Synthesis and Epoxidation of 1,3-, 1,4-, and 1,5-Alkadienes with Pentafluoro-\(\lambda^6\)-sulfanyl (SF\(_5\)) Groups

Valery K. Brel*  
Institute of Physiologically Active Compounds of Russian Academy of Science, Chernogolovka, Moscow region, 142432, Russia  
Fax +7(095)7857024; E-mail: brel@ipac.ac.ru  
Received 29 November 2004; revised 14 January 2005

Abstract: This paper describes a convenient and efficient synthesis of new pentafluoro-\(\lambda^6\)-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 \(^1\)H, \(^19\)F and \(^13\)C NMR spectroscopy data. All products are formed by attack of F\(_5\)S radical on terminal carbon atom, i.e., the studied photochemical reactions are completely regioselective.

The second step of the preparation of alkadienes 5 and 6 is the dehydrochlorination of monoadducts 1 and 3 respectively by heating with K\(_2\)CO\(_3\) in sulfolane at 60 °C during 3 hours (Scheme 2). Elimination of hydrogen chloride was monitored using thin layer chromatography. The formation of 1-pentafluorosulfanyllhexa-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.

We have tried to synthesize 1-pentafluorosulfanylbuta-1,3-diene by a similar two-step approach using photochemical addition of F\(_5\)SCl to unsaturated substrate followed by HCl elimination. For that we have used 3-
chlorination of observed with the increase of reaction time. The dehydro-
tations; elimination of a second HCl molecule is not
dichlorobut-1-ene (\[^{9}\text{SF}_{5}\text{Cl}\] from adduct of hydrogen chloride with \[^{12}\text{K}_{2}\text{CO}_{3}\text{ in DMF or sulfolane}
adduct into the 1,3-diene by elimination of two molecules
vacuum distillation. Unfortunately, transformation of this
formation of the mixture of \[^{8}\text{SF}_{5}\text{Cl}\text{ and }^{10}\text{Cl}\text{ at }^{11}55–60 \, ^{12}\text{C}\text{ leads to elimination of one HCl molecule
at }^{13}55–60 \, ^{14}\text{C}\text{ leads to elimination of one HCl molecule
of 1-pentafluorosulfanylbuta-1,3-diene. But-3-en-2-ol un-
Therefore, we have used another approach to the synthesis
obtained.

![Scheme 3](image)

The formation of dichloride \[^{15}9\text{ in this elimination has been proved by }^{15}\text{H, }^{19}\text{F and }^{13}\text{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 pres-
ure with simultaneous distillation of formed 1,3-diene into a cooled trap. This procedure provided 1-pentafluoro-
sulfanylbuta-1,3-diene (12) in 35–40% yield (Scheme 4).

![Scheme 4](image)

The structures of 1-pentafluorosulfanylhexa-1,5-diene (6), 1-pentafluorosulfanylpena-1,4-diene (5), and 1-pen-
tauflurosulfanylbuta-1,3-diene (12) have been unambigu-
ously proved using \[^{15}\text{H, }^{19}\text{F and }^{13}\text{C NMR spectroscopy. The most useful for this was the }^{13}\text{C NMR spectroscopy. Coupling constants }J_{CC,F}
for the compounds containing pentafluorosulfanyl substit-
ent: }^{15}\delta_{C,1} = 141.74 \text{ (doublet of a pentet, }^{15}J_{C,1,F} = 1.6 \, ^{17}\text{Hz, }^{15}J_{C,2,F} = 20.4 \, ^{18}\text{Hz); }^{15}\delta_{C,2} = 136.62 \text{ (pentet, }^{15}J_{C,2,F} = 7.5 \, ^{19}\text{Hz). }^{15}C-3 \text{ and }^{15}C-4 \text{ are singlets; their chemical shifts are the fol-
owing: }^{15}\delta_{C,3} = 131.35 \text{ (s) and }^{15}\delta_{C,4} = 126.54 \text{ (s). The }^{15}\text{F NMR spectra for compounds 5, 6 and 12 showed no sig-
nificant 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 }^{15}\delta = 140–141,
while the basal fluorines were observed at }^{15}\delta = 160–161, with the typical appearance of the AB\(_1\)-spin system,
^{15}J_{AB} = 144–151 \, ^{20}\text{Hz.}

We have studied the epoxidation of SF\(_5\)-containing unsatu-
rated compounds 5, 6 and 12 by m-chloroperoxybenzoic
acid. After 72 hours, these dienes were converted into monoepoxides 13–15 in 80–90% yields (Scheme 5). Ep-
oxides 14 and 15 were also synthesized from adducts 1
and 3 by a two-step procedure. In the first step, these chlo-
roalkenes 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 exclu-
sively epoxidized. Double bond connected directly to SF\(_5\)
\text{group fails to react with the electrophilic oxidant. This can be explained on account of the significant steric and elec-
tron-withdrawing effects of pentafluorosulfanyl groups.}

Synthesis 2005, No. 8, 1245–1250 © Thieme Stuttgart · New York
The epoxides 13–15 have been characterized by $^1$H, $^{19}$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-λ⁵-sulfanyl (SF₅) 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 SF₅ 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-λ⁵-sulfanyl (SF₅) 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 ($^1$H NMR), 188.3 MHz ($^{19}$F NMR) and 50.3 MHz ($^{13}$C NMR). Chemical shifts for $^1$H 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 CF₃CO₂H. Starting materials penta-1,4-diene, hexa-1,5-diene, 3-chlorobut-1-ene, but-3-en-2-ol, epoxide but-3-en-2-ol, 200 MHz ($^1$H NMR), 188.3 MHz ($^{19}$F NMR) and 50.3 MHz ($^{13}$C NMR) were currently in progress. Applications of 1,3-, 1,4-, and 1,5-alkadienes containing pentafluoro-λ⁵-sulfanyl (SF₅) groups to the synthesis of interesting heterocycles will be reported in due course.

**4-Chloro-5-(pentafluoro-λ⁵-sulfanyl)pent-1-ene (1)**: Typical Procedure

A mixture of penta-1,4-diene (8.16 g, 0.12 mol), F₅SCl (16.2 g, 0.1 mol) and Cl₂CF (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 Cl₂CF 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**

$^1$H NMR (200 MHz, CDCl₃): δ = 2.61 (m, 3 H, CH₃), 3.93 (ddpt, 2 H, Jₕₜ = 8.0 Hz, Jₕₜ = 6.0 Hz, F₅SCCH₃), 4.42 (pent, 1 H, Jₕₜ = 6.0 Hz, CH₂), 5.21 (dd, 1 H, Jₕₜ = 18.1 Hz, Jₕₜ = 1.4 Hz, =CCH₂), 5.23 (dd, 1 H, Jₕₜ = 9.0 Hz, Jₕₜ = 1.4 Hz, =CCH₂), 3.85 (ddt, 1 H, Jₕₜ = 18.1 Hz, Jₕₜ = 9.0 Hz, Jₕₜ = 6.9 Hz, CH₂).
1-(Pentafluoro-5-sulfanyl) penta-1,4-diene (5); Typical Procedure
To K₂CO₃ (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 vacuum (35-40 °C/2-2 mm Hg), washed with H₂O, and dried (MgSO₄). The crude product was purified by column chromatography on silica gel with pentane–CHCl₃ (10:2) as eluent; yield: 4.6 g (79%), Rf 0.53.

¹H NMR (200 MHz, CDCl₃): δ = 2.98 (m, 2 H, CH₃), 5.13 (ddt, 1 H, JCH₃ = 18.9 Hz, JHF = 1.4 Hz, JHH = 1.5 Hz, =CH(CH3)), 5.15 (ddt, 1 H, JCH₃ = 10.4 Hz, JHF = 2.1 Hz, =CH₂(CF3)), 5.78 (ddt, 1 H, JCH₃ = 10.4 Hz, JHF = 18.9 Hz, JHH = 6.4 Hz, CH₂), 6.47 (m, 2 H, F₃SCH=CH).

¹³C NMR (50.3 MHz, CDCl₃): δ = 34.61 (s, CH₃), 118.21 (s, =CH), 132.60 (s, CH₂), 136.93 (pent, JCF = 7.0 Hz, F₃SCH=CH), 141.30 (d, JCF = 19.6 Hz, JCF = 1.5 Hz, F₃SCH=CH).

¹⁹F NMR (188.3 MHz, CDCl₃): δ = 140.40 (d, 9 lines, 1 F, JHF = 153.7 Hz), 161.48 (dm, 4 F, JHF = 153.7 Hz).

Anal. Calcd for C₆H₉F₅S (208.19): C, 34.62; H, 4.36; F, 45.63; S, 13.67. Found: C, 34.60; H, 4.35; F, 45.76; S, 13.60.

2-Chloro-4-(pentafluoro-5-sulfanyl)butan-2-ol (10)
According to the procedure for the synthesis of 3, butan-2-ol (7.2 g, 0.1 mol) was allowed to react with F₃SCl (17.82 g, 0.11 mol). Distillation at 93 °C/12 mm Hg gave 17.8 g (76%) of compound 10.

¹H NMR (200 MHz, CDCl₃): δ = 2.23 (m, 4 H, 2 CH₂), 5.05 (dd, 1 H, JCH₂ = 10.4 Hz, JHF = 1.4 Hz, =CH₂(CH₃)), 5.07 (dd, 1 H, JCH₂ = 17.4 Hz, JHF = 1.4 Hz, =CH₂), 5.77 (ddt, 1 H, JCH₂ = 10.4 Hz, JCH₂ = 17.4 Hz, JHF = 6.6 Hz, CH₂), 6.44 (m, 2 H, F₃SCH=CH).

¹³C NMR (50.3 MHz, CDCl₃): δ = 29.71 (s, CH₂), 31.77 (s, CH₂), 116.11 (s, =CH₂), 136.18 (s, CH₂), 138.24 (pent, JCF = 7.1 Hz, F₃SCH=CH), 140.71 (d, JCF = 19.5 Hz, JCF = 1.6 Hz, F₃SCH=CH).

¹⁹F NMR (188.3 MHz, CDCl₃): δ = 140.62 (dm, 4 F, JHF = 153.6 Hz), 160.91 (9 lines, 1 F, JHF = 153.6 Hz).


2,3-Dichloro-1-(pentafluoro-5-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 F₃SCl (17.82 g, 0.11 mol). Distillation at 57 °C/10 mm Hg gave 22.9 g (91%) of compound 7.

¹H NMR (200 MHz, CDCl₃): δ = 1.62, 1.70 (d, 3 H, JHH = 7.1 Hz, CH₃), 4.20 (m, 2 H, F₃SCH₂), 4.63 (m, 2 H, 2 CH₂).

¹³C NMR (50.3 MHz, CDCl₃): δ = 21.38, 22.19 (s, CH₃), 50.81, 59.06 (pent, JCF = 1.4 Hz, CH₂(CH₃)₂), 59.20, 59.59 (pent, JCF = 4.2 Hz, F₃SCH₂CH₂), 74.39, 75.01 (d, JCF = 14.9 Hz, JCH₂ = 1.2 Hz, F₃SCH₂).

¹⁹F NMR (188.3 MHz, CDCl₃): δ = 144.21 (dm, 4 F, JHF = 146.0 Hz), 160.50 (9 lines, 1 F, JHF = 146.0 Hz).

Anal. Calcd for C₄H₉Cl₂F₅S (225.06): C, 18.89; 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-5-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 K₂CO₃ (11 g). Distillation at reduced pressure gave 2.17 g (50%) of compound 8; bp 58 °C/80 mm Hg.

Compounds 8
¹H NMR (200 MHz, CDCl₃): δ = 1.72 (d, 3 H, JCH₃ = 7.0 Hz, CH₃), 4.59 (dq, 1 H, JHH = 8.5 Hz, JHH = 12.0 Hz, CH₂Cl), 6.72 (m, 2 H, F₃SCH=CH).

¹³C NMR (50.3 MHz, CDCl₃): δ = 24.63 (s, CH₃), 53.39 (s, CH₂), 139.19 (pent, JCF = 7.1 Hz, F₃SCH=CH), 141.74 (d, JCF = 21.2 Hz, JCF = 1.7 Hz, F₃SCH=CH).

¹⁹F NMR (188.3 MHz, CDCl₃): δ = 141.15 (dm, 4 F, JHF = 146.9 Hz), 159.87 (9 lines, 1 F, JHF = 146.9 Hz), 159.87 (9 lines, 1 F, JHF = 146.9 Hz).

Anal. Calcd for C₄H₅ClF₅S (225.06): 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.
1-(Pentafluoro-α-sulfanyl)but-1,3-diene (12)

The 4-(pentafluoro-α-sulfanyl)but-3-en-2-ol (11; 4.0 g, 0.02 mol) was treated with conc. H2SO4 (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 crop tube 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 NaHCO3 and H2O. The organic layer was dried (Na2SO4). Distillation at 52 °C/100 mm Hg gave 1.44 g (40%) of compound 12.

1H NMR (200 MHz, CDCl3); δ = 5.55 (1H, JHH = 10.0 Hz, JHF = 0.9 Hz, CHF = CH2), 5.63 (d, 1H, JHH = 16.9 Hz, JHF = 0.9 Hz, CHF = CH2), 6.29 (dd, 1H, JHH = 16.9 Hz, JHF = 10.0 Hz, JHF = 11.5 Hz, CHF = CH2), 6.58 (d, 1H, JHH = 14.5 Hz, JHF = 6.7 Hz, F5SCH = CH), 6.88 (d, 1H, JHH = 14.5 Hz, JHF = 11.5 Hz, JHF = 0.8 Hz, F5SCH = CH).

13C NMR (50.3 MHz, CDCl3); δ = 126.54 (s, CH2), 131.35 (s, CHF = CH2), 136.62 (pent, JCF = 7.5 Hz, F5SCH = CH), 141.74 (pent, JCF = 20.4 Hz, JCF = 1.6 Hz, F5SCH = CH).

1F NMR (188.3 MHz, CDCl3); δ = 141.41 (dm, 4F, JFJF = 149.3 Hz), 161.53 (9 lines, 1F, JFJF = 149.3 Hz).

Anal. Calcd for C5H7F5OS (210.17): C, 28.58; H, 3.36; F, 45.20; S, 12.35. Found: 27.84; H, 3.53; F, 36.50; S, 12.31.

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

A solution of m-chloroperoxybenzoic acid (3.44 g, 0.02 mol) in CHCl3 (20 mL) was added to a well-stirred solution of the compound 12 (1.8 g, 0.01 mol) in CHCl3 (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 Na2SO4 and again with 10%aq NaHCO3 and H2O. The organic layer was dried (Na2SO4). Evaporation of the solvent and distillation at 80 °C/60 mm Hg gave 1.76 g (90%) of compound 13.

1H NMR (200 MHz, CDCl3); δ = 2.74 (1H, JHH = 2.4 Hz, JHF = 5.4 Hz, CHF = CH2), 3.12 (dd, 1H, JHH = 5.4 Hz, JHF = 4.4 Hz, CHF = CH2), 3.47 (m, 1H, CH), 6.33 (d, 1H, JHH = 6.2 Hz, JHF = 14.6 Hz, JHF = 1.2 Hz, F5SCH = CH), 6.79 (d, 1H, JHH = 14.6 Hz, JHF = 6.4 Hz, F5SCH = CH).

13C NMR (50.3 MHz, CDCl3); δ = 49.18 (s, CH3), 49.64 (pant, JCF = 1.0 Hz, CH), 136.59 (pent, JCF = 7.0 Hz, F5SCH = CH), 143.13 (d, JCF = 21.6 Hz, JCF = 1.5 Hz, F5SCH = CH).

1F NMR (188.3 MHz, CDCl3); δ = 140.73 (dm, 4F, JFJF = 150.0 Hz), 160.03 (9 lines, 1F, JFJF = 150.0 Hz).

Anal. Calcd for C5H7F5OS (210.17): C, 28.58; H, 3.36; F, 45.20; S, 12.35. Found: 27.84; H, 3.53; F, 36.50; S, 12.31.

3,4-Epoxy-1-(pentafluoro-α-sulfanyl)pent-1-ene (14)

According to the procedure for the synthesis of 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.

1H NMR (200 MHz, CDCl3); δ = 2.37 (3H, 1H, CH2), 2.52 (m, 1H, CHF), 2.56 (dd, 1H, JHH = 2.6 Hz, JHF = 4.6 Hz, CHF = CH2), 2.85 (dd, 1H, JHH = 4.6 Hz, JHF = 4.6 Hz, CHF = CH2), 3.07 (m, 1H, CH), 6.56 (m, 2H, F5SCH = CH).

13C NMR (50.3 MHz, CDCl3); δ = 32.58 (s, CH3), 45.84 (s, CH3), 49.15 (pant, JCF = 1.0 Hz, CH), 133.36 (pant, JCF = 7.0 Hz, F5SCH = CH), 141.92 (pant, JCF = 20.1 Hz, JCF = 1.5 Hz, F5SCH = CH).

1F NMR (188.3 MHz, CDCl3); δ = 140.21 (dm, 4F, JFJF = 150.6 Hz), 161.08 (9 lines, 1F, JFJF = 150.6 Hz).

Synthesis 2005, No. 8, 1245−1250 © Thieme Stuttgart · New York

13-, 14-, and 1,5-alkadienes with SF Groups

1249
Acknowledgment

This work was supported by the European Office of Aerospace Research and Development (EOARD # 037004) and International Science and Technology Center (ISTC 2791p). The author thanks Dr. M.D. Vorob’ev for the preparation of the starting compounds.

References


