Available online at www.sciencedirect.com
ScienceDirect
Journal of Fluorine Chemistry 128 (2007) 862–867
JOURNAL OF FLUORINE CHEMISTRY
www.elsevier.com/locate/fluor

Synthesis of new pentafluorosulfanylacrylates ($F_5SCH{=}CHCHO$, $F_5SCH{=}CHCN$, $F_5SCH{=}CHCOOCH_3$) and use of them as dienophiles in Diels-Alder reaction

Valery K. Brel *

Institute of Physiologically Active Compounds of Russian Academy of Science, Chernogolovka 142432, Moscow Region, Russia

Received 9 March 2007; received in revised form 7 April 2007; accepted 9 April 2007
Available online 19 April 2007

Abstract

New pentafluoro-λ^6-sulfanylacrylates ($F_5SCH{=}CHCHO$, $F_5SCH{=}CHCN$, $F_5SCH{=}CHCOOCH_3$) were synthesized by a convenient and efficient method. These compounds are useful as intermediates in the preparation of pentafluoro-λ^6-sulfanyl-containing cyclic and heterocyclic Diels-Alder cycloadducts.

Keywords: Alkenes; Diels-Alder; Fluorine; Sulfur

1. Introduction

Fluorinated acrylates have been widely used as building blocks in organic synthesis for construction of organic compounds and polymers. Though a great many number of fluorinated acrylates are known only a limited number containing the SF_5-group have been reported. The first SF_5-containing acrylates and its polymers in which the SF_5 is present in the acid moiety were synthesized at the end of 90 years [1–4]. At the same time, the methods for the synthesis of acrylates with pentafluorosulfanyl group in unsaturated moiety are still limited. Only in 2004, did Gard and coworkers report the preparation of esters of β-SF_5-acrylic and methacrylic acids [5]. More recently, in our laboratories, we have used new approach for synthesis of SF_5-containing unsaturated compounds and for the first time were synthesized the $F_5SCH{=}CHCOR$ (R=OH, CH_3) [6].

As a part of our interest in the development of synthetic methods for organic compounds with the pentafluorosulfanyl substituent, we synthesized of SF_5-containing acrylates that had not been described previously and used them for construction of cyclic, bicyclic and heterocyclic compounds. In this paper, the synthesis of $F_5SCH{=}CHR$ (CHO, CN, $COOCH_3$) and their use as Diels-Alder synthons for preparing F_5S-cyclic adducts are presented.

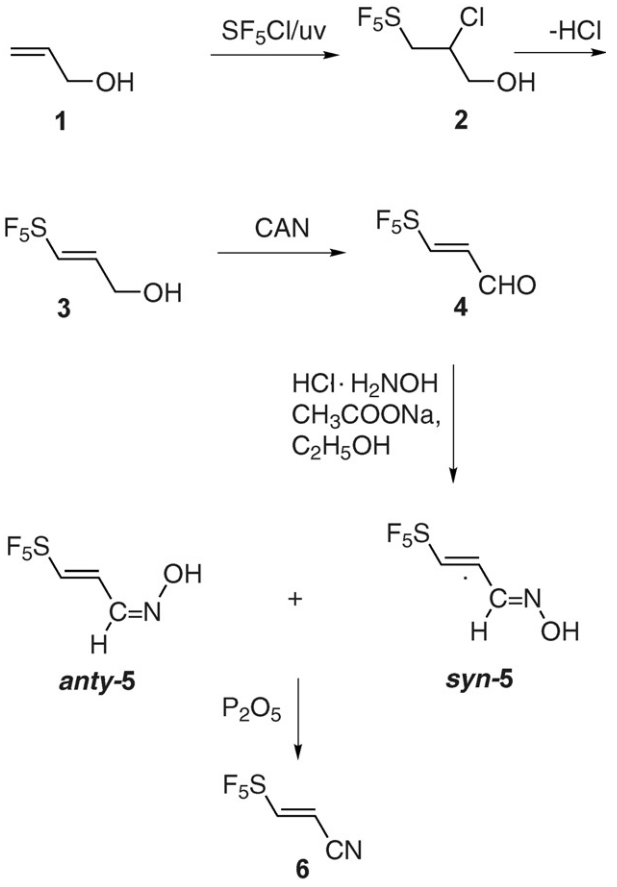
2. Results and discussion

As the starting compounds in the synthesis of pentafluorosulfanyl-containing dienophiles we used 1-pentafluorosulfanylprop-1-en-3-ol (**3**) [7,8]. Compound **3** were prepared in two-steps, the first step was the photo-induced radical addition of pentafluorosulfanyl chloride [9] to the allyl alcohol (**1**) leading to the formation of adduct **2**. Dehydrochlorination of **2** with potassium hydroxide gave **3** with good yield. The primary alcohol **3** was oxidized by CAN (cerium (IV) ammonium nitrate) [6,10] to afford *trans*-3-(pentafluoro-λ^6-sulfanyl)prop-2-enal (**4**) obtained as a colourless liquid in 90% yield after vacuum distillation by (Scheme 1).

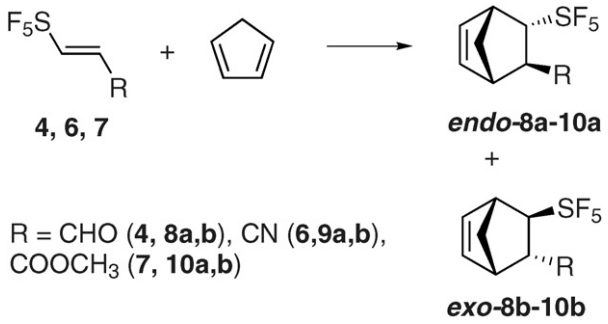
When aldehyde **4** was reacted with a hydroxylamine [11] the *trans*-3-(pentafluoro-λ^6-sulfanyl)prop-2-enal oxime (**5**) was obtained as a mixture of *syn*- and *anty*-isomers (1:1 ratio), which were separated by flash chromatography on silica gel. The final step of synthesis of *trans*-1-cyan-2-(pentafluoro-λ^6-sulfanyl)-ethen was dehydration of oxime **5** with used phosphorus pentoxide. We have found that removing the nitrile **6** from the reaction mixture increases the yield of target product. Hence, the reaction was performed under reduced pressure with simultaneous distillation of formed nitrile **6** into a

* Tel.: +7 496 5242539; fax: +7 496 5249508.
E-mail address: brel@ipac.ac.ru.

0022-1139/$ – see front matter © 2007 Elsevier B.V. All rights reserved.
doi:10.1016/j.jfluchem.2007.04.013



Scheme 1.



Scheme 2.

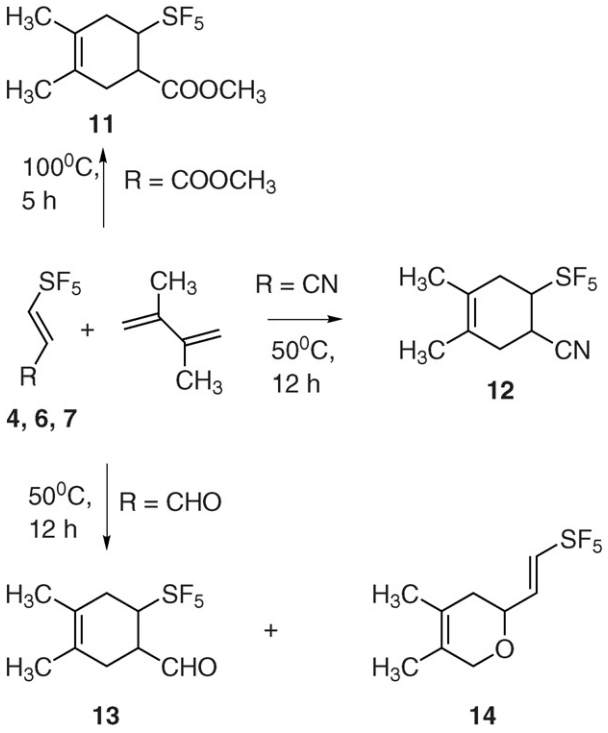
cooled trap. This procedure provided *trans*-1-cyan-2-(pentafluoro-λ^6-sulfanyl)-ethen **6** with 56% yield.

The structures of *trans*-3-(pentafluoro-λ^6-sulfanyl)prop-2-enal **4**, *syn*- and *anty*-isomers of *trans*-3-(pentafluoro-λ^6-sulfanyl)prop-2-enal oxime **5**, and *trans*-1-cyan-2-(pentafluoro-λ^6-sulfanyl)-ethen **6** have been unambiguously proved using ^{1}H, ^{19}F and ^{13}C NMR spectroscopy. The most useful for this was of the ^{13}C NMR spectroscopy. Coupling constants J_{CF} of carbon atom connected directly to F_5S group as well as J_{CF} of atom C(2) are characteristic to the compounds containing pentafluorosulfanyl substituent: $\delta_{C(1)}$ = 141.74 ppm, doublet of a pentet, $J_{C(1)-F'}$ = 1.6 Hz, $J_{C(1)-F}$ = 20.4 Hz; $\delta_{C(2)}$ = 136.62 ppm, pentet, $J_{C(2)-F}$ = 7.5 Hz. The ^{19}F NMR spectra for compounds **4**, **5** and **6** 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 140–141 ppm, while the basal fluorines were observed at 160–161 ppm, with the typical appearance of the AB4-spin system, J_{AB} = 144–151 Hz [6,12].

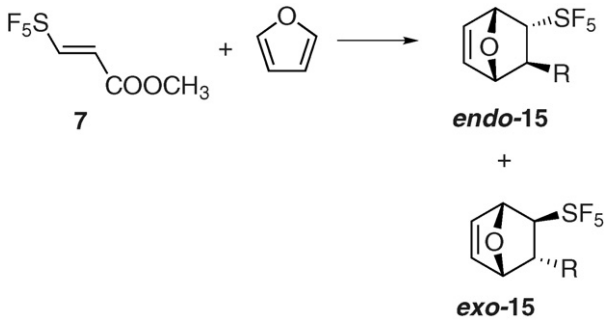
Compounds **7** and **8** participated in Diels-Alder cycloaddition reactions to yield F_5S-containing adducts. They react readily with both aliphatic and cyclic electron-releasing dienes with the formation of Diels-Alder cycloadducts **8–14** as mixture of *endo* and *exo*-isomers. For example, the reaction was performed by heating a mixture of dienophiles **4**, **6**, **7** with cyclopentadiene (10 equiv) under a nitrogen atmosphere in closed glass ampoules at 50 °C for **4**, **6** and at 110 °C for methyl ester **7** (Scheme 2).

After 10 h, ^{1}H NMR analysis showed that the reaction mixture contained the starting material cyclopentadiene, the dimer of cyclopentadiene, and the new compounds **8–10** as a mixture of *endo*- and *exo*-isomers (2.5:1 ratio) (Scheme 2). The reaction products were then separated by preparative column chromatography. Both *endo*-adducts **8a–10a** and both *exo*-adducts **8b–10b** were isolated in pure form. Reaction of 2,3-dimethylbutadiene with compounds **4**, **7** (at 110 °C and 50 °C, respectively) led to adducts **11** and **12** (Scheme 3). In contrast to β-SF_5-acrylates **6** and **7**, *trans*-3-(pentafluoro-λ^6-sulfanyl)-prop-2-enal **4** formed both Diels-Alder adduct 13 and *hetero*-Diels-Alder adduct **14** [13], under similar reaction conditions.

Heterocyclic compounds containing the SF_5 substituent are a class of compounds that can be interesting with regard to potential biological activity. At the same time, the methods for



Scheme 3.



Scheme 4.

the synthesis of heterocyclic compounds with pentafluorosulfanyl group are still limited [14–16]. Well know, that furans undergo Diels-Alder reactions with strong dienophiles and generally afford *exo*-cycloadducts which are thermodynamically more stable than the kinetically favored *endo*-adducts [17]. We have shown that reaction of furan with methyl ester **7** led to *hetero*-adduct **15** as a mixture of *endo*- and *exo*-isomers (3:1 ratio) (Scheme 4).

3. Experimental

3.1. General

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 CF_3COOH. Column chromatography on silica gel was performed with Fluka Silica gel 60 (0.035–0.070 mm). Preparative TLC was performed on Fluka Silica gel/TLC-cards (20 cm × 20 cm × × 0.2 cm). All reagents were of commercial quality or were purified before use. Organic solvents were purified and dried by standard procedures.

3.2. *trans*-3-(Pentafluoro-λ^6-sulfanyl)prop-2-enal (**4**)

A mixture of 3-pentafluorosulfanylprop-2-en-1-ol **3** (1.68 g, 0.01 mol) and ammonium cerium (IV) nitrate (25.11 g, 0.045 mol) in 50% solution of acetic acid (50 mL) was stirred at 85–90 °C 0.5 h. After the orange cerium (IV) solution had turned to a pale yellow cerium (III) solution containing a small amount of cerium (IV), the product mixture was extracted with ether. The ether solution was washed with 5% potassium hydroxide and dried. Removal of the ether and distillation at 74–75 °C/85 mm Hg, gave 1.5 g (90%) pure aldehyde **4**.

^{1}H NMR spectral data (200 MHz, $CDCl_3$): δ 6.75 (1H, dd, J_{HH} = 15.2 Hz, J_{HH} = 6.8 Hz, =C*H*CHO), 7.36 (1H, dquin, J_{HH} = 15.2 Hz, J_{HF} = 6.2 Hz, =CHSF$_5$), 9.71 (1H, d, J_{HH} = 6.8 Hz, CHO); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 134.26 (quin, J_{CF} = 6.0 Hz, =*C*HCHO), 157.61 (dquin, J_{CF} = 1.6 Hz, J_{CF} = 23.1 Hz, =CHSF$_5$), 189.72 (s, C=O); ^{19}F NMR (188.3 MHz, $CDCl_3$): δ 140.39 (4F, dm, J_{FF} = 146.6 Hz), 156.11–156.51 (1F, 9 lines). Anal. Calcd. for $C_3H_3F_5OS$ (182.112): C, 19.79; H, 1.66; F, 52.16. Found: C, 19.61; H, 1.74; F, 52.08.

3.3. *trans*-3-(Pentafluoro-λ^6-sulfanyl)prop-2-enal oxime (***syn-5***, ***anty-5***)

A mixture of 4.55 g (0.025 mol) of *trans*-3-(pentafluoro-λ^6-sulfanyl)prop-2-enal, 5.52 g (0.8 mol) of hydroxylamine hydrochloride, and 10.88 g (0.8 mol) of sodium acetate trihydrate in 70 mL of absolute ethanol was refluxed for 45 min, and then ca. 60 mL of ethanol was removed in vacuum at 25°. The residue was added to 100 mL of ice water and the product was extracted with 35 mL of methylene chloride. The extract was dried and concentrated to leave 4.45 g of oil which was purified by column chromatography on silica gel.

3.3.1. *syn*-Isomer

^{1}H NMR spectral data (200 MHz, $CDCl_3$): δ 6.83 (1H, dquin, J_{HH} = 15.0 Hz, J_{HF} = 6.0 Hz, =CHSF$_5$), 7.02 (1H, ddquin, J_{HH} = 15.0 Hz, J_{HH} = 9.4 Hz, J_{HF} = 1.4 Hz, =C*H*CHNOH), 7.79 (1H, d, J_{HH} = 9.4 Hz, C*H* =NOH), 8.61 (1H, br.s, OH); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 130.74 (quin, J_{CF} = 7.5 Hz, =CH–), 146.64 (dquin, J_{CF} = 1.0 Hz, J_{CF} = 22.6 Hz, =CHSF$_5$), 147.15 (s, CH=NOH); ^{19}F NMR (188.3 MHz, $CDCl_3$): δ 140.82 (4F, dm, J_{FF} = 150.4 Hz), 157.53–160.74 (1F, 9 lines). Anal. Calcd. for $C_3H_4F_5NOS$ (197.127): C, 18.28; H, 2.05; F, 48.19. Found: C, 28.39; H, 2.10; F, 48.02.

3.3.2. *anty*-Isomer

^{1}H NMR spectral data (200 MHz, $CDCl_3$): δ 6.91 (1H, dquin, J_{HH} = 15.0 Hz, J_{HF} = 6.4 Hz, =CHSF$_5$), 7.20 (1H, d, J_{HH} = 9.4 Hz, C*H*=NOH), 7.56 (1H, ddquin, J_{HH} = 15.0 Hz, J_{HH} = 9.4 Hz, J_{HF} = 1.5 Hz, =C*H*CHNOH), 8.50 (1H, br.s, OH); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 122.92 (quin, J_{CF} = 6.5 Hz, =CH−), 143.49 (s, CH=NOH), 148.08 (dquin, J_{CF} = 1.5 Hz, J_{CF} = 21.6 Hz, =CHSF$_5$); ^{19}F NMR (188.3 MHz, $CDCl_3$): δ 140.80 (4F, dm, J_{FF} = 150.4 Hz), 156.90–160.12 (1F, 9 lines). Anal. Calcd. for $C_3H_4F_5NOS$ (197.127): C, 18.28; H, 2.05; F, 48.19. Found: C, 28.20; H, 2.02; F, 48.31.

3.4. *trans*-1-Cyan-2-(pentafluoro-λ^6-sulfanyl)-ethen (**6**)

The *trans*-3-(pentafluoro-λ^6-sulfanyl)prop-2-enal oxime (3.34 g, 0.02 mol) were treated with P_2O_5 (8.5 g, 0.06 mol) at −30 °C in a 20 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 80–90 °C for 30 min. The liquid from trap was distillation at 100 °C (50 mm Hg) gave 2.90 g of liquid. Distillation at 68–69 °C/85 mm Hg, gave (56% yield) of compound **6**.

^{1}H NMR spectral data (200 MHz, $CDCl_3$): δ 6.30 (1H, dquin, J_{HH} = 15.4 Hz, J_{HF} = 1.4 Hz, =CHCN), 7.33 (1H, dquin, J_{HH} = 15.4 Hz, J_{HF} = 6.2 Hz, = CHSF$_5$); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 108.78 (quin, J_{CF} = 8.6 Hz, =*C*HCN), 112.78 (s, CN), 157.39 (dquin, J_{CF} = 2.0 Hz, J_{CF} = 24.1 Hz, =CHSF$_5$); ^{19}F NMR (188.3 MHz, $CDCl_3$): δ 139.71 (4F, dm,

J_{FF} = 146.6 Hz), 152.90–158.14 (1F, 9 lines). Anal. Calcd. for $C_3H_2F_5NS$ (179.112): C, 20.12; H, 1.13; F, 53.03. Found: C, 20.30; H, 1.28; F, 53.21.

3.5. trans-Methyl 3-(pentafluoro-λ^6-sulfanyl)prop-2-enate (7)

Solution of F_5SCH =CHCOOH (1.98 g, 0.01 mol), MeOH (10 mL), and H_2SO_4 (2–3 drops) was heated for 6 h. To reaction mixture was added H_2O (50 mL). The two layers were separated and the aqueous phase was extracted with Et_2O (3 mL × 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 1.7 g (80% yield) of compound **7**; bp 75–78 °C/65 mm Hg.

^{1}H NMR spectral data (200 MHz, $CDCl_3$): δ 3.85 (3H, s, CH_3), 6.58 (1H, dquin, J_{HH} = 14.8 Hz, J_{HF} = 1.5 Hz, = C*H*COOMe), 7.44 (1H, dquin, J_{HH} = 14.8 Hz, J_{HF} = 6.8 Hz, = $CHSF_5$); ^{13}C NMR (50.3 MHz, CDCl3): δ 53.29 (s, CH_2), 127.42 (quin, J_{CF} = 7.5 Hz, =*C*HCOOMe), 152.78 (dquin, J_{CF} = 2.0 Hz, J_{CF} = 22.6 Hz, =$CHSF_5$), 164.00 (s, C=O); ^{19}F NMR (188.3 MHz, $CDCl_3$): δ 140.55 (4F, dm, J_{FF} = 146.0 Hz), 155.21–158.43 (1F, 9 lines). Anal. Calcd. for $C_4H_5F_5O_2S$ (212.138): C, 22.65; H, 2.38; F, 44.78. Found: C, 22.71; H, 2.40; F, 44.63.

3.6. Methyl endo-2-(Pentafluoro-λ^6-sulfanyl)-5-norbornene-exo-3-carboxylate (endo-8) and methyl exo-2-(pentafluoro-λ^6-sulfanyl)-5-norbornene-endo-3-carboxylate (exo-8)

A mixture of **7** (2.12 g, 0.01 mol), cyclopentadiene (6.6 g, 0.1 mol) contained in a Pyrex seal tube was heated at 110 °C for 10 h. The reaction mixture was freed from pentadiene by evaporation under reduced pressure leaving 3.2 g of a brownish oil. Isomers ***endo-8*** and ***exo-8*** were isolated by column chromatography on silica gel.

(**endo-8**) 1.43 g (51.4%) as a colorless oil. R_f = 0.77 ($CHCl_3$). ^{1}H NMR spectral data (200 MHz, $CDCl_3$): δ 1.53 (1H, ddquin, J_{HH} = 10.0 Hz, J_{HH} = 2.0 Hz, J_{HF} = 2.1 Hz, CHH), 1.65 (1H, dquin, J_{HH} = 10.0 Hz, J_{HF} = 1.0 Hz, CHH), 2.92 (1H, dd, J_{HH} = 2.0 Hz, J_{HF} = 5.0 Hz, $CHCOOCH_3$), 3.08 (1H, br.s, CH), 3.48 (1H, br.s, CH), 3.77 (3H, s, CH_3), 4.98 (1H, m, $CHSF_5$), 6.21 (1H, m, CH=), 6.41 (1H, dd, J_{HH} = 3.3 Hz, J_{HH} = 5.5 Hz, CH=); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 45.98 (quin, J_{CF} = 3.0 Hz, CH_2), 47.82 (quin, J_{CF} = 3.0 Hz, CH), 48.02 (s, CH), 49.4 (quin, J_{CF} = 3.0 Hz, CH), 53.01 (s, CH_3), 88.3 (dquin, J_{CF} = 0.8 Hz, J_{CF} = 9.6 Hz, $CHSF_5$), 135.90 (s, CH=), 137.60 (s, CH=), 173.66 (s, C=O); ^{19}F NMR (188.3 MHz, $CDCl_3$): δ 140.08 (4F, dm, J_{FF} = 146.9 Hz), 163.0–166.05 (1F, 9 lines). Anal. Calcd. for $C_9H_{11}F_5O_2S$ (278.241): C, 38.85; H, 3.99; F, 34.14. Found: C, 38.94; H, 3.92; F, 34.25.

(**exo-8**) 0.57 g (20.51%) as a colorless oil. R_f = 0.71 ($CHCl_3$). ^{1}H NMR spectral data (200 MHz, $CDCl_3$): δ 1.73 (1H, d, J_{HH} = 9.0 Hz, CH*H*), 1.88 (1H, d, J_{HH} = 9.0 Hz, CH*H*), 3.32 (1H, br.s, CH), 3.56 (1H, dquin, J_{HH} = 1.4 Hz, J_{HH} = 2.0 Hz, CH), 3.66 (1H, quin, J_{HF} = 4.5 Hz, *C*HCOOCH$_3$), 3.71 (3H, s, CH_3), 4.21 (1H, ddquin, J_{HH} = 2.2 Hz, J_{HH} = 6.7 Hz, J_{HH} = 5.1 Hz, $CHSF_5$), 6.14 (1H, dd, J_{HH} = 2.8 Hz, J_{HH} = 5.6 Hz, CH=), 6.23 (1H, dd, J_{HH} = 3.5 Hz, J_{HH} = 5.6 Hz, CH=); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 46.25 (s, CH), 48.36 (quin, J_{CF} = 1.5 Hz, CH_2), 48.66 (quin, J_{CF} = 4.0 Hz, CH), 48.83 (quin, J_{CF} = 4.5 Hz, CH), 52.77 (s, CH_3), 88.80 (dquin, J_{CF} = 1.0 Hz, J_{CF} = 8.0 Hz, $CHSF_5$), 136.21 (s, CH=), 137.80 (s, CH=), 174.00 (s, C=O); ^{19}F NMR (188.3 MHz, $CDCl_3$): δ 139.78 (4F, dm, J_{FF} = 144.8 Hz), 162.7–166.3 (1F, 9 lines). Anal. Calcd. for $C_9H_{11}F_5O_2S$ (278.241): C, 38.85; H, 3.99; F, 34.14. Found: C, 38.90; H, 3.82; F, 34.30.

3.7. exo-3-Carboxaldehyde-endo-2-(pentafluoro-λ^6-sulfanyl)-5-norbornene (endo-9) and endo-3-carboxaldehyde-exo-2-(pentafluoro-λ^6-sulfanyl)-5-norbornene (exo-9)

A mixture of **4** (1.82 g, 0.01 mol), cyclopentadiene (6.6 g, 0.1 mol) contained in a Pyrex seal tube was heated at 50–55 °C for 6 h. The reaction mixture was freed from pentadiene by evaporation under reduced pressure leaving 3.6 g of a brownish oil. Isomers ***endo-9*** and ***exo-9*** were isolated by column chromatography on silica gel.

(**endo-9**) 1.31 g (52.8%) as a colorless oil. R_f = 0.8 ($CHCl_3$). ^{1}H NMR spectral data (200 MHz, $CDCl_3$): δ 1.32 (1H, d, J_{HH} = 9.2 Hz, C*H*H), 1.54 (1H, dddquin, J_{HH} = 1.8 Hz, J_{HH} = 2.0 Hz, J_{HH} = 9.2 Hz, J_{HF} = 2.2 Hz, C*H*H), 3.11 (1H, dd, J_{HH} = 2.0 Hz, J_{HH} = 4.6 Hz, C*H*CHO), 3.20 (1H, m, CH), 3.50 (1H, m, CH), 4.99 (1H, ddquin, J_{HH} = 1.4 Hz, J_{HH} = 4.6 Hz, J_{HF} = 6.5 Hz, $CHSF_5$), 6.26 (1H, m, = CH), 6.43 (1H, dd, J_{HH} = 5.8 Hz, J_{HH} = 3.4 Hz, =CH), 9.82 (1H, s, CHO); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 44.24 (s, CH), 45.52 (quin, J_{CF} = 3.0 Hz, CH_2), 47.79 (quin, J_{CF} = 3.0 Hz, CH), 57.60 (quin, J_{CF} = 3.0 Hz, *C*HCHO), 84.31 (dquin, J_{CF} = 1.0 Hz, J_{CF} = 9.6 Hz, $CHSF_5$), 136.61 (s, CH=), 136.99 (s, CH=), 198.34 (s, CHO); ^{19}F NMR (188.3 MHz, $CDCl_3$): δ 140.11 (4F, dm, J_{FF} = 148.52 Hz), 162.92–166.02 (1F, 9 lines). Anal. Calcd. for $C_8H_9F_5OS$ (248.215): C, 38.71; H, 3.66; F, 38.27. Found: C, 38.63; H, 3.58; F, 38.41.

(**exo-9**) 0.52 g (21.00%) as a colorless oil. R_f = 0.77 ($CHCl_3$). ^{1}H NMR spectral data (200 MHz, $CDCl_3$): δ 1.81 (1H, dddquin, J_{HH} = 0.8 Hz, J_{HH} = 1.0 Hz, J_{HH} = 9.2 Hz, J_{HF} = 0.7 Hz, C*H*H), 1.96 (1H, d, J_{HH} = 9.2 Hz, CH*H*), 3.47 (1H, br.s, CH), 3.65 (1H, br.s, CH), 3.81 (1H, dd, J_{HH} = 1.8 Hz, J_{HH} = 4.4 Hz, C*H*CHO), 4.23 (1H, ddquin, J_{HH} = 1.2 Hz, J_{HH} = 4.4 Hz, J_{HF} = 6.5 Hz, $CHSF_5$), 6.21 (2H, m, CH =CH), 9.64 (1H, s, CHO); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 44.12 (s, CH), 47.94 (quin, J_{CF} = 1.5 Hz, CH_2), 48.75 (quin, J_{CF} = 3.5 Hz, CH), 57.2 (quin, J_{CF} = 3.0 Hz, *C*HCHO), 85.56 (dquin, J_{CF} = 1.3 Hz, J_{CF} = 8.6 Hz, $CHSF_5$), 136.03 (quin, J_{CF} = 1.0 Hz, CH=), 137.43 (quin, J_{CF} = 0.5 Hz, CH=), 198.36 (s, CHO); ^{19}F NMR (188.3 MHz, $CDCl_3$): δ 39.13 (4F, dm, J_{FF} = 142.9 Hz), 162.95–166.0 (1F, 9 lines). Anal. Calcd. for $C_8H_9F_5OS$ (248.215): C, 38.71; H, 3.66; F, 38.27. Found: C, 38.60; H, 3.52; F, 38.45.

3.8. exo-3-Cyan-endo-2-(pentafluoro-λ^6-sulfanyl)-5-norbornene (**endo-10**) and endo-3-cyan-exo-2-(pentafluoro-λ^6-sulfanyl)-5-norbornene (**exo-10**)

According to the procedure 3.7 for the synthesis of **endo-9,** and **exo-9**, *trans*-1-cyan-2-(pentafluoro-λ^6-sulfanyl)-ethen **6** (1.79 g, 0.01 mol) was allowed to react with pentadiene (6.6 g, 0.1 mol).

(**endo-10**) 1.07 g (44.00%) as a colorless oil. R_f = 0.62 ($CHCl_3$/C_6H_{14} = 10:2). ^{1}H NMR spectral data (200 MHz, $CDCl_3$): δ 1.74 (1H, dquin, J_{HH} = 9.6 Hz, J_{HF} = 2.0 Hz, C*H*H), 1.85 (1H, ddquin, J_{HH} = 1.6 Hz, J_{HH} = 9.6 Hz, J_{HF} = 2.2 Hz, CH*H*), 2.92 (1H, dd, J_{HH} = 1.6 Hz, J_{HH} = 5.2 Hz, CHCN), 3.36 (1H, br.s, CH), 3.62 (1H, br.s, CH), 4.67 (1H, ddquin, J_{HH} = 2.6 Hz, J_{HH} = 5.6 Hz, J_{HF} = 5.8 Hz, $CHSF_5$), 6.25 (1H, m, =CH), 6.40 (1H, dd, J_{HH} = 5.8 Hz, J_{HH} = 3.2 Hz, =CH); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 34.37 (quin, J_{HF} = 3.5 Hz, *C*HCN), 46.86 (quin, J_{CF} = 2.5 Hz, CH_2), 47.60 (quin, J_{CF} = 2.5 Hz, CH), 47.74 (s, CH), 88.52 (dquin, Jcf = 0.5 Hz, J_{CF} = 10.5 Hz, $CHSF_5$), 120.4 (s, CN), 135.22 (s, CH=), 135.97 (s, CH=); ^{19}F NMR (188.3 MHz, $CDCl_3$): δ 140.16 (4F, dm, J_{FF} = 146.6 Hz), 160.72–163.72 (1F, 9 lines). Anal. Calcd. for $C_8H_8F_5NS$ (245.215): C, 39.19; H, 3.29; F, 38.74. Found: C, 39.32; H, 3.32; F, 38.57.

(**exo-10**) 0.43 g (17.6%) as a colorless oil. R_f = 0.59 ($CHCl_3$/C_6H_{14} = 10:2). ^{1}H NMR spectral data (200 MHz, $CDCl_3$): δ 1.88 (1H, dquin, J_{HH} = 9.4 Hz, J_{HF} = 2.0 Hz, C*H*H), 1.98 (1H, dquin, J_{HH} = 9.4 Hz, J_{HF} = 2.0 Hz, CH*H*), 2.53 (1H, m, CHCN), 3.43 (1H, br.s, CH), 3.71 (1H, br.s, CH), 3.89 (1H, ddquin, J_{HH} = 5.0 Hz, J_{HF} = 6.0 Hz, $CHSF_5$), 6.42 (1H, m, =CH), 6.51 (1H, dd, J_{HH} = 5.6 Hz, J_{HH} = 3.3 Hz, =CH); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 35.07 (quin, J_{HF} = 3.0 Hz, *C*HCN), 48.74 (quin, J_{CF} = 1.0 Hz, CH_2), 49.0 (quin, J_{CF} = 2.4 Hz, CH), 49.14 (s, CH), 88.95 (dquin, J_{CF} = 1.0 Hz, J_{CF} = 9.8 Hz, $CHSF_5$), 122.4 (s, CN), 135.67 (s, CH=), 136.05 (s, CH=); ^{19}F NMR (188.3 MHz, $CDCl_3$): δ 138.51 (4F, dm, J_{FF} = 148.0 Hz), 159.54–163.92 (1F, 9 lines). Anal. Calcd. for $C_8H_8F_5NS$ (245.215): C, 39.19; H, 3.29; F, 38.74. Found: C, 39.36; H, 3.30; F, 38.51.

3.9. Methyl 1,2-dimethyl-4-(pentafluoro-λ^6-sulfanyl)-cyclohex-1-en-5-carboxylate (**11**)

According to the procedure for the synthesis of **endo-8**, and **exo-8**, methyl 3-(pentafluoro-λ^6-sulfanyl)prop-2-enate (2.12 g, 0.01 mol) was allowed to react with 2,3-dimethylbutadiene (8.2 g, 0.1 mol). Yield **11** 1.91 g (65%) as a colorless oil. R_f = 0.76 ($CHCl_3$).

^{1}H NMR spectral data (200 MHz, $CDCl_3$): δ 1.66 (6H, m, $2CH_3$), 2.36 (2H, dm, J_{HH} = 6.4 Hz, CH_2), 2.65 (2H, m, CH_2), 3.26 (2H, dt, J_{HH} = 7.4 Hz, J_{HH} = 7.0 Hz, C*H*COOCH_3), 3.77 (3H, s, OCH_3), 4.60 (1H, dquin, J_{HH} = 6.8 Hz, J_{HF} = 6.2 Hz, $CHSF_5$); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 18.55 (s, CH_3), 19.10 (s, CH_3), 33.68 (quin, J_{CF} = 4.5 Hz, CH_2), 34.57 (quin, J_{CF} = 1.5 Hz, CH_2), 43.76 (quin, J_{CF} = 3.0 Hz, CH_2), 52.86 (s, OCH_3), 84.07 (dquin, J_{CF} = 0.8 Hz, J_{CF} = 10.0 Hz, $CHSF_5$), 122.76 (s, CH=), 123.44 (s, CH=), 173.86 (s, C=O); ^{19}F NMR (188.3 MHz, $CDCl_3$): δ 134.16 (4F, dm, J_{FF} = 141.0 Hz), 161.98–164.99 (1F, 9 lines). Anal. Calcd. for $C_{10}H_{15}F_5O_2S$ (294.284): C, 40.81; H, 5.14; F, 32.28. Found: C, 40.94; H, 5.29; F, 32.50.

3.10. 5-Cyano-1, 2-dimethyl-4-(pentafluoro-λ^6-sulfanyl)-cyclohex-1-en (**12**)

According to the procedure 3.7 for the synthesis of **endo-9**, and **exo-8**, *trans*-1-cyan-2-(pentafluoro-λ^6-sulfanyl)-ethen **6** (1.79 g, 0.01 mol) was allowed to react with 2,3-dimethylbutadiene (8.2 g, 0.1 mol). Yield **12** 1.41 g (54%) as a colorless oil. R_f = 0.81 ($CHCl_3$). ^{1}H NMR spectral data (200 MHz, $CDCl_3$): δ 1.61 (3H, s, CH_3), 1.65 (3H, s, CH_3), 2.32 (2H, dm, J_{HH} = 6.4 Hz, CH_2), 2.64 (2H, m, CH_2), 3.22 (1H, dt, J_{HH} = 7.4 Hz, J_{HH} = 7.0 Hz, C*H*CN), 4.49 (1H, dquin, J_{HH} = 7.0 Hz, J_{HF} = 6.0 Hz, $CHSF_5$); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 18.76 (s, CH_3), 19.07 (s, CH_3), 31.70 (quin, J_{CF} = 1.5 Hz, CH_2), 36.03 (quin, J_{CF} = 6.0 Hz, CH_2), 46.62 (quin, J_{CF} = 2.5 Hz, *C*HCN), 86.67 (dquin, J_{CF} = 0.6 Hz, J_{CF} = 10.6 Hz, $CHSF_5$), 120.51 (s, CN), 123.09 (s, CH=), 123.59 (s, CH=); ^{19}F NMR (188.3 MHz, $CDCl_3$): δ 133.33 (4F, dm, J_{FF} = 143.0 Hz), 161.03–164.05 (1F, 9 lines). Anal. Calcd. for $C_9H_{12}F_5NS$ (261.258): C, 41.38; H, 4.63; F, 36.36. Found: C, 41.50; H, 4.64; F, 36.42.

3.11. 5-Carboxaldehyd-1,2-dimethyl-4-(pentafluoro-λ^6-sulfanyl)-cyclohex-1-en (**13**) and 4,5-dimethyl-2-(2-(pentafluoro-λ^6-sulfanyl)ethen-1-yl)-3,6-dihydro-2H-pyran (**14**)

According to the procedure 3.7 for the synthesis of **endo-9**, and **exo-8**, *trans*-3-(pentafluoro-λ^6-sulfanyl)prop-2-enal **4** (1.82 g, 0.01 mol) was allowed to react with 2,3-dimethylbutadiene (8.2 g, 0.1 mol).

(**13**) Yield 1.53 g (58%). R_f = 0.79 ($CHCl_3$). ^{1}H NMR spectral data (200 MHz, $CDCl_3$): δ 1.62 (3H, s, CH_3), 1.66 (3H, s, CH_3), 2.35 (2H, d, J_{HH} = 5.0 Hz, CH_2), 2.45 (1H, dd, J_{HH} = 17.5 Hz, J_{HH} = 1.2 Hz, C*H*H), 2.63 (1H, dd, J_{HH} = 17.5 Hz, J_{HH} = 2.0 Hz, CH*H*), 3.13 (1H, ddt, J_{HH} = 1.8 Hz, J_{HH} = 6.4 Hz, J_{HH} = 6.6 Hz, C*H*CHO), 4.53 (1H, dquin, J_{HH} = 6.4 Hz, J_{HF} = 6.6 Hz, $CHSF_5$), 9.54 (1H, m, CHO); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 18.84 (s, CH_3), 19.16 (s, CH_3), 30.70 (quin, J_{CF} = 1.5 Hz, CH_2), 33.03 (quin, J_{CF} = 6.0 Hz, CH_2), 49.62 (quin, J_{CF} = 2.5 Hz, *C*HCHO), 81.87 (dquin, J_{CF} = 0.6 Hz, J_{CF} = 10.6 Hz, $CHSF_5$), 123.11 (s, CH=), 123.60 (s, CH=), 199.77 (quin, J_{CF} = 1.5 Hz, CHO); ^{19}F NMR (188.3 MHz, $CDCl_3$): δ 134.45 (4F, dm, J_{FF} = 141.0 Hz), 162.03–165.05 (1F, 9 lines). Anal. Calcd. for $C_9H_{13}F_5OS$ (264.258): C, 40.91; H, 4.96; F, 35.95. Found: C, 40.80; H, 4.88; F, 36.13.

(**14**) Yield 0.55 g (21%). R_f = 0.89 ($CHCl_3$). ^{1}H NMR spectral data (200 MHz, $CDCl_3$): δ 1.56 (3H, s, CH_3), 1.66 (3H, s, CH_3), 1.98 (1H, d, J_{HH} = 16.0 Hz, C*H*H), 2.15 (1H, dd, J_{HH} = 16.0 Hz, J_{HH} = 10.8 Hz, CHH), 4.05 (2H, m, OCH_2), 4.19 (1H, dddquin, J_{HH} = 10.8 Hz, J_{HH} = 3.8 Hz, J_{HH} = 1.8 Hz, J_{HF} = 2.0 Hz, OCH), 6.56 (1H, m, ddquin, J_{HH} = 14.6 Hz,

J_{HH} = 3.8 Hz, J_{HF} = 1.0 Hz, =CH), 6.75 (1H, m, ddquin, J_{HH} = 14.6 Hz, J_{HH} = 1.8 Hz, J_m = 6.2 Hz, =CHSF$_5$); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 14.23 (s, CH_3), 18.67 (s, CH_3), 36.04 (s, CH_2), 69.91 (s, OCH_2), 71.67 (s, OCH), 123.04 (s, =C), 124.96 (s, =C), 138.47 (quin, J_{CF} = 2.6 Hz, =CH), 140.75 (dquin, J_{CF} = 1.5 Hz, J_{CF} = 20.0 Hz, =CHSF$_5$); ^{19}F NMR (188.3 MHz, $CDCl_3$): δ 141.03 (4F, dm, J_{FF} = 148.5 Hz), 159.91–169.91 (1F, 9 lines). Anal. Calcd. for $C_9H_{13}F_5OS$ (264.258): C, 40.91; H, 4.96; F, 35.95. Found: C, 40.74; H, 4.78; F, 36.10.

*3.12. 5-Methoxycarbonyl-6-(pentafluoro-λ^6-sulfanyl)-7-oxabicyclo[2.2.1]hept-2-en (**endo-15**) and (**exo-15**)*

According to the procedure for the synthesis of **endo-8**, and **exo-8**, methyl 3-(pentafluoro-λ^6-sulfanyl)prop-2-enate (2.12 g, 0.01 mol) was allowed to react with furane (6.8 g, 0.1 mol).

(**endo-15**) 1.00 g (35.7%) as a colorless oil. R_f = 0.49 ($CHCl_3$). ^{1}H NMR spectral data (200 MHz, $CDCl_3$): δ 3.07–4 (1H, d, J_{HH} = 4.6 Hz, CH), 3.86 (3H, s, CH_3), 5.00 (1H, ddquin, J_{HH} = 4.4 Hz, J_{HH} = 4.4 Hz, J_{HF} = 7.0 Hz, $CHSF_5$), 5.20 (1H, dquin, J_{HH} = 0.6 Hz, J_{HF} = 1.0 Hz, CH), 5.37 (1H, J_{HH} = 5.6 Hz, CH), 6.54 (1H, dd, J_{HH} = 1.8 Hz, J_{HH} = 5.8 Hz, CH=), 6.71 (1H, dd, J_{HH} = 1.6 Hz, J_{HH} = 5.8 Hz, CH=); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 49.46 (quin, J_{CF} = 3.0 Hz, *C*HCOOCH$_3$), 53.30 (s, CH_3), 83.34 (quin, J_{CF} = 5.0 Hz, OCH), 83.39 (s, OCH), 86.58 (dquin, J_{CF} = 0.5 Hz, J_{CF} = 11.0 Hz, $CHSF_5$), 137.27 (s, CH=), 137.36 (s, CH=), 169.63 (s, C=O); ^{19}F NMR (188.3 MHz, $CDCl_3$): δ 140.02 (4F, dm, J_{FF} = 144.8 Hz), 161.40–164.52 (1F, 9 lines). Anal. Calcd. for $C_7H_9F_5O_3S$ (268.202): C, 31.35; H, 3.58; F, 35.42. Found: C, 31.50; H, 3.62; F, 35.60.

(**exo-15**) 0.3 g (10.7%) as a colorless oil. R_f = 0.47 ($CHCl_3$). ^{1}H NMR spectral data (200 MHz, $CDCl_3$): δ 3.77 (3H, s, CH_3), 3.87 (1H, d, J_{HH} = 4.5 Hz, CH), 4.26 (1H, dquin, J_{HH} = 4.0 Hz, J_{HF} = 6.3 Hz, $CHSF_5$), 5.30 (1H, d, J_{HH} = 5.3 Hz, CH), 5.54 (1H, br.s, CH), 6.43 (1H, dd, J_{HH} = 5.7 Hz, J_{HH} = 0.7 Hz, CH=), 6.51 (1H, dd, J_{HH} = 5.7 Hz, J_{HH} = 1.0 Hz, CH=); ^{13}C NMR (50.3 MHz, $CDCl_3$): δ 48.88 (quin, J_{CF} = 3.5 Hz, *C*HCOOCH$_3$), 53.00 (s, CH_3), 79.58 (quin, J_{CF} = 4.0 Hz, OCH), 79.58 (s, OCH), 82.67 (dquin, J_{CF} = 1.0 Hz, J_{CF} = 10.6 Hz, $CHSF_5$), 135.58 (s, CH=), 135.68 (s, CH=), 171.28 (s, C=O); ^{19}F NMR (188.3 MHz, $CDCl_3$): δ 142.42 (4F, dm, J_{FF} = 146.6 Hz), 161.44–164.52 (1F, 9 lines). Anal. Calcd. for $C_7H_9F_5O_3S$ (268.202): C, 31.35; H, 3.58; F, 35.42. Found: C, 31.48; H, 3.60; F, 35.50.

4. Conclusions

In conclusion, our results demonstrate a simple and efficient synthesis of novel pentafluorosulfanyl-containing dienophiles and their reaction with cyclic and aliphatic electron-releasing dienes and with furane. Further application of this methodology to the synthesis of potentially interesting pentafluorosulfany derivatives as well as the exploration of their properties will be reported.

Acknowledgements

This work was supported by the European Office of Aerospace Research and Development (EOARD #037004) and the International Science and Technology Center (ISTC 2791p).

References

[1] J.C. Hansen, P.M. Savu, United States Patent 5,159,105 (1992).
[2] J.C. Hansen, P.M. Savu, United States Patent 5,286,352 (1992).
[3] R. Winter, P.G. Nixon, G.L. Gard, D.G. Castner, N.R. Holcomb, Y.-H. Hu, D.W. Grainger, Chem. Mater. 11 (1999) 3044.
[4] R. Winter, P.G. Nixon, R.J. Terjeson, J. Mohtasham, N.R. Holcomb, D.W. Grainger, D. Graham, D.G. Caster, G.L. Gard, J. Fluorine Chem. 115 (2002) 107.
[5] R. Winter, R. Dodean, L. Holmes, G.L. Gard, J. Fluorine Chem. 125 (2004) 37.
[6] V.K. Brel, Synthesis (2006) 339.
[7] R. Winter, G.L. Gard, J. Fluorine Chem. 66 (1994) 109.
[8] I.V. Trushkov, V.K. Brel, Tetrahedron Lett. 46 (2005) 4777.
[9] V.K. Brel, Synthesis (2005) 1245.
[10] K. Itoh, S. Takahashi, T. Ueki, T. Sogiyama, T.T. Takahashi, C.A. Horiuchi, Tetrahedron Lett. 43 (2002) 7035.
[11] V. Grakautas, J. Org. Chem. 38 (1973) 2999.
[12] P.G. Nixon, J. Renn, R.J. Terjeson, Y.S. Choi, R. Winter, R. Gard, J. Fluorine Chem. 115 (1998) 13.
[13] F. Fringuelly, A. Taticchi (Eds.), The Diels-Alder Reaction: Selected Practical Methods, John Wiley & Sons, Ltd, 2002, pp. 122–123.
[14] F.W. Hoover, D.D. Coffman, J. Org. Chem. 29 (1964) 3567.
[15] R.W. Dolbier, A. Mitani, W. Xu, I. Ghiviriga, Org. Lett. 8 (2006) 5573.
[16] V.K. Brel, Synthesis (2006) 2665.
[17] F. Fringuelly, A. Taticchi (Eds.), The Diels-Alder Reaction: Selected Practical Methods, John Wiley & Sons, Ltd, 2002, pp. 40–42.