and distilled. Compound **XVI** (0.75 g, 51.0%) (b.p. 92–94 °C/1 mmHg) was obtained. Analysis: Found: C, 34.90; H, 2.88; F, 37.26; S, 7.79%. Calc. for $C_{12}H_{12}F_8Cl_2S$: C, 35.05; H, 2.94; F, 36.97; S, 7.798%. MS: 410 $[M^+]$ 4.0; 333 $[C_9H_6F_8ClS]^+$ 12.0; 305 $[C_7H_2F_8ClS]^+$ 7.0; 83 $[C_6H_{11}]^+$ 100.0; 77 $[(CH_3)_2CCl]^+$ 12.4; 69 $[CF_3]^+$ 91.5; 55 $[(CH_3)_2C_2H]^+$ 58.5; 42 $[(CH_3)_2C]^+$ 22.0. IR (ν, cm^{-1}): 1590 (C=C). ^1H NMR δ: 1.22 (d, CH_3^3); 1.55 (s, CH_3^1); 1.63 (s, CH_3^2); 1.9 (d q d, H^3); 2.8 (d d, H^1); 3.65 (d d, H^2) ppm; $J(CH_3^3-H^3)=7.0$ Hz, $J(H^3-H^1)=10.5$ Hz, $J(H^3-H^2)=2.5$ Hz, $J(H^1-H^2)=12.5$ Hz.



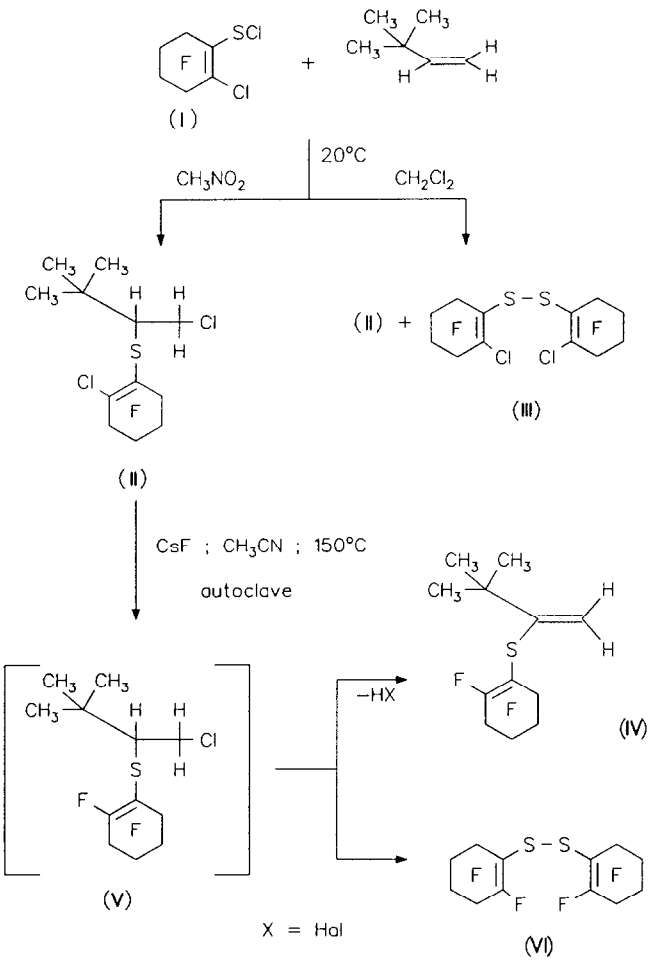
Results and discussion

The goal of the present study was to investigate the interaction of the alicyclic fluorine-containing α,β-unsaturated sulfenyl chloride, 2-chloroperfluoro-1-cyclohexenesulfenyl chloride-1 (**I**) with t-butylethene, styrene, allylbenzene and *p*-methoxyallylbenzene in polar solvents (CH_2Cl_2, CH_3NO_2) as well as in the $LiClO_4$/CH_3NO_2 system.

The reaction of **I** with t-butylethene resulted in the formation of adduct **II** (Scheme 1).

In CH_2Cl_2, disulfide **III** is formed in addition to product **II**. Only the addition product which does not accord with the Markovnikov rule (AM-adduct) is formed in the reaction; in general, exclusive formation of the AM-adduct is typical for interaction of terminal alkenes [6] (in particular, t-butylethene [7], see review in ref. 5) with sulfur-containing electrophiles.

The presence of the AM-adduct is confirmed by further experiments: the interaction of **II** with CsF leads to dehydrohalogenation of **II** giving sulfide **IV**. The coupling constant $^2J(H-H)=2$ Hz for the olefinic protons demonstrates the vinylidene sub-structure of **IV** [8]. Nucleophilic substitution of chlorine in the 2-position of the cyclohexenyl ring by fluorine is observed



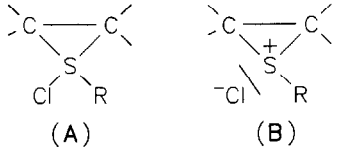
Scheme 1.

under the reaction conditions, as reported for reactions of polyfluorinated cyclic olefins with alkaline metal fluorides [9]. It has been shown that nucleophilic substitution precedes dehydrohalogenation, since the sequence of these conversions could be observed by GLC analysis when the reaction was carried out under reflux in CH_3CN at ambient pressure*. Under the reaction conditions, partial degradation of sulfide **V** is also noted since the disulfide **VI** was found amongst the reaction products.

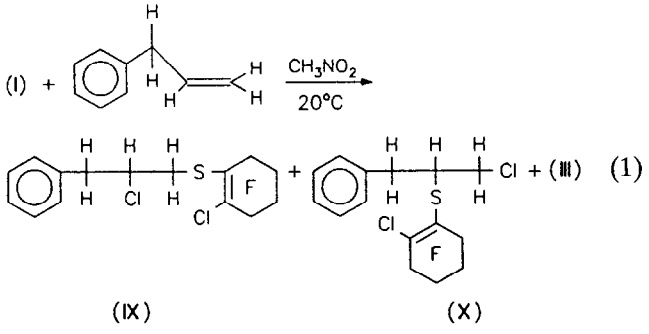
When **I** interacts with styrene in CH_3NO_2, the reaction ends in the formation of a single addition product (**VII**) according to Markovnikov's rule (the M-adduct) (Scheme 2), which has also been observed for similar reactions of styrene [5, 7, 10].

The structure of **VII** was proved by analysis of the ^1H NMR spectra of its dehydrohalogenation product (**VIII**) (reaction with CsF), when a coupling constant $^3J(H-H) = 15.3$ Hz (*trans*-coupling) was observed for the olefinic protons (Scheme 2).

Thus, the addition of sulfenyl chloride **I** to t-butylethene and styrene proceeds regiospecifically to give the AM- or M-adducts exclusively. The fact that the direction of addition of the sulfur-containing fragment and chlorine is not different from that in similar reactions with non-fluorinated sulfenyl chlorides implies that the sulfur atom in sulfenyl chloride **I** behaves as an electrophilic particle in this case. These reactions may be considered to be of the Ad_E type. In addition to this, the above reactions are likely to proceed via the intermediate formation of episulfurane (A) or a close ion pair (B), the presence of the latter have been postulated in similar cases recently [10].



The interaction of **I** with allylbenzene and *p*-methoxyallylbenzene proved to be quite different. Thus, addition of **I** to allylbenzene [eqn. (1)]



leads to the formation of both the adducts M (**IX**) and AM (**X**) with the kinetically-controlled product AM (**X**) predominating; the formation of disulfide **III** also takes place. The product ratio (%) M/AM/**III** is 20:76:4 (according to GLC, ^1H and ^{19}F NMR methods).

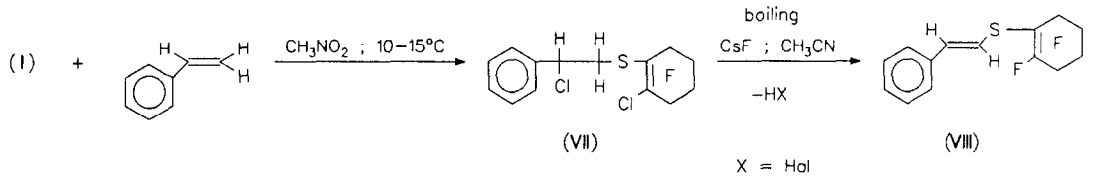
The addition of **I** to *p*-methoxyallylbenzene yields three isomeric products (Scheme 3).

On the basis of ^1H NMR spectra, GC–MS data and literature data (see below), we have come to the conclusion that the two compounds M (**XI**) and AM (**XII**) are adducts and that **XIII** is the product of a skeletal rearrangement with 1,2-migration of the *p*-methoxyphenyl group.

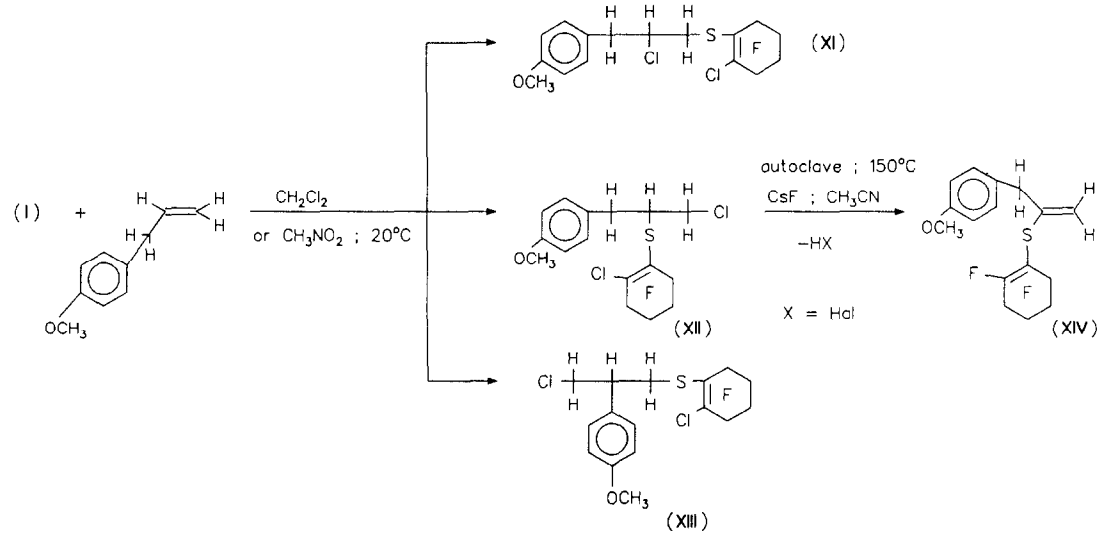
The sulfides **XI**, **XII** and **XIII** obtained from reaction in CH_2Cl_2* [with the ratio (%) (**XI**, **XIII**)/(**XII**) = 56:44]

*Nucleophilic substitution only takes place in the case of the t-butylethene derivative when the process is not carried out in an autoclave; the sequence of nucleophilic substitution and dehydrohalogenation can be followed successfully for the styrene derivative.

*Reaction in CH_3NO_2 proceeds in a similar manner, but the ratio (%) of the products is different: (**XI**, **XIII**)/(**XII**) = 50:50.



Scheme 2.



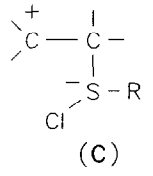
Scheme 3.

were isolated by column chromatography. A mixture of the isomers **XI** and **XIII** and the pure product **XII** were obtained.

The structure of **XII**, like that of **II** and **VII**, was proved by its dehydrohalogenation reaction (Scheme 3), which gave the unsaturated sulfide **XIV**.

Chromatographic separation of the isomers **XI** and **XIII** was unsuccessful, but one of the isomers was enriched. Thus, unambiguous assignment of the ^1H NMR signals was possible.

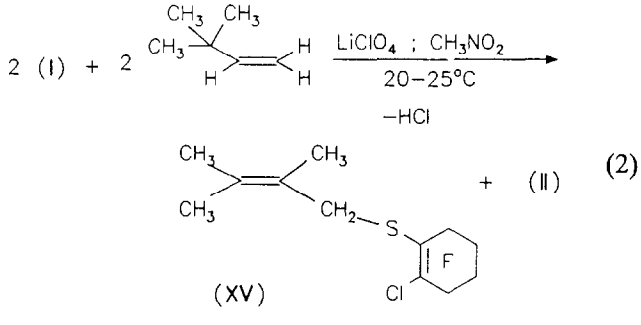
The reactions of **I** with allylbenzene and *p*-methoxyallylbenzene [eqn. (1), Scheme 3] are likely to proceed via formation of intermediates of A and B type as in the case of t-butylethene and styrene (Schemes 1 and 2). However, 1,2-migration of the *p*-methoxyphenyl group, taking place as shown in Scheme 3, apparently requires the contribution of more polar intermediates, for instance, of a zwitterion C [cf. refs. 11 and 12].



(C)

A similar interaction, proceeding with normal addition along with 1,2-migration of an aryl group, has been observed previously in the reaction of phenylsulfenyl chloride with 2-methyl-3-aryl-1-buten-3-ols [13, 14] or on the thiocyanation of *p*-substituted allylbenzenes [15]. However, it should be noted that, in general, skeletal rearrangements in addition reactions involving bivalent sulfur as an electrophilic centre and olefins are observed quite rarely [14]. Nevertheless, the absence of a skeletal rearrangement in the reaction of **I** with allylbenzene [see eqn. (1)] is, as yet, not unambiguous.

We have observed a similar 1,2-migration of a methyl group in the reaction of **I** with t-butylethene in the presence of a salt additive, e.g. in the $LiClO_4/CH_3NO_2$ system [eqn. (2)].

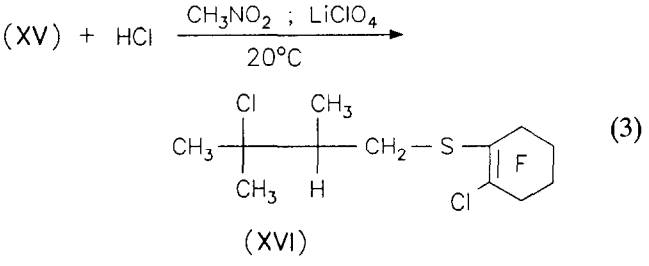


(2)

The adduct AM (**II**) is formed together with the rearrangement product **XV** in a ratio (%) of 24:76.

Lithium perchlorate is known [16, 17] to enhance the polarization of intermediates in the reactions of sulfenyl chlorides with alkenes; this fact explains the rearrangement in the presence of $LiClO_4$ [eqn. (2)], because formation of the zwitterion of type C predominates, and the absence of a 1,2-migration when the reaction is performed without a salt additive (see Scheme 1).

When the reaction mixture is left standing for several hours, formation of sulfide **XVI** (the product of HCl addition to **XV**) together with **XV** and **II** is noted. Product **XVI** may also be obtained by another method [eqn. (3)].



Conversions similar to those in eqns. (2) and (3) took place on reaction of 2,4-dinitrobenzylsulfenyl chloride with t-butylethene [18].

In addition to the reactions presented in eqn. (1) and Scheme 3, we also carried out the reaction of **I** with allylbenzene and *p*-methoxyallylbenzene in the $LiClO_4/CH_3NO_2$ system but no salt effect was observed in these cases.

Thus, the results obtained show that polyfluorinated alicyclic α,β-unsaturated sulfenyl chlorides readily undergo electrophilic addition to alkenes. This offers a convenient method for the introduction of fluorine-containing polyfunctional fragments into various types of olefin.

Specific formation of AM or M-adducts depends on the electronic structure and the size of the substituents at the double bond of the olefin. The skeletal rearrangements described in this paper should provide suitable model systems for detailed investigation of similar processes.

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