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Synthesis and reactions of 2-SF_5-butadiene

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Abstract

A stable and storable precursor of 2-SF_5-butadiene, 3-SF_5-3-sulfolene, has been synthesized and its reactivity studied with several olefinic compounds. When SF_5Br is added to sulfolene, 3-bromo-4-SF_5-sulfolane is formed and when reacted further with silver tosylate forms 4-SF_5-2-sulfolene. The 4-SF_5-2-sulfolene undergoes rearrangement with silicic acid to give 3-SF_5-3-sulfolene and when heated forms 2-SF_5-butadiene; in the absence of a dienophile, dimerization does occur. The new 2-SF_5-butadiene is a reactive diene undergoing a Diels–Alder reaction with olefinic sytems such as maleic anhydride, *p*-naphthoquinone, and methyl acrylate.

Keywords: SF_5-butadiene; SF_5-cycloaddition reactions; SF_5-synthon; SF_5-building block

1. Introduction

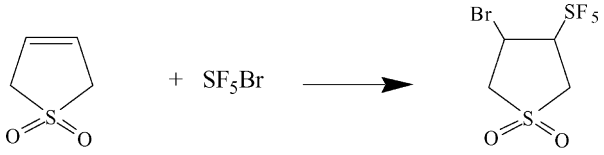
Research in SF_5-organic compounds is currently being carried out in several laboratories through out the world. Organic compounds containing an SF_5-group exhibit a number of useful properties that include increased chemical and thermal stability, increased surface activity, increased dielectric properties and increased energetics, making these compounds of interest in the fields of pharmaceutical chemistry, polymer sciences, explosive studies and electronic applications [1].

Three methods are available to prepare SF_5-compounds [1]: the fluorination of sulfides (for example, AgF_2 with diphenyldisulfide), addition of SF_5-halides to multiple bonds (for example, SF_5Br with ethylene or acetylene) and build-up of complex compounds from SF_5-precursors ($SF_5C_6H_5$ from SF_5Br and diacetoxycyclohexene). The latter method is the least explored but has the greatest potential for generating new and unique SF_5-compounds. This paper describes the synthesis of 3-SF_5-3-sulfolene, a stable and storable precursor of 2-SF_5-1,3-butadiene and its use as a diene in several Diels–Alder reactions. Previously, Diels–Alder reactions have been reported for $SF_5C{\equiv}CH$ [2], $SF_5CF{=}CF_2$ [3], SF_5-cyclopentadiene [4], 1-SF_5-butadiene, β-SF_5-acrylic acid and γ-SF_5-crotonic ester [5,6].

2. Results and discussion

The pathway to 2-SF_5-butadiene involves several stages:

The first step is to add SF_5Br to sulfolene (butadiene sulfone) in CH_2Cl_2; after irradiation with a sunlamp, the product 3-bromo-4-SF_5-sulfolan (**1**) is obtained by evaporation of the volatile materials and re-crystallization from CH_2Cl_2/hexane. It was not possible to carry out this addition reaction via thermal methods:



(**1**)

Treatment of (**1**) in CH_3CN with excess silver tosylate results in three compounds:

4-SF_5-2-sulfolene (**2**), a trace quantity of 3-SF_5-3-sulfolene (**4**), and 4-tosyloxy-2-sulfolene (**3**). The products were separated by column chromatography into a fraction containing (**2**) and (**4**) and another fraction which was pure (**3**):

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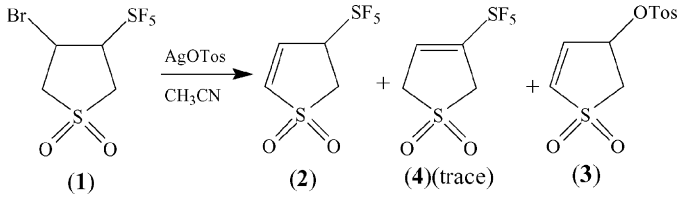
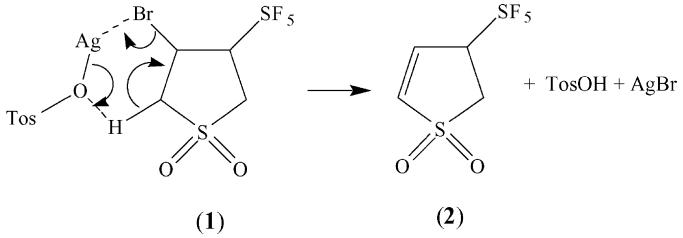
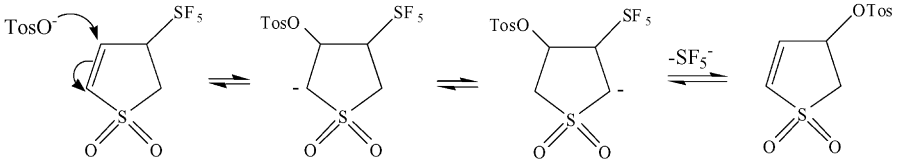


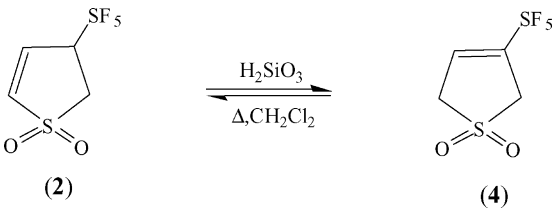
The following mechanisms are proposed for the formation of compounds (**2**) and (**3**):





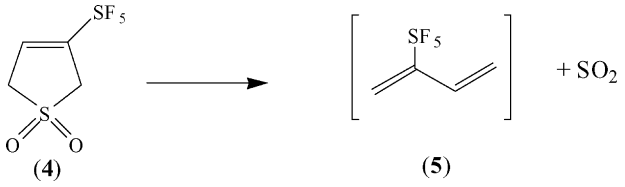
It should be noted that, as was found in this work, silver salt reactions with secondary alkyl halides can proceed by an elimination pathway, instead of a substitution pathway [7]. However, it has been found that *t*-butyl tosylate, obtained by the silver salt method from $(CH_3)_3CCl$, is an unstable compound and at ≈30 °C forms isobutylene and toluenesulfonic acid [8]. In our present paper, it was found that silver salt reactions with the SF_5-containing alkyl halide (**1**) produce only olefinic products; no evidence was found for an ester-stage as was reported in earlier work [9].

The final step for preparing 3-SF_5-3-sulfolene (**4**), the stable precursor to 2-SF_5-butadiene (**5**), is to heat (**2**) with silicic acid in CH_2Cl_2 in a Carius tube to 120 °C for 2 h and then to quickly chill in a −78 °C bath. The isomerization process for 2-sulfolene → 3-sulfolene is normally carried out under basic conditions [10]; these conditions destroyed the SF_5-sulfolene system. A similar decomposition is also found with 3-bromo-4-trichloromethyl sulfolane, formed from $CBrCl_3$ and butadiene sulfone; it is possible in this case to isolate a small amount of the intermediate *exo*-dichloromethylenesulfolene [11]. It was therefore necessary to find a new method to carry out the isomerization of the 4-SF_5-2-sulfolene (**2**). Surprisingly, it was found that silicic acid catalyzes the reaction:

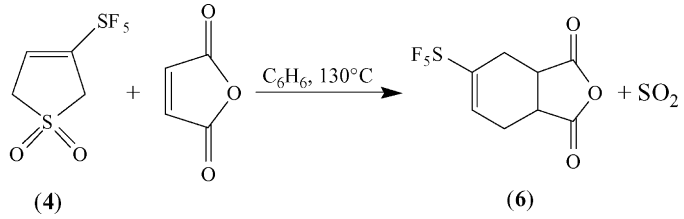


Solvents other than methylene chloride (benzene, ethylenedichloride) are much less desirable; with benzene, slow darkening occurs while with ethylenedichloride the reaction is extremely slow. In methylene chloride no color change is observed. In a much improved method of obtaining (**4**) from (**1**), a small excess (≈10%) of silver acetate in CH_3CN is used; with silver tosylate, despite using a large excess, this isomerization occurred to only a minor extent.

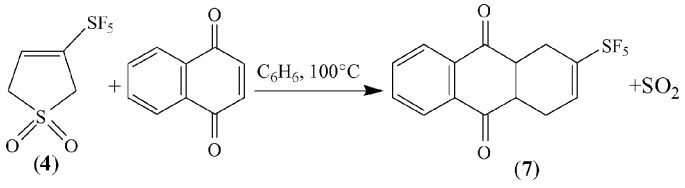
In the final step, heating 3-SF_5-3-sulfolene (**4**) produces the intermediate 2-SF_5-butadiene:



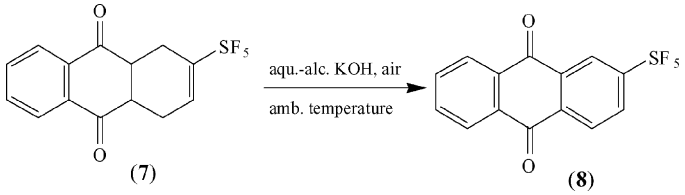
When 3-SF_5-3-sulfolene (**4**) is heated with an olefin, a Diels–Alder product is formed; with maleic anhydride, 4-SF_5-1,2,3,6-tetrahydrophthalic anhydride (**6**) is produced in a quantitative yield:



Likewise, with *p*-naphthoquinone the following adduct (**7**) is formed:



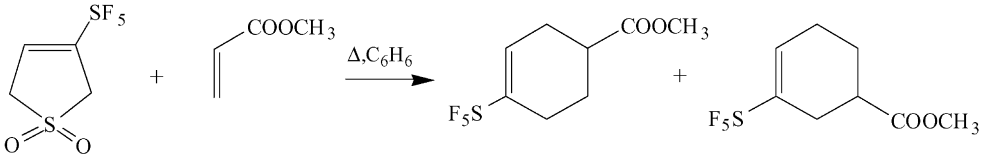
Compound (**7**) apparently exist in several tautomeric forms; it was not isolated but further oxidized in alkaline solution:



There was no reaction found for the 2-SF_5-butadiene and dichloromaleic anhydride; it is interesting to note that a reaction

occurs with butadiene and leads directly to phthalic anhydride [12]. A similar direct aromatization is observed with the diene reaction of 1,4-diacetoxy-butadiene and maleic anhydride [13].

The reaction with methyl acrylate with the SF_5-butadiene (**5**), produced from (**4**), gave the following two isomeric products that could not be separated:



(**4**) (**9**) (**10**)

It was of interest to see if the intermediate (**5**), 2-SF_5-butadiene, could be isolated and characterized. We have found that by heating compound (**4**) in $CDCl_3$ it was possible to obtain (**5**) and obtain its ^1H and ^{19}F NMR spectra and mass spectrum; upon prolonged heating at 135–145 °C in $CDCl_3$ or heating without solvent at 150–170 °C only produced the dimer (**11**). At room temperature, slow dimerization of (**5**) occurs in solution.

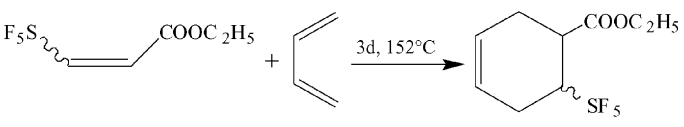
The infrared spectra for all new compounds, except compound (**3**), exhibit strong absorption bands in the 814–893 cm^{-1} range due to the S–F stretching modes of the SF_5-group. One of the SF_5-group deformation modes occurs between 593 and 602 cm^{-1}. The C–H stretching bands were located near 3000 cm^{-1}. For compounds (**1**), (**2**) and (**4**) the asym. and sym. SO_2 stretching modes were found at 1310–1313 and 1130–1145 cm^{-1}, respectively.

The mass spectral peaks contained, for some of the compounds, a parent ion but all compounds have peaks supporting the assigned structures.

The ^1H and ^{19}F NMR spectral data for all new compounds are given in Section 3.

All the compounds, except compound (**3**), show a typical AB_4 splitting pattern in the ^{19}F NMR spectrum for the SF_5-group. The axial fluorine (A) appears as a nine line pattern and is located in the range of 78–86 ppm; the equatorial fluorines (B) appear as a doublet of multiplets in the range of 56–62 ppm. The values for these compounds are in excellent agreement with SF_5-carbon compounds [14].

Some of our early cycloaddition studies centered around the use of SF_5-acrylic esters [15]. In one study, an adduct in low yields (32%) was obtained with an SF_5-acrylic ester (see below). This work was presented at the 17th Winter Fluorine Conference [16]. While this work was in progress, Brel reported that the corresponding SF_5-acid is effective with 2,3-dimethyl-butadiene [5]. A new direction, as reported in this article was taken because of the low yield found in the reaction below:



(**12**)

3. Experimental

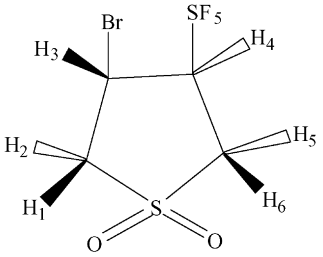
The reactant SF_5Br was prepared from SF_4, BrF_3, Br_2 and CsF via a method previously described by our laboratory [17]. The compounds butadiene sulfone, methylene chloride, acetonitrile, benzene, maleic anhydride, and *p*-naphthoquinone, were purchased from Aldrich Chemicals and were used as received. The silver tosylate reagent was prepared by reacting toluenesulfonic acid and silver oxide in acetontrile at room temperature and in the dark; the product was obtained by evaporation.

The infrared spectra of the reactants and products were obtained on a Perkin-Elmer 2000 FTIR spectrometer operating at 1.0 cm^{-1} resolution using KBr windows. The NMR spectroscopy values were obtained by use of the following instruments: ^{19}F Varian EM-390 (84.7 MHz) and ^1H General Electric (500 MHz) in $CDCl_3$ with CCl_3F and $Si(CH_3)_4$ as internal standards. Gas chromatography–mass spectroscopy (GC–MS) results were obtained using a Hewlett-Packard HP5890 mass selective detector (operating at 70 eV) and a DB5, 30 m column; the temperature profile used was 50 °C for 2 min, then 11 °C min^{-1} up to 280 °C. The HRMS values were determined on a Kratos MS 50TC; chemical ionization with methane. Spectral simulation values were obtained using the ACD/HNMR-Viewer program.

3.1. 3-Bromo-4-SF_5-sulfolan (*1*)

To butadiene sulfone (3.72 g, 31.5 mmol) and methylene chloride (50 ml) in a 100 ml Carius tube, SF_5Br (8.02 g, 38.7 mmol) was vacuum-condensed (−196 °C); the tube was immersed in an ice-bath to a depth of one-half of the liquid level in the Carius tube and irradiated with a sunlamp at a distance of 30 cm for 6 h, while magnetic stirring was maintained. Butadiene sulfone was absent after 6 h; evaporation of the volatile components, re-crystallizing from methylene chloride and hexane solution gave 6.87 g (67%) of a white solid, mp = 81–82 °C.

^1H NMR spectrum ($CDCl_3$, 500 MHz, $Si(CH_3)_4$): $\delta_1 = 3.57$ (d–d, $J_{12} = 14.45$ Hz, $J_{13} = 5.86$, 1H); $\delta_2 = 3.88$ (d–d, $J_{12} = 14.45$, $J_{23} = 7.42$, 1H, H(1), H(2) form an AB-system); $\delta_3 = 4.99$ (d–d–d, $J_{23} = 7.42$, $J_{13} = 5.82$, $J_{34} = 6.25$, 1H); $\delta_4 = 4.85$ (d–d–d–p, $J_{34} = 6.25$, $J_{45} = 7.03$, $J_{46} = 5.9$, $J_{4SF4} = 8.2$, 1H); $\delta_5 = 3.818$, 1H; $\delta_6 = 3.814$ (H(5) + H(6) form an asym. d–d, 2H); additional coupling values and chemical shifts, $J_{45} = 7.03$, $J_{46} = 5.9$, $J_{56} = 0$, $J_{5SF4} = 0.65$, δ_5 and δ_6 were determined by trial and error through the use of a spectral simulation program:



^{19}F NMR spectrum (84.7 MHz, $CDCl_3$, CCl_3F): (AB_4-type) $\delta_A = 81.0$ (nine lines, 1F); $\delta_B = 60.7$ (asym. dm, $J_{AB} = 149$ Hz, 4F).

Infrared spectrum (cm^{-1}): 3024, m–w, br.; 2900, w, sh.; 1407, m–w; 1329, s; 1310, s–vs; 1256, m–s; 1229, w; 1190, w–vw; 1138, s–vs; 971, vw; 918, w–m; 893, m–s; 840, vs; 819, m–s, sh.; 731, w–vs; 706, w–vw; 655, st–vs.

Mass spectrum (ion (*m*/*z*), %, assignment): 259, 261, each <1, $(M - SO_2–H)^+$; 245, 16, $(M - Br)^+$; 197, 199, 6, 6, $(M - SF_5)^+$; 181, 10, $(M - SO_2–Br)^+$; 133, 135, 55, 52, $(M - SO_2–SF_5)^+$; 127, 7, SF_5^+; 117, 12, $(C_4H_5SO_2)^+$; 106, 108, 9, 9, $C_2H_3Br^+$; 89, 18, SF_3^+; 73, 28, C_2HSO^+, $C_3H_5S^+$; 53, 100, $C_4H_5^+$; 39, 22, $C_3H_3^+$; 27, 22, $C_2H_3^+$.

High-resolution mass spectrum—calcd. for $^{12}C_4{}^1H_7{}^{79}Br^{19}F_5{}^{16}O_2{}^{32}S_2$ (*M* + H): 324.89910. Found: 324.89887.

3.2. 4-SF_5-2-sulfolene (**2**)

3-Bromo-4-SF_5-sulfolan (2.86 g, 8.8 mmol), 15 ml of CH_3CN and 13 g of silver tosylate (38.7 mmol added in four portions on consecutive days) were refluxed for 5.5 days. After cooling, the filtrate was diluted with ether to volume of 200 ml, filtered again, evaporated, re-dissolved in 50 ml methylene chloride, re-filtered and evaporated, leaving 2.70 g of a light-beige crystalline solid. The product was chromatographed twice on silica gel (50 g, column diameter 7 cm) with methylene chloride. The sulfolene product eluted first (1.12 g, 52%, mp = 83–85 °C, colorless crystals (**2**)), then a second compound, which is identified as (**3**), 4-tosyloxy-2-sulfolene (0.35 g, 14%, mp = 139.5–140.5 °C).

^{1}H NMR spectrum of (**2**) ($CDCl_3$, 500 MHz, $Si(CH_3)_4$): $\delta_2 = 6.968$; $\delta_3 = 6.950$ $J_{23} \approx 7.5$ Hz, $J_{24} \approx 1$, $J_{34} \approx 2.3$, 2H (m, interpreted as AB-system with close-lying and overlying branches, the appearance of which was approximated by estimating parameters by simulation); $\delta_4 = 5.22$ (m, $J_{4SF4} \approx 7.5$ estd., 1H); $\delta_5 = 3.88$ (d–d, $J_{45} = 5.08$, $J_{56} = 14.45$, 1H); $\delta_6 = 3.68$ (d–d, each line with suggested pentet splitting, $J_{46} = 8.60$, $J_{6SF4} \approx 1$, 1H).

^{19}F NMR spectrum (84.7 MHz, $CDCl_3$, CCl_3F): (AB_4-type) $\delta_A = 81.5$ (nine lines, 1F); $\delta_B = 61.5$ (dm, $J_{AB} = 148$ Hz, 4F).

Infrared spectrum (cm^{-1}): 3099, w; 3047, w; 2994, w; 1415, w–m; 1313, s; 1224, m; 1191, w; 1178, w; 1157, m; 1145, m–s; 1115, m; 1090, m–w–m; 1045, w–m; 969, w–m; 955, w–m; 886, m; 864, sh., m–s; 833, vs; 771, s; 745, m; 726, m; 695, w; 679, w; 657, w–m; 629, w; 611, w–m; 596, m; 571, w; 562, w.

Mass spectrum (ion (*m*/*z*), %, assignment), $R_t = 6.01$ min: 180, 11 $(M - SO_2)^+$; 127, 9, SF_5^+; 117, 59, $(M - SF_5)^+$; 99, 11, $C_4H_3OS^+$; 89, 47, SF_3^+; 68, 12, C_3S^+; 61, 12, $CHOS^+$; 53, 100, $C_4H_5^+$; 51, 14, SF^+, $C_4H_3^+$; 45, 11, CHS^+; 39, 8, $C_3H_3^+$; 27, 24, $C_2H_3^+$.

High-resolution mass spectrum—calcd. for $^{12}C_4{}^1H_6{}^{19}F_5{}^{16}O_2{}^{32}S$ (*M* + H): 244.97234. Found: 244.97924.

3.3. 4-Tosyloxy-2-sulfolene (**3**)

This compound was eluted as the second component in the chromatography of 4-SF_5-2-sulfolene (see above); it appears to be unstable over long periods of time.

^{1}H NMR spectrum ($CDCl_3$, 500 MHz, $Si(CH_3)_4$): for the tosyl group: $\delta = 7.81$ (d, $J = 8.21$ Hz, 2H); $\delta = 7.41$ (d, $J = 8.21$, 2H); $\delta = 2.49$ (s, CH_3).

For the sulfolene portion: $\delta_2 = 6.83$ (d–d, $J_{23} = 6.64$ Hz, $J_{24} = 2.36$, 1H); $\delta_3 = 6.65$ (d–d, $J_{23} = 6.64$, $J_{34} = 2.24$); $\delta_4 = 6.968$ (d–d–d–d, 1H); $\delta_5 = 3.548$ (d–d, $J_{56} = 14.3$ (average), $J_{45} = 7.82$, 1H); $\delta_5 = 3.336$ (d–d, $J_{56} = 14.3$, $J_{46} = 3.90$, 1H).

Mass spectrum (70 eV: ion (*m*/*z*), %, assignment), $R_t = 18.31$ min: 288, 9, M^+; 223, 11, $(M - SO_2–H)^+$; 172, 29, $TosOH^+$; 171, 18, $TosO^+$; 155, 47, Tos^+; 117, 8, $(M - TosO)^+$; 116, 4, $(M - TosOH)^+$; 91, 100, $C_7H_7^+$; 65, 20, HSO_2^+; 53, 13, $C_4H_5^+$; 39, 10, $C_3H_3^+$.

High-resolution mass spectrum—calcd. for $^{12}C_{11}{}^1H_{12}{}^{16}O_5{}^{32}S_2$: 288.01262. Found: 288.01278.

3.4. 3-SF_5-3-sulfolene (**4**)

In a 200 ml round bottomed flask, crude 3-Br-4-SF_5-sulfolan (26.24 g, 80.6 mmole) was dissolved in 100 ml of CH_3CN; the solution was then stirred in an ice-bath for several minutes, and 14.8 g of silver acetate (0.089 mol) was added. Stirring was maintained overnight while room temperature was attained by allowing the ice to melt. After 18 h very little starting material was present, and substantial and roughly equal (by GC–MS) amounts of 3-SF_5-3-sulfolene and 4-SF_5-2-sulfolene were present; 4-Br-2-sulfolene was the major by-product. After heating the mixture for 3.5 h in a boiling-water bath, very little 4-SF_5-2-sulfolene was left and a very strong GC–MS signal of 3-SF_5-3-sulfolene was obtained. The mixture was filtered and the residue washed thoroughly with CH_3CN. The solvent was removed at 35 °C and under vacuum; 15.5 g of crude product was obtained. It was dissolved in ≈0.25 l of CH_2Cl_2, passed through a short column of Kieselgel, dried and crystallized from ether (≈0.4 l, −12 °C). First crystallization, 5.03 g; second crystallization, 1.95 g; total 6.98 g, 35%, mp = 139–140 °C.

^{1}H NMR spectrum (500 MHz, $CDCl_3$, $Si(CH_3)_4$): 1,1′ and 4,4′ are AB-type spectra with pentet coupling to SF_5 and doublet coupling to 3, $\delta_1 = 4.081$; $\delta_{1'} = 4.066$ ($J_{11'} = 2$ Hz, $J_{1SF4} = J_{1'SF4} = 2.5$, br., 2H); $\delta_3 = 6.70$ (br., m, 1H); $\delta_4 = 4.1765$; $\delta_{4'} = 4.1690$ (br. AB-system, 2H). A good simulation of the spectrum was obtained with the above values and further estimated couplings were determined: $J_{3SF4} = 1.4$, $J_{13} = J_{1'3} = 0.7$, $J_{34} = J_{34'} = 0.4$, $J_{44'} = 1.8$, $J_{4SF4} = J_{4'SF4} = 0.2$ Hz.

^{19}F NMR spectrum (84.7 MHz, $CDCl_3$, CCl_3F): $\delta_A = 78.3$ (nine lines, 1F); $\delta_B = 60.0$ (dm, $J_{AB} = 152$ Hz, 4F).

Infrared spectrum (cm^{-1}): 3084, w; 3018, vw–w; 2976, w; 2930, vw–w; 1404, w; 1313, s; 1293, w–m; 1253, m–s; 1240,

m–s; 1130, s; 1058, w–m; 1009, w; 935, vw–w; 908, w; 875, m–s; 838, vs; 814, s–vs; 717, w–m; 703, w–m; 668, w–m; 606, m; 600, m; 577, m.

Mass spectrum (ion (*m*/*z*), %, assignment), R_t = 5.20 min: 180, 39, $(M - SO_2)^+$; 127, 8, SF_5^+; 89, 11, SF_3^+; 72, 40, $(C_3H_3S + H)^+$; 64, 15, SO_2^+; 53, 100, $C_4H_5^+$; 51, 18, SF^+, $C_4H_3^+$; 39, $C_3H_3^+$.

High-resolution mass spectrum—calcd. for $^{12}C_4{}^1H_6{}^{19}F_5{}^{16}O_2{}^{32}S$ (M + H): 244.97234. Found: 244.97160.

3.5. 4-SF_5-1,2,3,6-tetrahydrophthalic anhydride (**6**)

Benzene (10 ml), 3-SF_5-3-sulfolene (**4**) (0.54 g, 2.21 mmol) and maleic anhydride (0.22 g, 2.24 mmol) are heated in a 40 ml Carius tube (three fourths of the Carius tube was immersed in an oil bath) at 130 °C for 5 h; after 5 h no more (**4**) could be detected by GC–MS. The solvent was removed under reduced pressure and the residue pale brown solid, 0.54 g (87%), virtually pure by GC–MS was re-crystallized (much loss) from C_6H_{12} (4 °C), yielding shiny platelets, mp = 115 °C.

^{1}H NMR spectrum ($CDCl_3$, 500 MHz, $Si(CH_3)_4$ = 0): δ_1 = 3.56 (d–d–d, J_{12} = 10.8 Hz, J_{16} = 7.3 (*trans*), $J_{16'}$ = 3.4 (*cis*), 1H); δ_2 = 3.47 (d–d–d, J_{24} = 8.10, J_{23} = 3.3 (*trans*), 1H); δ_3 = 2.560 (d–m, $J_{33'} \approx 16.6$, 1H); $\delta_{3'}$ = 2.910 (d–m, 1H); δ_5 = 6.727 (m, 1H); δ_6 = 2.74 (d–d–d–d, J_{56} = 2.2, J_{36} = 2.2, 1H); $\delta_{6'}$ = 3.19 (d–d, $J_{66'}$ = 16.6, 1H).

^{19}F NMR spectrum (84.7 MHz, $CDCl_3$, CCl_3F): δ_A = 81.9 (nine lines, 1F); δ_B = 56.8 (dm, J_{AB} = 150 Hz, 4F).

Infrared spectrum (cm^{-1}); 3094, vvw; 2989, vw; 2968, vw; 1845, w–m; 1787, m; 1774, m; 1448, w; 1440, w; 1358, vw; 1342, vw; 1312, w; 1242, m; 1208, w–m; 1197, w; 1173, w–m; 1109, vw–w; 1096, w–m; 1080, vw–w; 1015, m; 967, w; 958, m; 946, w; 931, w; 876, m; 860, m; 841, m–s; 833, s; 826, vs; 773, m; 711, w–m; 669, w; 665, w; 650, vw; 626, vw; 602, w; 598, w; 587, w–m; 576, w–m; 567, w.

Mass spectrum (ion (*m*/*z*), %, assignment); R_t = 9.25 min: 258, <1, $(M - HF)^+$; 230, 4, $(M - HF–CO)^+$; 206, 24, $(M - CO–CO_2)^+$; 127, 5, SF_5^+; 122, 27, $(M - SF_5–CO–H)^+$; 105, 12, $C_7H_5O^+$=$C_6H_5CO^+$; 97, 9, $C_4HO_3^+$; 89, 9, SF_3^+; 79, 100, $C_6H_7^+$; 78, 35, $C_6H_6^+$; 77, 55, $C_6H_5^+$; 70, 2, SF_2^+; 51, 11, SF^+; 39.8, $C_3H_3^+$.

High-resolution mass spectrum—calcd: for $^{12}C_8{}^1H_7{}^{19}F_5{}^{16}O_3{}^{32}S$: 278.00362. Found: 278.00417.

3.6. 2-SF_5-anthraquinone (**8**)

3-SF_5-3-sulfolene (2.40 g, 9.8 mmol), *p*-naphthoquinone (1.55 g, 9.9 mmol) and 60 ml of toluene were heated in a 200 ml Carius tube in an oil-bath at 150 °C for 2.5 h and then for 4 h at 160–165 °C. There was very little of the sulfolene left, but extensive tar formation had taken place. The solvent was removed under diminished pressure, the residue containing compound (**7**) taken up in 200 ml of acetone and this solution (homogeneous, wine-red) stirred together with 50 ml (1.0N) KOH, while air was bubbled through the solution. After 2 h, the volume was halved by evaporation, and the solution extracted (3× 100 ml) with ethyl acetate; the combined extracts were brought to a small volume, and the residue passed through a short column of Kieselgel. Re-crystallization of the dried residue from acetone (−11 °C) left 0.54 g (16%) of brownish needles, mp = 182–183 °C.

Infrared spectrum (cm^{-1}): 3101, w; 3085, w; 3079, w; 3042, w; 3012, vw; 1677, s; 1590, m; 1332, m; 1320, m; 1295, s; 1267, w–m; 1175, w–m; 1130, vw; 1119, w; 1082, w–m; 965, s; 934, w; 924, w; 840, b, vs with sh. at 865; 793, vs; 726, m; 711, s; 696, w–m; 662, m; 645, m; 632, w–m; 598, m; 583, w–m; 573, w.

^{1}H NMR spectrum ($CDCl_3$, 500 MHz, $Si(CH_3)_4$): δ_1 = 8.697 (d, 1H); δ_3 = 8.163 (d, d, J_{13} = 2.30 Hz, J_{34} = 8.40, 1H); δ_4 = 8.424 (d, br., 1H); δ_5 = 8.358; δ_8 = 8.341 (m, overlapping H5 with H8, 2H); δ_6 = 7.878; δ_7 = 7.876 (m, overlapping H6 with H7, $J_{56} = J_{78}$ = 8.2, J_{58} = 0.4, J_{67} = 10.6, 2H).

^{19}F NMR spectrum (84.7 MHz, $CDCl_3$, CCl_3F): δ_A = 80.8 (nine lines, 1F); δ_B = 61.66 (dm, J_{AB} = 152 Hz).

Mass spectrum (ion (*m*/*z*), %, assignment), R_t = 13.78 min: 334, 100, M^+; 206, 30, $(M - CO)^+$; 207, 25, $(M - SF_5)^+$; 198, 41, $(M - 5F–CO–CH)^+$; 179, 24, $(M - SF_5–CO)^+$; 170, 42, $(M - 5F–2CO–CH)^+$; 151, 83, $C_5H_2SF_3^+$, $C_2SF_5^+$; 150, 56, $C_5HSF_3^+$; 127, 1, SF_5^+; 125, 8, $C_3SF_3^+$; 99, 14, $C_8H_3^+$; 89, 12, SF_3^+; 85, 16, C_7H^+; 76, 14, $C_6H_4^+$; 75, 32, $C_6H_3^+$; 73, 10, C_6H^+; 51, 4, SF^+, $C_4H_3^+$; 50, 7, $C_4H_2^+$; 28, 4, CO^+.

High-resolution mass spectrum—calcd: for $^{12}C_{14}{}^1H_8{}^{19}F_5{}^{16}O_2{}^{32}S$ (M + H): 335.01652. Found: 335.01736.

3.7. Reaction of sulfolene (**4**) with methyl acrylate preparation of (**9**) and (**10**)

Sulfolene **4** (0.33 g, 1.3 mmol), benzene (10 ml), hydroquinone (14 mg) and methyl acrylate (0.39 g, 4.5 mmol) are heated in a 30 ml Carius tube in an oil bath at 125–135 °C for 4 h. The benzene is distilled away at atmospheric pressure and the residue was taken up in 2 ml of methylene chloride; this solution was passed through 2 g of Kieselgel, and after evaporation, 0.24 g of a colorless oil (65%) remained; an isomeric mixture of compounds (**9**) and (**10**).

Mass spectrum (ion (*m*/*z*), %, assignment), only one band eluted, R_t = 5.92 min: 235, 10, $(M - CH_3O)^+$; 207, 8, $(M - COOCH_3)^+$; 138, 21, $(M - SF_5–H)^+$; 127, 1, SF_5^+; 110, 19, $C_6H_6S^+$; 107, 12, $C_6H_7CO^+$; 95, 5, $C_5H_3S^+$; 89, 3, SF_3^+; 79, 100, $C_6H_7^+$; 59, 20, $COOCH_3^+$; 51, 2, SF^+; 39, 4, $C_3H_3^+$.

^{1}H NMR spectrum (500 MHz, $CDCl_3$, $Si(CH_3)_4$): series of multiplets from δ = 1.7 to 2.85 (asym., m at 6.52 and two singlets at δ = 3.718 and 3.724, ratio 3:4).

^{19}F NMR spectrum (84.7 MHz, $CDCl_3$, CCl_3F): two signals, evident in the A-portion of the AB_4-spectra: δ_{A1} = 85.12, δ_{A2} = 85.02 (nine lines), respectively, area A1:A1 ≈ 4:3; $\delta_{B1} = \delta_{B2}$ = 55.8 (dm); area A:B = 1:4; $J \approx 148$ Hz in both cases.

Infrared spectrum (cm^{-1}): 3088, vvw; 3001, vw; 2958, w–m; 2871, w; 2850, w; 1740, vs; 1457, w–m, sh.; 1440, m; 1382, w; 1365, w; 1323, w–m; 1311, w–m; 1256, w–m; 1250, m; 1197, m; 1175, m; 1152, w–m, sh.; 1076, w; 1030, w; 1000, w;

985, w; 943, w–m; 832, vs; 814, vs; 774, w–m; 728, w–m; 656, m; 595, m; 560, m; 575, w–m, sh.

3.8. Synthesis of 2-SF_5-butadiene (**5**) and its dimer (**11**)

3.8.1. Synthesis of monomer and dimer

Into a 30 ml Carius tube, 0.50 g of compound (**4**) and 8.5 g of $CDCl_3$ are added and heated at 135–145 °C for 110 h; during the heating period, samples are taken at 8, 20, 40 and 110 h. An analysis of these samples by GC–MS shows a decrease in the starting compound (**4**) and the increase in the monomer (**5**) and dimer (**11**). After 110 h, essentially only the dimer was present and isolated by vacuum transfer. During the first 20 h the GC–MS shows that a large amount of the monomer (**5**) is formed; an aliquot is taken for NMR analysis. In this manner it was possible to determine the proton and fluorine NMR values of the monomer (**5**).

^{1}H NMR spectrum of monomer (500 MHz, $CDCl_3$, $Si(CH_3)_4$): $\delta_{11'} = 5.8$ ppm (m (narrow), 2H); $\delta_3 = 6.42$ (dd, 1H, $J_{trans} = 17.1$ Hz, $J = 11.0$); $\delta_4 = 5.61$ (d, 1H, $J_{trans} = 17.1$ Hz); $\delta_{4'} = 5.34$ (d, 1H, $J = 11.0$, $J_{44'} = 0$ Hz).

^{19}F NMR spectrum of monomer (84.7 MHz, $CDCl_3$, CCl_3F): $\delta_A = 82.5$ (nine lines, 1F); $\delta_B = 58.0$ (dm, 4F, $J_{AB} = 149$ Hz).

Mass spectrum of monomer (ion (*m*/*z*), %, assignment): $R_t = 1.5$ min; 180, 11, M^+; 127, 13, SF_5^+; 89, 2, SF_4^+; 84, 12, $C_4H_4S^+$; 72, 23, $C_3H_4S^+$; 70, 7, SF_3^+; 53, 100, $C_4H_5^+$; 52, 15, $C_4H_4^+$; 51, 30, $C_4H_3^+$; 50, 20, $C_4H_2^+$; 49, 7, C_4H^+; 39, 4, $C_3H_3^+$; 27, 20, $C_2H_3^+$.

In addition to generating the dimer in solution (see above) it is possible by heating (**4**) neat to form the dimer: Into a 30 ml Carius tube, 0.50 g of compound (**4**) was added and heated to 150–170 °C for 2 h. The Carius tube was opened at room temperature and vented (loss of SO_2); 0.33 g of a viscous light orange-brown liquid was transferred from the tube.

^{1}H NMR spectrum of dimer (500 MHz, $CDCl_3$, $Si(CH_3)_4$): a series of multiplets from $\delta = 1.4$ to 3.0 ppm; three pairs of olefinic protons centered at $\delta = 5.6$, 6.0, 6.5 ppm.

^{19}F NMR spectrum of dimer (84.7 MHz, $CDCl_3$, CCl_3F): $\delta_{A123} = 84.7$, 83.9, 83.8 ppm, nine lines, 1F; $\delta_B = 56.1$, 56.4 (overlapping, dm, 4F).

Infrared spectrum of dimer (cm^{-1}): 2961, w; 2935, w; 2868, vw; 2843, vvw; 1645, w; 1457, w; 1443, m; 1431, m; 1394, vw; 1364, vw; 1356, vw; 1329, w; 1254, vw; 1231, w; 1200, w; 1157, wm; 1128, vw; 1109, vw; 1019, w; 977, w; 952, s with sh. at 941; 829, b, vs with sh. at 878 and 812; 750, ms; 737, s; 659, s; 638, m; 593, s; 580, ms, with sh. at 565; 535, vw; 519, w.

Mass spectrum of dimer (ion (*m*/*z*), %, assignment), two bands, $R_t = 5.20$ and 6.00 min (at 100 °C and 2 min): 360, <1, M^+; 318, 3, $(M - C_3H_6)^+$; 233, 21, $(M - SF_5)^+$; 205, 15, $(M - SF_5–C_2H_3)^+$; 185, 11, $(M - SF_6–C_2H_2–HF)^+$; 125, 38, $C_3SF_3^+$; 106, 36, $(M - 2SF_5)^+$; 105, 92, $(M - 2SF_5–H)^+$; 97, 52, $C_5H_5S^+$; 91, 39, $C_7H_7^+$; 79, 79, $C_6H_7^+$; 78, 34, $C_6H_6^+$; 77, 64, $C_6H_5^+$, $C_2H_2SF^+$; 72, 100, $C_3H_4S^+$; 53, 90, $C_4H_5^+$; 39, 30, $C_3H_3^+$; 27, 18, $C_2H_3^+$.

3.8.2. Cis/trans-ethyl-2-SF_5-4-cyclohexenecarboxylate (**12**)

Into a dry steel bomb equipped with a Whitey stainless-steel value, $SF_5CH{=}CHC(O)OEt$ (2.09 g, 9.25 mmol), hydroquinone (0.090 g), and benzene (10 ml) were added; butadiene (2.41 g, 44.63 mmol) was then added to the evacuated and cooled bomb (−196 °C). The mixture was heated to 135–145 °C for 21 days; GC–MS analysis confirmed the presence of two isomeric adducts. The reaction mixture was distilled and the product boiling at 60 °C/5 Torr was collected; the product was further purified by column chromatography on silica gel with CH_2Cl_2. The *cis*/*trans* colorless liquid product, 0.83 g was obtained in 32% yield. This reaction was not further studied because of the low yield.

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