Synthesis and Epoxidation of 1,3-, 1,4-, and 1,5-Alkadienes with Pentafluoro-λ^6-sulfanyl (SF_5) Groups

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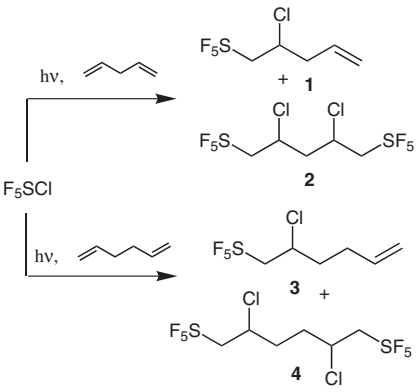
Abstract: This paper describes a convenient and efficient synthesis of new pentafluoro-λ^6-sulfanyl-containing 1,3-, 1,4- and 1,5-alkadienes and their epoxidation. These compounds are useful as monomers or as intermediates in the preparation of polymers, polymer surface coating and SF_5-containing heterocyclic compounds.

Key words: alkenes, epoxidations, fluorine, sulfur

Compounds in which a pentafluorothio group is present are of special interest because they often possess the advantageous properties of the parent compound SF_6, among which are a high group electronegativity, large steric bulk, a nonfunctional hexacoordinate stereochemistry, and high thermal and hydrolytic stability. These new properties are manifested in a multitude of uses, or potential uses, such as fumigants, as perfluorinated blood substitutes, as thermally and chemically stable systems,[1] as energetic materials[2] and rocket fuels.[3] Besides, the high radiative and chemical stability of the pentafluorothio group make these compounds attractive as replacements for compounds that contain a trifluoromethyl group.

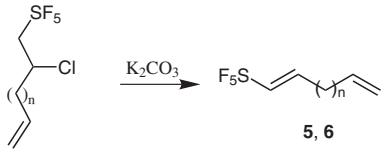
One of the most promising methods of preparation of pentafluorosulfanyl-containing compounds is pentafluorosulfanylation of unsaturated substrates.[4] Compounds with the pentafluorosulfanyl group have been synthesized earlier.[5] At the same time, the preparation of SF_5-alkadienes with terminal CH_2-group, to the best of our knowledge, has not been described hitherto. Therefore, we have developed a convenient approach to the synthesis of pentafluorosulfanyl-containing 1,3-, 1,4- and 1,5-alkadienes and studied their reactivity.

1-Pentafluorosulfanylpenta-1,4-diene (**5**) and 1-pentafluorosulfanylhexa-1,5-diene (**6**) have been prepared by similar two-step syntheses. In both cases, the first step is the photo-induced radical addition of pentafluorosulfanyl chloride to the corresponding 1,4- and 1,5-dienes with the formation of adducts **1** and **3**, respectively (Scheme 1). These reactions were performed at room temperature in a quartz ampule with Hg lamp as a source of irradiation. In reactions with 1,4- and 1,5-dienes, bis-adducts **2** and **4**, respectively, are formed as by-products in the yields of 10–15%. Products **1**–**4** were isolated by vacuum distillation and their structures proved by ^1H, ^{19}F and ^{13}C NMR spectroscopy data. All products are formed by attack of F_5S radical on terminal carbon atom, i.e., the studied photochemical reactions are completely regioselective.



Scheme 1

The second step of the preparation of alkadienes **5** and **6** is the dehydrochlorination of monoadducts **1** and **3** respectively by heating with K_2CO_3 in sulfolane at 60 °C during 3 hours (Scheme 2). Elimination of hydrogen chloride was monitored using thin layer chromatography. The formation of 1-pentafluorosulfanylhexa-1,5-diene (**6**) is straightforward. The formation of 1-pentafluorosulfanylpenta-1,4-diene (**5**) is accompanied by its partial isomerization to 1-pentafluorosulfanylpenta-2,4-diene. The extent of this isomerization increased with temperature. Therefore, 1,4-pentadiene **5** was isolated by column chromatography on silica gel where as distillation at reduced pressure was used for isolation of thermally stable product **6**.



Scheme 2

We have tried to synthesize 1-pentafluorosulfanylbuta-1,3-diene by a similar two-step approach using photochemical addition of F_5SCl to unsaturated substrate followed by HCl elimination. For that we have used 3-

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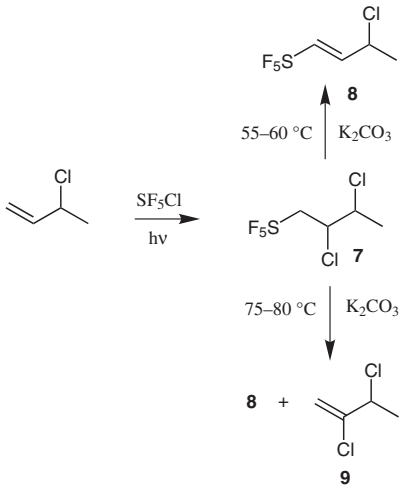
chlorobut-1-ene as the substrate. Indeed, adduct **7** is formed in good yield. It has been isolated in pure form by vacuum distillation. Unfortunately, transformation of this adduct into the 1,3-diene by elimination of two molecules of hydrogen chloride with K_2CO_3 in DMF or sulfolane failed.

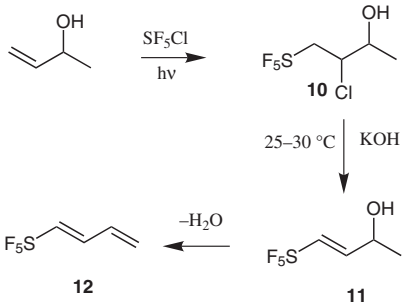
We have now found that heating **7** with potassium carbonate at 55–60 °C leads to elimination of one HCl molecule only with formation of 3-chloro-1-pentafluorosulfanylbut-1-ene (**8**). Compound **8** is stable under these conditions; elimination of a second HCl molecule is not observed with the increase of reaction time. The dehydrochlorination of **7** at higher temperature (75–80 °C) proceeds with formation of the mixture of **8** and 2,3-dichlorobut-1-ene (**9**) in a ratio of 2:1 (Scheme 3).



Scheme 3

The formation of dichloride **9** is the result of elimination of HSF_5 from adduct **7**. So, under these conditions the F_5S group behaves as a pseudohalide and competes with the chlorine atom in a base-induced elimination reaction. This is unexpected while the interaction between bases and alkyl halides containing a F_5S group leads usually to elimination of hydrogen halide but not HSF_5. The formation of **9** can be explained by the increased acidity of H-2 atom in 2,3-dichloro-1-pentafluorosulfanylbutane (**7**) due to inductive effects of electron-withdrawing substituents both at C-1 and at C-3 atoms. Therefore, dehydrochlorination of **7** at 55–60 °C leads to elimination of one HCl molecule only. Increase of reaction temperature to 80 °C gives rise to both the same dehydrochlorination and to elimination of HSF_5 but 1-pentafluorosulfanylbuta-1,3-diene is not obtained.

Therefore, we have used another approach to the synthesis of 1-pentafluorosulfanylbuta-1,3-diene. But-3-en-2-ol underwent photochemical reaction with F_5SCl to yield adduct **10**. Treatment of compound **10** with KOH in diethyl ether affords allyl alcohol **11**. The reaction is mild and relatively fast: full conversion of **10** required 3 hours at 25–30 °C. Unsaturated alcohol **11** has been isolated by vacuum distillation. Exclusive formation of the *trans*-isomer in this elimination has been proved by ^1H, ^{19}F and ^{13}C NMR spectroscopy. The final step of our synthesis of 1-pentafluorosulfanylbuta-1,3-diene (**12**) was dehydration of alcohol **11**. We have found that removing the product from the reaction mixture increases the yield of **12**. Hence, the reaction was performed under reduced pressure with simultaneous distillation of formed 1,3-diene into a cooled trap. This procedure provided 1-pentafluorosulfanylbuta-1,3-diene (**12**) in 35–40% yield (Scheme 4).

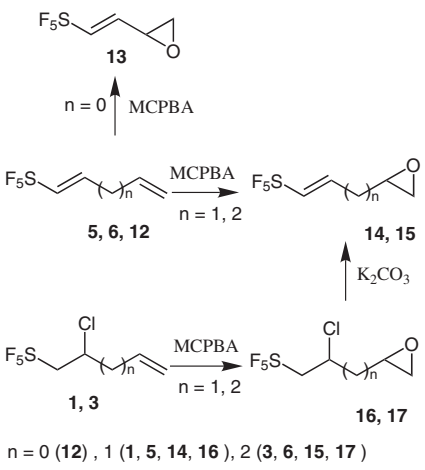


Scheme 4

The structures of 1-pentafluorosulfanylhexa-1,5-diene (**6**), 1-pentafluorosulfanylpenta-1,4-diene (**5**), and 1-pentafluorosulfanylbuta-1,3-diene (**12**) have been unambiguously proved using ^1H, ^{19}F and ^{13}C NMR spectroscopy. The most useful for this was the ^{13}C NMR spectroscopy. Coupling constants $J_{C,F}$ of carbon atom connected directly to F_5S group as well as $J_{C,F}$ of atom C-2 are characteristic for the compounds containing pentafluorosulfanyl substituent: $\delta_{C\text{-}1} = 141.74$ (doublet of a pentet, $J_{C\text{-}1,F'} = 1.6$ Hz, $J_{C\text{-}1,F} = 20.4$ Hz); $\delta_{C\text{-}2} = 136.62$ (pentet, $J_{C\text{-}2,F} = 7.5$ Hz). C-3 and C-4 are singlets; their chemical shifts are the following: $\delta_{C\text{-}3} = 131.35$ (s) and $\delta_{C\text{-}4} = 126.54$ (s). The ^{19}F NMR spectra for compounds **5**, **6** and **12** showed no significant deviations from the chemical shifts or coupling constants found for other unsaturated derivatives of sulfur hexafluoride. The chemical shifts of the apical fluorine atom in the SF_5-group were in the range of δ = 140–141, while the basal fluorines were observed at δ = 160–161, with the typical appearance of the AB_4-spin system, $J_{A,B} = 144$–151 Hz.

We have studied the epoxidation of F_5S-containing unsaturated compounds **5**, **6** and **12** by *m*-chloroperoxybenzoic acid.[6] After 72 hours, these dienes were converted into monoepoxides **13**–**15** in 80–90% yields (Scheme 5). Epoxides **14** and **15** were also synthesized from adducts **1** and **3** by a two-step procedure. In the first step, these chloroalkenes were epoxidized with *m*-chloroperoxybenzoic acid; the second step is HCl elimination from the obtained chloroalkyl epoxides **16** and **17**.

In all cases, unsubstituted terminal double bond is exclusively epoxidized. Double bond connected directly to F_5S group fails to react with the electrophilic oxidant. This can be explained on account of the significant steric and electron-withdrawing effects of pentafluorosulfanyl groups.



Scheme 5

The epoxides **13–15** have been characterized by ^1H, ^{19}F and ^{13}C NMR spectroscopy.

In summary, we have described an easy and convenient method for the preparation of new, synthetically valuable 1,3-, 1,4-, and 1,5-alkadienes with pentafluoro-λ^6-sulfanyl (SF_5) groups. The epoxidations of compounds **1**, **3**, **5**, **6**, **12** with *meta*-chloroperoxybenzoic acid occur in high yield. In all cases, double bond connected directly to F_5S group fails to react with the electrophilic oxidant. Future studies on this potentially important synthetic methodology are currently in progress. Applications of 1,3-, 1,4-, and 1,5-alkadienes containing pentafluoro-λ^6-sulfanyl (SF_5) groups to the synthesis of interesting heterocycles will be reported in due course.

NMR spectra were recorded on a Bruker CXP-200 spectrometer at 200 MHz (^1H NMR), 188.3 MHz (^{19}F NMR) and 50.3 MHz (^{13}C NMR). Chemical shifts for ^1H NMR and ^{13}C NMR are reported in ppm relative to TMS as internal standard. ^{19}F downfield shifts (δ) are expressed with a positive sign, relative to external CF_3CO_2H. Starting materials penta-1,4-diene, hexa-1,5-diene, 3-chlorobut-1-ene, but-3-en-2-ol, *meta*-chloroperoxybenzoic acid are commercially available. SF_5 was prepared from F_4S according to the literature procedure.[7]

4-Chloro-5-(pentafluoro-λ^6-sulfanyl)pent-1-ene (1); Typical Procedure

A mixture of penta-1,4-diene (8.16 g, 0.12 mol), F_5SCl (16.2 g, 0.1 mol) and Cl_3CF (10 mL) contained in a Pyrex ampule was irradiated for 2 h with UV light from a Hanovia S500 lamp placed at a distance of 30 cm. The reaction mixture was freed from Cl_3CF by distillation leaving 24 g of a brownish oil. The oil was distilled in vacuo, giving 18.5 g (80%) of **1**; bp 48 °C/8 mm Hg and 3.4 g (15%) of **2**; bp 101 °C/2 mm Hg.

Compound 1

^1H NMR (200 MHz, $CDCl_3$): δ = 2.61 (m, 3 H, CH_2), 3.93 (dpent, 2 H, $J_{H,F}$ = 8.0 Hz, $J_{H,F}$ = 6.0 Hz, F_5SCH_2), 4.42 (pent, 1 H, $J_{H,H}$ = 6.0 Hz, CHCl), 5.21 (dd, 1 H, $J_{H,H}$ = 18.1 Hz, $J_{H,H}$ = 1.4 Hz, = C*CH*H), 5.23 (dd, 1 H, $J_{H,H}$ = 9.0 Hz, $J_{H,H}$ = 1.4 Hz, =CCH*H*), 5.85 (ddt, 1 H, $J_{H,H}$ = 18.1 Hz, $J_{H,H}$ = 9.0 Hz, $J_{H,H}$ = 6.9 Hz, CH=).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 41.38 (s, CH_2), 54.26 (pent, $J_{C,F}$ = 4.2 Hz, CHCl), 75.74 (dpent, $J_{C,F}$ = 13.4 Hz, $J_{C,F}$ = 1.0 Hz, F_5SCH_2), 120.04 (s, =CH_2), 131.62 (s, CH=).

^{19}F NMR (188.3 MHz, $CDCl_3$): δ = 144.01 (dm, 4 F, $J_{F,F}$ = 146.0 Hz), 160.83 (9 lines, 1 F, $J_{F,F}$ = 146.0 Hz).

Anal. Calcd for $C_5H_8ClF_5S$ (230.63): C, 26.04; H, 3.50; F, 41.19; S, 13.90. Found: C, 26.12; H, 3.49; F, 41.36; S, 14.02.

Compound 2

^1H NMR (200 MHz, $CDCl_3$): δ = 2.29 (d, 1 H, $J_{H,F}$ = 5.5 Hz, C*H*H), 2.33 (d, 1 H, $J_{H,H}$ = 5.7 Hz, CH*H*), 3.91 (ddpent, 2 H, $J_{H,F}$ = 8.0 Hz, $J_{H,H}$ = 14.3 Hz, $J_{H,H}$ = 7.7 Hz, 2 F_5SCHH), 4.10 (ddpent, 2 H, $J_{H,F}$ = 8.5 Hz, $J_{H,H}$ = 14.3 Hz, $J_{H,H}$ = 5.1 Hz, 2 F_5SCHH), 4.69 (m, 2 H, 2 CHCl).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 44.54 (pent, $J_{C,F}$ = 1.2 Hz, CH_2), 52.44 (pent, $J_{C,F}$ = 4.8 Hz, 2 CHCl), 75.75 (dpent, $J_{C,F}$ = 14.0 Hz, $J_{C,F}$ = 1.0 Hz, 2 F_5SCH_2).

^{19}F NMR (188 MHz, $CDCl_3$): δ = 144.40 (dm, 4 F, $J_{F,F}$ = 146.0 Hz), 161.20 (9 lines, 1 F, $J_{F,F}$ = 146.0 Hz).

Anal. Calcd for $C_5H_8Cl_2F_{10}S_2$ (393.14): C, 15.28; H, 2.05; F, 48.32; S, 16.31. Found: C, 15.12; H, 1.97; F, 48.46; S, 16.44.

5-Chloro-6-(pentafluoro-λ^6-sulfanyl)hex-1-ene (3)

According to the procedure for the synthesis of **1**, hexa-1,5-diene (9.8 g, 0.12 mol) was allowed to react with F_5SCl (16.2 g, 0.1 mol). Distillation at reduced pressure gave 20.7 g (85%) of compound **3**; bp 61/7 mm Hg and 3.1 g (13%) of compound **4**; bp 110 °C/2 mm Hg.

Compound 3

^1H NMR (200 MHz, $CDCl_3$): δ = 1.85 (m, 1 H, C*H*H), 2.03 (m, 1 H, CH*H*), 2.31 (m, 2 H, CH_2), 3.90 (ddpent, 1 H, $J_{H,H}$ = 6.2 Hz, $J_{H,H}$ = 14.3 Hz, $J_{H,F}$ = 8.0 Hz, F_5SCHH), 4.03 (ddpent, 1 H, $J_{H,H}$ = 6.2 Hz, $J_{H,H}$ = 14.3 Hz, $J_{H,F}$ = 8.0 Hz, F_5SCHH), 4.36 (tt, 1 H, $J_{H,H}$ = 6.2 Hz, $J_{H,H}$ = 9.6 Hz, CHCl), 5.11 (ddd, 1 H, $J_{H,H}$ = 17.1 Hz, $J_{H,H}$ = 1.5 Hz, $J_{H,H}$ = 1.5 Hz, =C*CH*H), 5.07 (dd, 1 H, $J_{H,H}$ = 10.1 Hz, $J_{H,H}$ = 1.5 Hz, $J_{H,H}$ = 1.0 Hz, =CCH*H*), 5.77 (ddt, 1 H, $J_{H,H}$ = 17.1 Hz, $J_{H,H}$ = 10.1 Hz, $J_{H,H}$ = 6.3 Hz, C*H*=CH_2).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 30.05 (s, CH_2), 36.45 (pent, $J_{C,F}$ = 14.2 Hz, CH_2), 54.92 (pent, $J_{C,F}$ = 4.4 Hz, CHCl), 76.72 (dpent, $J_{C,F}$ = 13.8 Hz, $J_{C,F}$ = 0.9 Hz, F_5SCH_2), 118.57 (s, =CH_2), 135.82 (s, CH=).

^{19}F NMR (188.3 MHz, $CDCl_3$): δ = 144.03 (dm, 4 F, $J_{F,F}$ = 146.1 Hz), 160.96 (9 lines, 1 F, $J_{F,F}$ = 146.1 Hz).

Anal. Calcd for $C_6H_{10}ClF_5S$ (244.66): C, 29.46; H, 4.12; F, 38.83; S, 13.11. Found: C, 29.30; H, 4.07; F, 38.97; S, 13.25.

Compound 4

^1H NMR (200 MHz, $CDCl_3$): δ = 2.11 (m, 4 H, 2 CH_2), 3.90 (ddpent, 2 H, $J_{H,F}$ = 8.1 Hz, $J_{H,H}$ = 14.4 Hz, $J_{H,H}$ = 7.1 Hz, 2 F_5SCHH), 4.08 (ddpent, 2 H, $J_{H,F}$ = 8.4 Hz, $J_{H,H}$ = 14.4 Hz, $J_{H,H}$ = 5.0 Hz, 2 F_5SCHH), 4.42 (m, 2 H, 2CHCl).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 33.23 (pent, $J_{C,F}$ = 1.5 Hz, CH_2), 34.19 (pent, $J_{C,F}$ = 1.5 Hz, CH_2), 54.35 (pent, $J_{C,F}$ = 5.5 Hz, CHCl), 54.98 (pent, $J_{C,F}$ = 5.4 Hz, CHCl), 76.21 (dpent, $J_{C,F}$ = 13.6 Hz, $J_{C,F}$ = 1.0 Hz, F_5SCH_2), 76.27 (dpent, $J_{C,F}$ = 13.4 Hz, $J_{C,F}$ = 1.0 Hz, F_5SCH_2).

^{19}F NMR (188.3 MHz, $CDCl_3$): δ = 144.12, 144.19 (dm, 4 F, $J_{F,F}$ = 146.1 Hz), 160.47, 160.48 (9 lines, 1 F, $J_{F,F}$ = 146.1 Hz).

Anal. Calcd for $C_6H_{10}Cl_2F_{10}S_2$ (407.16): C, 17.70; H, 2.48; F, 46.66; S, 15.75. Found: C, 17.54; H, 2.39; F, 46.80; S, 15.85.

1-(Pentafluoro-λ⁶-sulfanyl)penta-1,4-diene (5); Typical Procedure

To K_2CO_3 (20 g) in sulfolane (50 mL) contained in a 100 mL round-bottomed flask equipped with a magnetic stirring bar, a dropping funnel, a thermometer and a reflux condenser was added adduct **1** (6.9 g, 0.03 mol) dissolved in sulfolane (10 mL). The mixture was stirred at r.t. for 0.5 h and at 60 °C for 3 h. When the reaction was complete, the crude product was distilled out under vacuum (35–40 °C/1–2 mm Hg), washed with H_2O, and dried ($MgSO_4$). The crude product was purified by column chromatography on silica gel with pentane–$CHCl_3$ (10:2) as eluent; yield: 4.6 g (79.0%); R_f 0.53.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.98 (m, 2 H, CH_2), 5.13 (ddt, 1 H, $J_{H,H}$ = 18.9 Hz, $J_{H,H}$ = 1.4 Hz, $J_{H,H}$ = 1.5 Hz, =CC*H*H), 5.15 (ddt, 1 H, $J_{H,H}$ = 10.4 Hz, $J_{H,H}$ = 1.4 Hz, $J_{H,H}$ = 2.1 Hz, =CCH*H*), 5.78 (ddt, 1 H, $J_{H,H}$ = 10.4 Hz, $J_{H,H}$ = 18.9 Hz, $J_{H,H}$ = 6.4 Hz, CH=), 6.47 (m, 2 H, F_5SCH=CH).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 34.61 (s, CH_2), 118.21 (s, =CH_2), 132.60 (s, CH=), 136.93 (pent, $J_{C,F}$ = 7.0 Hz, F_5SCH=C*H*), 141.30 (dpent, $J_{C,F}$ = 19.6 Hz, $J_{C,F}$ = 1.5 Hz, F_5SCH=).

^{19}F NMR (188.3 MHz, $CDCl_3$): δ = 140.65 (9 lines, 1 F, $J_{F,F}$ = 153.7 Hz), 161.48 (dm, 4 F, $J_{F,F}$ = 153.7 Hz).

Anal. Calcd for $C_5H_7F_5S$ (194.17): C, 30.93; H, 3.63; F, 48.92; S, 16.52. Found: C, 30.80; H, 3.58; F, 49.10; S, 16.61.

1-(Pentafluoro-λ⁶-sulfanyl)hexa-1,5-diene (6)

According to the procedure for the synthesis of **5**, adduct **3** (7.32 g, 0.03 mol) was allowed to react with K_2CO_3 (20 g). Distillation at reduced pressure gave 5.37 g (86% yield) of compound **6**; bp 74–75 °C/60 mm Hg.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.23 (m, 4 H, 2 CH_2), 5.05 (dd, 1 H, $J_{H,H}$ = 10.4 Hz, $J_{H,H}$ = 1.4 Hz, =C*H*H), 5.07 (dd, 1 H $J_{H,H}$ = 17.4 Hz, $J_{H,H}$ = 1.4 Hz, =CH*H*), 5.77 (ddt, 1 H, $J_{H,H}$ = 10.4 Hz, $J_{H,H}$ = 17.4 Hz, $J_{H,H}$ = 6.6 Hz, CH=), 6.44 (m, 2 H, F_5SCH=CH).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 29.71 (s, CH_2), 31.77 (s, CH_2), 116.11 (s, =CH_2), 136.18 (s, CH=), 138.24 (pent, $J_{C,F}$ = 7.1 Hz, F_5SCH=C*H*), 140.71 (dpent, $J_{C,F}$ = 19.5 Hz, $J_{C,F}$ = 1.6 Hz, F_5SCH=).

^{19}F NMR (188.3 MHz, $CDCl_3$): δ = 140.62 (dm, 4 F, $J_{F,F}$ = 153.6 Hz), 160.91 (9 lines, 1 F, $J_{F,F}$ = 153.6 Hz).

Anal. Calcd for $C_6H_9F_5S$ (208.19): C, 34.62; H, 4.36; F, 45.63; S, 15.40. Found: C, 34.60; H, 4.35; F, 45.76; S, 15.50.

2,3-Dichloro-1-(pentafluoro-λ⁶-sulfanyl)butane (7)

According to the procedure for the synthesis of **1**, 3-chlorobut-1-ene (9 g, 0.1 mol) was allowed to react with F_5SCl (17.8 g, 0.11 mol). Distillation at 57 °C/10 mm Hg gave 22.9 g (91%) of compound **7**.

^{1}H NMR (200 MHz, $CDCl_3$): δ (diastereomeric mixture) = 1.62, 1.70 (d, 3 H, $J_{H,H}$ = 7.1 Hz, CH_3), 4.20 (m, 2 H, F_5SCH_2), 4.63 (m, 2 H, 2 CHCl).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ (diastereomeric mixture) = 21.38, 22.19 (s, CH_3), 58.81, 59.06 (pent, $J_{C,F}$ = 1.4 Hz, C*H*ClCH_3), 59.20, 59.59 (pent, $J_{C,F}$ = 4.2 Hz, F_5SCH_2C*H*Cl), 74.39, 75.01 (dpent, $J_{C,F}$ = 14.9 Hz, $J_{C,F}$ = 1.2 Hz, F_5SCH_2).

^{19}F NMR (188.3 MHz, $CDCl_3$): δ (diastereomeric mixture) = 144.21 (dm, 4 F, $J_{F,F}$ = 146.0 Hz), 160.50 (9 lines, 1 F, $J_{F,F}$ = 146.0 Hz).

Anal. Calcd for $C_4H_7Cl_2F_5S$ (253.06): C, 18.99; H, 2.79; F, 37.54; S, 12.67. Found: C, 18.84; H, 2.75; F, 37.68; S, 12.75.

3-Chloro-1-(pentafluoro-λ⁶-sulfanyl)but-1-ene (8)

According to the procedure for the synthesis of **5**, adduct **7** (5.06 g, 0.02 mol) was allowed to react with K_2CO_3 (11 g). Distillation at reduced pressure gave 2.17 g (50%) of compound **8**; bp 58 °C/80 mm Hg.

Compound 8

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.72 (d, 3 H, $J_{H,H}$ = 7.0 Hz, CH_3), 4.59 (dq, 1 H, $J_{H,H}$ = 8.5 Hz, $J_{H,H}$ = 12.0 Hz, CHCl), 6.72 (m, 2 H, F_5SCH=CH).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 24.63 (s, CH_3), 53.39 (s, CHCl), 139.19 (pent, $J_{C,F}$ = 7.1 Hz, F_5SCH=C*H*), 141.74 (dpent, $J_{C,F}$ = 21.2 Hz, $J_{C,F}$ = 1.7 Hz, F_5SCH=).

^{19}F NMR (188.3 MHz, $CDCl_3$): δ = 141.15 (dm, 4 F, $J_{F,F}$ = 146.9 Hz), 159.87 (9 lines, 1 F, $J_{F,F}$ = 146.9 Hz). 159.87 (9 lines, 1 F, $J_{F,F}$ = 146.9 Hz),

Anal. Calcd for $C_4H_6ClF_5S$ (216.60): C, 22.18; H, 2.79; F, 43.86; S, 14.80. Found: C, 22.30; H, 2.83; F, 43.92; S, 14.85.

2,3-Dichlorobut-1-ene (9)

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.75 (d, 3 H, $J_{H,H}$ = 6.6 Hz, CH_3), 4.67 (q, 1 H, $J_{H,H}$ = 6.6 Hz, CHCl), 5.38 (d, 1 H, $J_{H,H}$ = 1.8 Hz, =C*H*H), 5.59 (d, 1 H, $J_{H,H}$ = 1.8 Hz, =CH*H*).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 15.24 (s, CH_3), 47.10 (s, CHCl), 125.06 (s, =CH_2), 134.05 (s, =CCl).

3-Chloro-4-(pentafluoro-λ⁶-sulfanyl)butan-2-ol (10)

According to the procedure for the synthesis of **1**, 3-buten-2-ol (7.2 g, 0.1 mol) was allowed to react with F_5SCl (17.82 g, 0.11 mol). Distillation at 93 °C/12 mm Hg gave 17.8 g (76%) of compound **10**.

^{1}H NMR (200 MHz, $CDCl_3$): δ (diastereomeric mixture) = 1.28 (d, 3 H, $J_{H,H}$ = 7.4 Hz, CH_3), 1.86 (br s, 1 H, OH), 4.00 (m, 2 H, F_5SCH_2), 4.18 (m, 1 H, C*H*OH), 4.31 (m, 1 H, CHCl).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ (diastereomeric mixture) = 18.80, 20.05 (s, CH_3), 60.84, 60.83 (pent, $J_{C,F}$ = 4.0 Hz, CHCl), 68.73, 70.22 (s, CHOH), 73.68, 74.07 (dpent, $J_{C,F}$ = 14.2 Hz, $J_{C,F}$ = 1.0 Hz, F_5SCH_2).

^{19}F NMR (188.3 MHz, $CDCl_3$): δ (diastereomeric mixture) = 144.16 (dm, 4 F, $J_{F,F}$ = 146.1 Hz), 144.22 (dm, 4 F, $J_{F,F}$ = 145.8 Hz), 160.82 (9 lines, 1 F, $J_{F,F}$ = 146.1 Hz), 161.00 (9 lines, 1 F, $J_{F,F}$ = 145.8 Hz).

Anal. Calcd for $C_4H_8ClF_5OS$ (234.62): C, 20.48; H, 3.44; F, 40.49; S, 13.67. Found: C, 20.36; H, 3.37; F, 40.53; S, 13.75.

4-(Pentafluoro-λ⁶-sulfanyl)but-3-en-2-ol (11)

To a mixture of KOH (11.2 g, 0.2 mol) in anhyd Et_2O (100 mL) in a 200 mL flask equipped with a magnetic stirring bar, thermometer and dropping funnel, was added a solution consisting of **10** (11.7 g, 0.05 mol) in anhyd Et_2O (20 mL) dropwise at 20–25 °C. The mixture was stirred at 25–30 °C for 1.5 h, and then was added to H_2O (100 mL). The two layers were separated and the aqueous phase was extracted with Et_2O (3 × 30 mL). The combined organic fractions were dried ($MgSO_4$) and the solvent was evaporated in vacuum and the resulting crude was distilled to give 7.52 g (76%) of compound **11**; bp 71 °C/12 mm Hg.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.39 (d, 3 H, $J_{H,H}$ = 6.6 Hz, CH_3), 1.79 (br s, 1 H, OH), 4.53 (m, 1 H, C*H*OH), 6.53 (ddpent, 1 H, $J_{H,H}$ = 4.4 Hz, $J_{H,H}$ = 14.5 Hz, $J_{H,F}$ = 1.1 Hz, =CH), 6.68 (dpent, 1 H, $J_{H,H}$ = 14.5 Hz, $J_{H,F}$ = 6.5 Hz, F_5SCH=).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 22.61 (s, CH_3), 65.86 (s, CHOH), 139.86 (dpent, $J_{C,F}$ = 20.5 Hz, $J_{C,F}$ = 1.6 Hz, F_5SCH=), 141.39 (pent, $J_{C,F}$ = 6.5 Hz, =CH).

^{19}F NMR (188.3 MHz, $CDCl_3$): δ = 141.16 (dm, 4 F, $J_{F,F}$ = 150.6 Hz), 161.28 (9 lines, 1 F, $J_{F,F}$ = 150.6 Hz).

Anal. Calcd for $C_4H_7F_5OS$ (198.16): C, 24.25; H, 3.56; F, 47.94; S, 16.18. Found: C, 24.33; H, 3.59; F, 47.86; S, 16.10.

1-(Pentafluoro-λ⁶-sulfanyl)but-1,3-diene (12)

The 4-(pentafluoro-λ⁶-sulfanyl)but-3-en-2-ol (**11**; 4.0 g, 0.02 mol) was treated with conc. H_2SO_4 (1 mL) at –20 °C in a 10 mL flask equipped with a magnetic stirring bar, thermometer and connected with the vacuum pump (50 mm Hg) through trap cooled to –196 °C. The mixture was stirred at 40–50 °C for 20 min and at 60–70 °C for 1 h. The liquid from the trap was washed with 10% aq $NaHCO_3$ and H_2O. The organic layer was dried (Na_2SO_4). Distillation at 52 °C/100 mm Hg gave 1.44 g (40%) of compound **12**.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 5.55 (dd, 1 H, $J_{H,H}$ = 10.0 Hz, $J_{H,H}$ = 0.9 Hz, =C*H*H), 5.63 (ddpent, 1 H, $J_{H,H}$ = 16.9 Hz, $J_{H,H}$ = 0.9 Hz, $J_{H,F}$ = 0.9 Hz, =CH*H*), 6.29 (ddd, 1 H, $J_{H,H}$ = 16.9 Hz, $J_{H,H}$ = 10.0 Hz, $J_{H,H}$ = 11.5 Hz, C*H*=CH_2), 6.58 (dpent, 1 H, $J_{H,H}$ = 14.5 Hz, $J_{H,F}$ = 6.7 Hz, F_5SC*H*=CH), 6.88 (ddpent, 1 H, $J_{H,H}$ = 14.5 Hz, $J_{H,H}$ = 11.5 Hz, $J_{H,F}$ = 0.8 Hz, F_5SCH=C*H*).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 126.54 (s, =CH_2), 131.35 (s, C*H*=CH_2), 136.62 (pent, $J_{C,F}$ = 7.5 Hz, F_5SCH=C*H*), 141.74 (dpent, $J_{C,F}$ = 20.4 Hz, $J_{C,F}$ = 1.6 Hz, F_5SCH=).

^{19}F NMR (188.3 MHz, $CDCl_3$): δ = 141.41 (dm, 4 F, $J_{F,F}$ = 149.3 Hz), 161.53 (9 lines, 1 F, $J_{F,F}$ = 149.3 Hz).

Anal. Calcd for $C_4H_5F_5S$ (180.14): C, 26.67; H, 2.80; F, 52.73; S, 17.80. Found: C, 26.65; H, 2.81; F, 52.76; S, 17.82.

3,4-Epoxy-1-(pentafluoro-λ⁶-sulfanyl)but-1-ene (13); Typical Procedure

A solution of *m*-chloroperoxybenzoic acid (3.44 g, 0.02 mol) in CH_2Cl_2 (20 mL) was added to a well-stirred solution of the compound **12** (1.8 g, 0.01 mol) in CH_2Cl_2 (20 mL) at r.t. The reaction mixture was stirred for 2 h at 40 °C and 3 d at r.t. Progress of the reaction was monitored by TLC analysis. The mixture was filtered, and washed with 20% aq Na_2SO_3, and again with 10% aq $NaHCO_3$ and H_2O. The organic layer was dried (Na_2SO_4). Evaporation of the solvent and distillation at 80 °C/60 mm Hg gave 1.76 g (90%) of compound **13**.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.74 (dd, 1 H, $J_{H,H}$ = 2.4 Hz, $J_{H,H}$ = 5.4 Hz, C*H*H), 3.12 (dd, 1 H, $J_{H,H}$ = 5.4 Hz, $J_{H,H}$ = 4.4 Hz, CH*H*), 3.47 (m, 1 H, CH), 6.33 (ddpent, 1 H, $J_{H,H}$ = 6.2 Hz, $J_{H,H}$ = 14.6 Hz, $J_{H,H}$ = 1.2 Hz, F_5SCH=C*H*), 6.79 (dpent, 1 H, $J_{H,H}$ = 14.6 Hz, $J_{H,F}$ = 6.4 Hz, F_5SCH=).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 49.18 (s, CH_2), 49.64 (pent, $J_{C,F}$ = 1.0 Hz, CH), 136.59 (pent, $J_{C,F}$ = 7.0 Hz, F_5SCH=C*H*), 143.13 (dpent, $J_{C,F}$ = 21.6 Hz, $J_{C,F}$ = 1.5 Hz, F_5SCH=).

^{19}F NMR (188.3 MHz, $CDCl_3$): δ = 140.73 (dm, 4 F, $J_{F,F}$ = 150.0 Hz), 160.03 (9 lines, 1 F, $J_{F,F}$ = 150.0 Hz).

Anal. Calcd for $C_4H_5F_5OS$ (196.14): C, 24.50; H, 2.57; F, 48.43; S, 16.35. Found: C, 24.53; H, 2.56; F, 48.40; S, 16.33.

4,5-Epoxy-1-(pentafluoro-λ⁶-sulfanyl)pent-1-ene (14)

According to the procedure for the synthesis of **13**, compound **5** (1.94 g, 0.01 mol) was allowed to react with *m*-chloroperoxybenzoic acid (3.44 g, 0.02 mol). Distillation at 73 °C/25 mm Hg gave 1.85 g (88%) of compound **14**.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 2.37 (m, 1 H, C*H*H), 2.52 (m, 1 H, CH*H*), 2.56 (dd, 1 H, $J_{H,H}$ = 2.6 Hz, $J_{H,H}$ = 4.6 Hz, C*H*H), 2.85 (dd, 1 H, $J_{H,H}$ = 4.6 Hz, $J_{H,H}$ = 4.6 Hz, CH*H*), 3.07 (m, 1 H, CH), 6.56 (m, 2 H, F_5SCH=CH).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ = 32.58 (s, CH_2), 45.84 (s, CH_2), 49.15 (pent, $J_{C,F}$ = 1.0 Hz, CH), 133.36 (pent, $J_{C,F}$ = 7.0 Hz, F_5SCH=C*H*), 141.92 (dpent, $J_{C,F}$ = 20.1 Hz, $J_{C,F}$ = 1.5 Hz, F_5SCH=).

^{19}F NMR (188,3 MHz, $CDCl_3$): δ = 140.21 (dm, 4 F, $J_{F,F}$ = 150.6 Hz), 161.08 (9 lines, 1 F, $J_{F,F}$ = 150.6 Hz).

Anal. Calcd for $C_5H_7F_5OS$ (210.17): C, 28.58; H, 3.36; F, 45.20; S, 15.26. Found: C, 28.62; H, 3.38; F, 45.17; S, 15.24.

5,6-Epoxy-1-(pentafluoro-λ⁶-sulfanyl)hex-1-ene (15)

According to the procedure for the synthesis of **13**, compound **6** (2.08 g, 0.01 mol) was allowed to react with *m*-chloroperoxybenzoic acid (3.44 g, 0.02 mol). Distillation at 87–88 °C/8 mm Hg gave 2.06 g (92%) of compound **15**.

^{1}H NMR (200 MHz, $CDCl_3$): δ = 1.77 (m, 2 H, CH_2), 2.39 (m, 2 H, CH_2), 2.54 (dd, 1 H, $J_{H,H}$ = 2.6 Hz, $J_{H,H}$ = 4.8 Hz, C*H*H), 2.83 (dd, 1 H, $J_{H,H}$ = 4.0 Hz, $J_{H,H}$ = 4.8 Hz, C*H*H), 2.98 (m, 1 H, CH), 6.54 (m, 2 H, F_5SCH=CH).

^{13}C NMR (50.3 MHz, MHz, $CDCl_3$): δ = 27.54 (s, CH_2), 31.19 (pent, $J_{C,F}$ = 1.0 Hz, CH_2), 47.40 (s, CH_2), 51.50 (s, CH), 138.25 (pent, $J_{C,F}$ = 7.0 Hz, F_5SCH=C*H*), 141.49 (dpent, $J_{C,F}$ = 20.0 Hz, $J_{C,F}$ = 1.5 Hz, F_5SCH=).

^{19}F NMR (188.3 MHz, $CDCl_3$): δ = 140.44 (dm, 4 F, $J_{F,F}$ = 150.6 Hz), 161.65 (9 lines, 1 F, $J_{F,F}$ = 150.6 Hz).

Anal. Calcd for $C_6H_9F_5OS$ (224.19): C, 32.15; H, 4.05; F, 42.37; S, 14.30. Found: C, 32.31; H, 4.09; F, 42.30; S, 14.24.

2-Chloro-4,5-epoxy-1-(pentafluoro-λ⁶-sulfanyl)pentane (16)

According to the procedure for the synthesis of **13**, adduct **1** (2.3 g, 0.01 mol) was allowed to react with *m*-chloroperoxybenzoic acid (3.44 g, 0.02 mol). Distillation at 78 °C/5 mm Hg gave 2.21 g (80%) of compound **16**.

^{1}H NMR (200 MHz, $CDCl_3$): δ (diastereomeric mixture) = 1.86–2.96 (m, 2 H, CH_2), 2.91 (dd, 1 H, $J_{H,H}$ = 2.4 Hz, $J_{H,H}$ = 4.4 Hz, C*H*H), 2.90 (dd, 1 H, $J_{H,H}$ = 4.4 Hz, $J_{H,H}$ = 4.8 Hz, C*H*H), 3.24 (m, 1 H, CH), 4.08 (dpent, 2 H, $J_{H,H}$ = 6.4 Hz, $J_{H,F}$ = 8.0 Hz, F_5SCH_2), 4.62 (m, 1 H, CHCl).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ (diastereomeric mixture) = 40.52, 41.35 (pent, $J_{C,F}$ = 0.8 Hz, CH_2), 46.38, 47.80 (s, CH_2), 48.81, 49.57 (s, CH), 53.46, 53.51 (pent, $J_{C,F}$ = 4.6 Hz, CHCl), 76.90 (pent, 13.8 Hz, F_5SCH_2).

^{19}F NMR (188.3 MHz, $CDCl_3$): δ (diastereomeric mixture) = 143.89 (dm, 4 F, $J_{F,F}$ = 143.1 Hz), 144.27 (dm, 4 F, $J_{F,F}$ = 146.9 Hz), 160.54 (9 lines, 1 F, $J_{F,F}$ = 143.1 Hz), 160.74 (9 lines, 1 F, $J_{F,F}$ = 146.9 Hz).

Anal. Calcd for $C_5H_8ClF_5OS$ (246.63): C, 24.35; H, 3.27; F, 38.52; S, 13.00. Found: C, 24.42; H, 3.29; F, 38.43; S, 13.08.

2-Chloro-5,6-epoxy-1-(pentafluoro-λ⁶-sulfanyl)hexane (17)

According to the procedure for the synthesis of **13**, adduct **3** (2.44 g, 0.01 mol) was allowed to react with *m*-chloroperoxybenzoic acid (3.44 g, 0.02 mol). Distillation at 80 °C/2 mm Hg gave 2.08 g (80%) of compound **17**.

^{1}H NMR (200 MHz, $CDCl_3$): δ (diastereomeric mixture) = 1.52–2.29 (m, 4 H, 2 CH_2), 2.54 (dd, 1 H, $J_{H,H}$ = 2.5 Hz, $J_{H,H}$ = 4.6 Hz, C*H*H), 2.83 (dd, 1 H, $J_{H,H}$ = 4.2 Hz, $J_{H,H}$ = 4.6 Hz, C*H*H), 2.96 (m, 1 H, CH), 4.00 (dpent, 2 H, $J_{H,H}$ = 6.2 Hz, $J_{H,F}$ = 8.0 Hz, F_5SCH_2), 4.50 (m, 1 H, CHCl).

^{13}C NMR (50.3 MHz, $CDCl_3$): δ (diastereomeric mixture) = 29.16, 29.70 (s, CH_2), 34.06, 34.69 (pent, $J_{C,F}$ = 1.4 Hz, CH_2), 47.18, 47.33 (s, CH_2), 51.29, 51.80 (s, CH), 55.58, 55.86 (pent, $J_{C,F}$ = 4.5 Hz, CHCl), 73.10 (dpent, $J_{C,F}$ = 0.8 Hz, $J_{C,F}$ = 13.4 Hz, F_5SCH_2).

^{19}F NMR (188.3 MHz, $CDCl_3$): δ (diastereomeric mixture) = 144.1 (dm, 4 F, $J_{F,F}$ = 145.0 Hz), 160.8 (9 lines, 1 F, $J_{F,F}$ = 145.0 Hz).

Anal. Calcd for $C_6H_9ClF_5OS$ (259.65): C, 27.76; H, 3.49; F, 36.58; S, 12.35. Found: 27.84; H, 3.53; F, 36.50; S, 12.31.

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References

(1) (a) Woolf, C. W.; Gard, G. L. US Patent 3448121, **1969**; *Chem. Abstr.* **1970**, *72*, 12547. (b) Allied Chem. Corp.; Brit. Patent 1167112, **1969**; *Chem Abstr.* **1970**, *72*, 21366. (c) Gilbert, E. E.; Gard, G. L. US Patent 3475453, **1969**; *Chem. Abstr.* **2000**, *72*, 20877. (d) Banks, R. E.; Haszeldine, R. N. Brit. Patent 1145263, **1969**; *Chem. Abstr.* **1969**, *70*, 97807. (e) Shepard, W. A. US Patent 3219690, **1965**; *Chem. Abstr.* **1966**, *64*, 43553.

(2) (a) Witucki, E. F.; Frankel, M. B. *J. Chem. Eng. Data* **1979**, *24*, 382. (b) Sitzmann, M. E.; Gilligan, W. H.; Ornellas, D. L.; Thrasher, J. S. *J. Energ. Mater.* **1990**, *8*, 352. (c) Sitzmann, M. E. *J. Fluorine Chem.* **1991**, *52*, 195. (d) Sitzmann, M. E.; Gilardi, R. D. *J. Fluorine Chem.* **1993**, *63*, 203.

(3) Bovin, J. L. Can. Patent 1085875, **1980**; *Chem. Abstr.* **1981**, *94*, 156285.

(4) Case, J. R.; Ray, N. H.; Roberts, H. L. *J. Chem. Soc.* **1961**, 2066.

(5) (a) Verma, R. D.; Kirchmeier, R. L.; Shreeve, J. M. *Adv. Inorg. Chem.* **1994**, *41*, 125. (b) Winter, R.; Gard, G. L. In *Inorganic Fluorine Chemistry: Toward the 21st Century*; Trasher, J. S.; Strauss, S. H., Eds.; ACS Symposium Series 555: Washington DC, **1994**, Chap. 8, 128.

(6) (a) Hudlicky, M. *Oxidation in Organic Chemistry*; American Chemical Society: Washington DC, **1990**. (b) Haines, A. H. *Methods for the Oxidation of Organic Compounds*; Academic Press: New York, **1985**. (c) Dryuk, V. G. *Russ. Chem. Rev.* **1985**, *54*, 986.

(7) Schack, C. J.; Wilson, R. D.; Warner, M. G. *Inorg. Synth.* **1986**, *24*, 8.