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Hexafluorothioacetone based synthesis of fluorinated heterocycles

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Abstract

Cycloadducts of hexafluorothioacetone (HFTA) were prepared in high yield by a CsF catalyzed reaction between readily available 2,2,4,4-tetrakis-(trifluoromethyl)-1,3-dithietane (as a source of HFTA) with conjugated electron-rich hydrocarbon dienes, such as cyclopentadiene, 2,3-dimethylbuta-1,3-diene, cyclohexa-1,3-diene or (1*Z*,3*Z*)-cyclohepta-1,3-diene. Cyclohexa-1,4- and (1*Z*,5*Z*)-cycloocta-1,5-dienes, also undergo the reaction with *in situ* generated HFTA, but form the products of insertion of HFTA into the C–H bond of the diene as a result of ene-reaction. The highly selective reaction of HFTA with (1*Z*,3*Z*,5*Z*)-cyclohepta-1,3,5-triene and (1*Z*,3*Z*,5*Z*,7*Z*)-cycloocta-1,3,5,7-tetraene leads to the formation of cycloadducts derived from exclusive addition of thioacetone to the corresponding bicyclic isomers—bicyclo[4.1.0]hepta-2,4-diene or bicyclo[4.2.0]octa-2,4,7-triene, respectively. The corresponding cycloadducts of HFTA with 2,3-dimethylbutadiene-1,3-cyclohexa-1,3-cyclohexa-1,4-dienes and (1*Z*,3*Z*,5*Z*)-cyclohepta-1,3,5-triene were also prepared by direct reaction of sulfur/hexafluoropropene/KF and the corresponding hydrocarbon substrate at 35–45 °C in DMF.

Keywords: 2,2,3,3-Tetrakis(trifluoromethyl)-1,3-dithietane; Hexafluorothioacetone; Diels–Alder reaction

1. Introduction

Hexafluorothioacetone (HFTA), discovered by W. Middleton over 50 years ago [1,2] is a potent heterodienophile. It reacts with variety of dienes under extremely mild conditions [3]. Unfortunately, the gaseous nature (bp 6 °C) of HFTA and its limited stability at ambient temperature, exemplified by pronounced ability to undergo dimerization, forming 2,2,4,4-tetrakis-(trifluoromethyl)-1,3-dithietane (**1**) [4], makes it a difficult to handle material. In recent years it was demonstrated that readily available **1** [5,6] treated with alkali metal fluoride in polar solvent generates HFTA which can be subsequently trapped by a variety of electron-rich dienes [7–11]. Quadricyclane, which is known to have high reactivity towards electron deficient unsaturated hydrocarbons [12] and polyfluorinated materials [13–16], was reported recently to undergo cycloaddition with HTFA, producing 3-thia-4,4-bis(trifluoromethyl)tricyclo[5.2.1.0^{2,5}]non-7-ene [17].

This paper, reports new data on cycloaddition reactions of generated *in situ* HFTA with a variety of electron-rich dienes, and cyclic polyenes.

2. Results and discussion

Addition of dry cyclopenta-1,3-diene (**2**) or 2,3-dimethylbuta-1,3-diene (**3**) to the mixture of **1** and catalytic amount of dry CsF in tetrahydrofuran (THF) results in a fast, exothermic reaction leading to the high yield formation of cycloadduct **4** or **5** [3], respectively (Eq. (1), Table 1, entries 1 and 2):

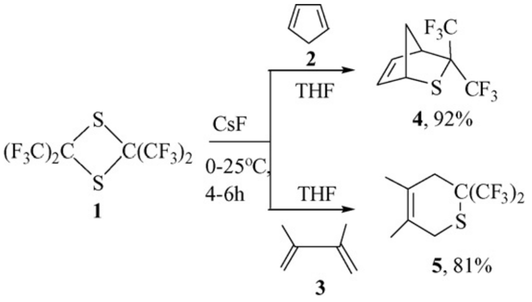

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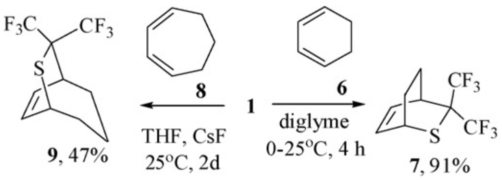
Table 1
Reaction of **1** with dienes—ratio of reactants and reaction conditions

Entry no.	**1** (mol)	Diene (mol)	Solvent (mL)	Catalyst (mol)	Temperature (°C)	Time (at 25 °C, h)	Product (yield %)
1	0.1	**2** (0.2)	THF (50)	CsF (0.03)	0–25	4	**4** (92)
2	0.1	**3** (0.2)	THF (100)	CsF (0.03)	10–25	6	**5** (81)
3	0.1	**6** (0.2)	Diglyme (100)	CsF (0.03)	25–30	4	**7**[a] (81)
4	0.027	**8** (0.054)	THF (60)	CsF (0.02)	25	48	**9** (47)
5	0.1	**10** (0.2)	THF (100)	CsF (0.03)	25	7 days	**11a**,**b** (45)
6	0.027	**12** (0.054)	THF (60)	CsF (0.02)	25	30 days	**13** (69)
7	0.05	**16** (0.1)	THF (60)	CsF (0.02)	25	24	**18** (57)
8	0.04	**17** (0.05)	CH_3CN (50)	CsF (0.03)	78, 25	5 days, 2 days	**19** (69)

[a] Purity 96%, isolated product contained 4% of diglyme.

In contrast to the unstable cycloadduct of hexafluoroacetone and cyclopentadiene, which readily undergoes retro-Diels–Alder reaction, generating the starting materials at ambient temperature [18], the cycloadduct **4** is stable and can be distilled without decomposition. Even significantly less active cyclohexa-1,3-diene (**6**) [19], reacted exothermally with a mixture of **1**/CsF in THF or diglyme solvent, producing adduct **7** in high yield:



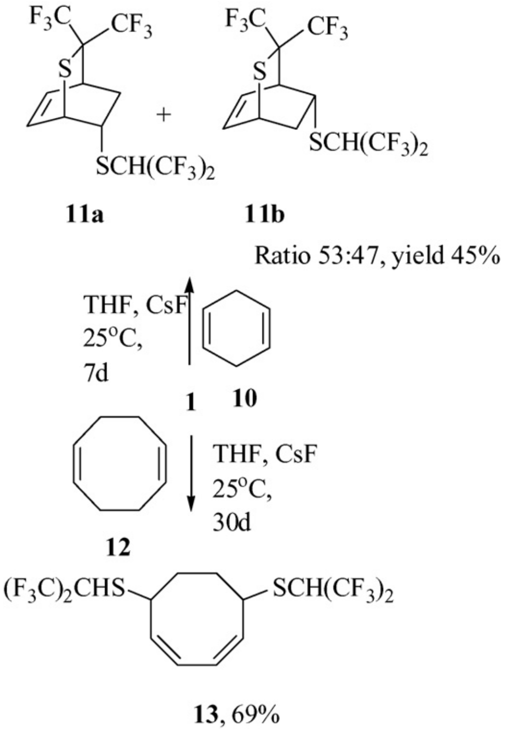
(2)

A significantly slower reaction (4 days, at 25 °C) between (1*Z*,3*Z*)-cyclohepta-1,3-diene (**8**) and *in situ* generated HFTA results in the formation of cycloadduct **9** (Eq. (2)).

The reaction of compound **1** with nonconjugated, cyclic dienes produced unexpected results. Cyclohexa-1,4-diene (**10**) when reacted with **1**, formed the mixture of two isomeric 1:2 adducts, **11a**,**b** (ratio 53:47, Eq. (3), Table 1, entry 5). The structure of one of isomer **11a**(**b**) was established by single crystal X-ray diffraction (Fig. 1).

Moderate yield of adducts **11a**,**b** in this case is the result of insufficient amount of **1** relative to **10** (ratio 1: 2, see Table 1, entry 5) and adjustment of the ratio to 1:1 should result in higher yield of **11a**,**b**. Although sufficient difference in the ratio of isomers **11a** and **11b**, and reasonable separation most of resonances in ^{1}H and ^{19}F NMR spectra allowed assignment of signals to major (**11a**) and minor (**11b**) isomers in the mixture, it should be pointed out that the assignment of structure **11a** to major isomer at this point is arbitrary.

(1*Z*,5*Z*)-Cycloocta-1,5-diene (**12**) in reaction with **1** produced **13** as a result of insertion of two molecules of HFTA. In this case quite slow reaction (Eq. (3)) stopped at the stage of conjugated cycloocta-1,3-diene, since compound **13** did not underwent further cycloaddition reaction with HTFA. Lower activity of **13** correlates well with general trend of reactivity reduction with increase of diene ring size observed in Diels–Alder process for cyclic dienes [19]:



(3)

Monitoring of this reaction by NMR revealed that compound **13** forms with selectivity ~95% and crude product contains ~5% isomeric material. It should be also pointed out that compound **13** is thermally unstable readily undergoes rearrangement upon heating, producing a mixture of several isomeric species. ^{1}H and ^{19}F NMR spectra of material isolated through the low temperature crystallization of crude product from hexane showed the presence mostly one isomer (over >95% of sample). Due to broadening of signals and complexity of ^{1}H and ^{19}F spectra NMR method was not sufficient for proving the structure of **13** and it was resolved by single crystal X-ray diffraction (see Fig. 2).

Interestingly, the product previously isolated in reaction of **12** with two equivalents of $(CF_3)_2C{=}C{=}S$ was reported to have structure of cyclootadiene-1,5 with both fluorinated substituents connected to same double bond [20].

We believe that the formation of isomers **11a**,**b** is the result of two consecutive reactions. First step includes well-known ene-reaction of HFTA [7] with diene **10** resulting in formation

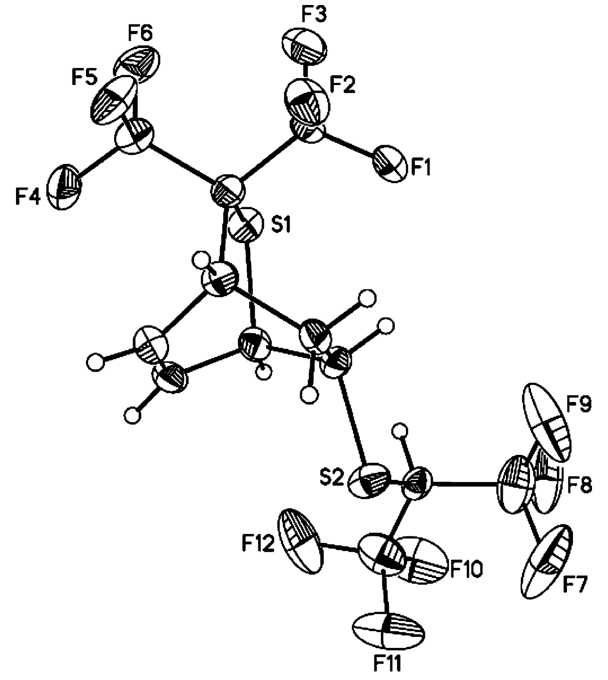
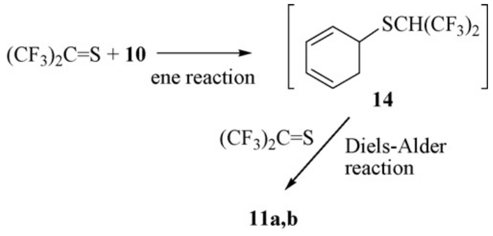


Fig. 1. ORTEP drawing of structure **11a**(**b**). Thermal ellipsoids are drawn at the 50% probability level. The racemic structure was determined in space group $P2_1/c$.

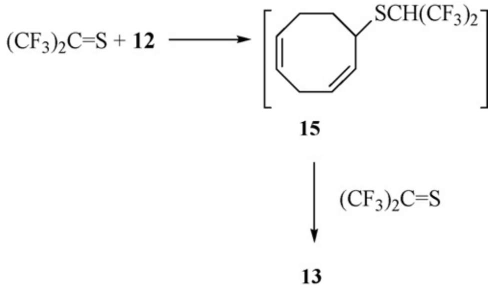
of conjugated diene **14**, which is followed by Diels–Alder cycloaddition of HFTA and nonsymmetrical **14**, leading to the formation of two isomers **11a** and **11b** (Scheme 1).

The formation of intermediate **14** was observed in the reaction of **10** and **1** by NMR, but its isolation was not attempted.

The first step of the mechanism for reaction **1** and cycloocta-1,5-diene (**12**) involves insertion of HFTA into the allylic C–H as the result of ene-reaction, leading to the intermediate **15** (see Scheme 2) and the second step—the selective hydrogen abstraction from the allylic CH_2 group of **15** leading to conjugated diene **13** as major product. The formation of **15** was not observed in this process, however, the adduct of similar structure was isolated in reaction of $(CF_3)_2C{=}C{=}S$ and **12** [20].

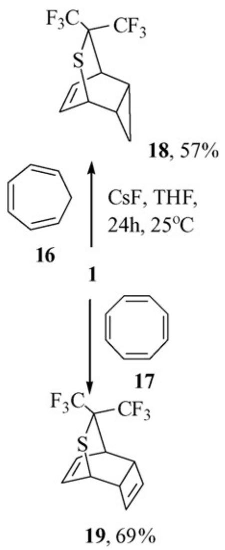


Scheme 1.



Scheme 2.

Interesting results were obtained in reaction of **1** with (1*Z*,3*Z*,5*Z*)-cyclohepta-1,3,5-triene (**16**) and (1*Z*,3*Z*,5*Z*,7*Z*)-cycloocta-1,3,5,7-tetraene (**17**). The treatment of cycloheptatriene **16** by mixture **1**/CsF in THF at ambient temperature resulted in exclusive formation of cycloadduct **18** (Eq. (4), Table 1, entry 7):



(4)

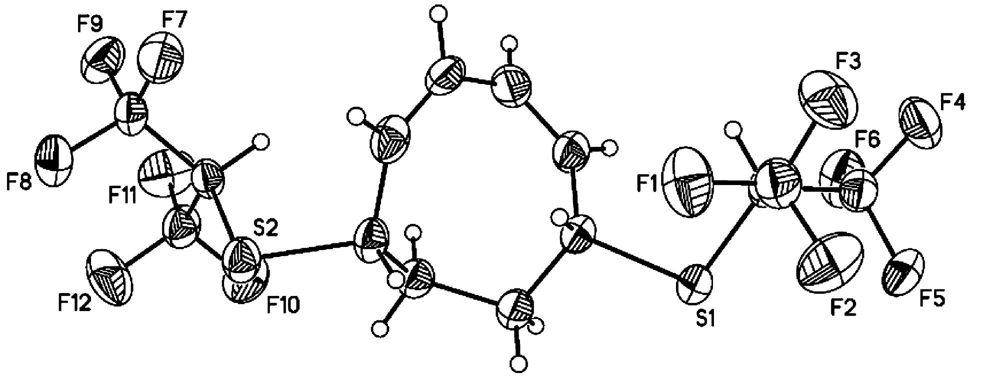


Fig. 2. ORTEP drawing of **13**. Thermal ellipsoids are drawn at the 50% probability level. The absolute configuration was determined in space group $P2_1$.

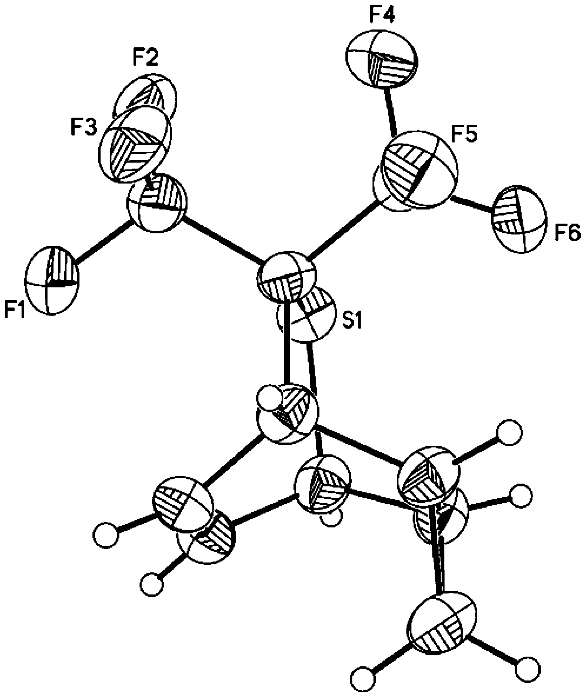


Fig. 3. ORTEP drawing of **18**. Thermal ellipsoids are drawn at the 50% probability level. The absolute configuration was determined in space group *Aba*2.

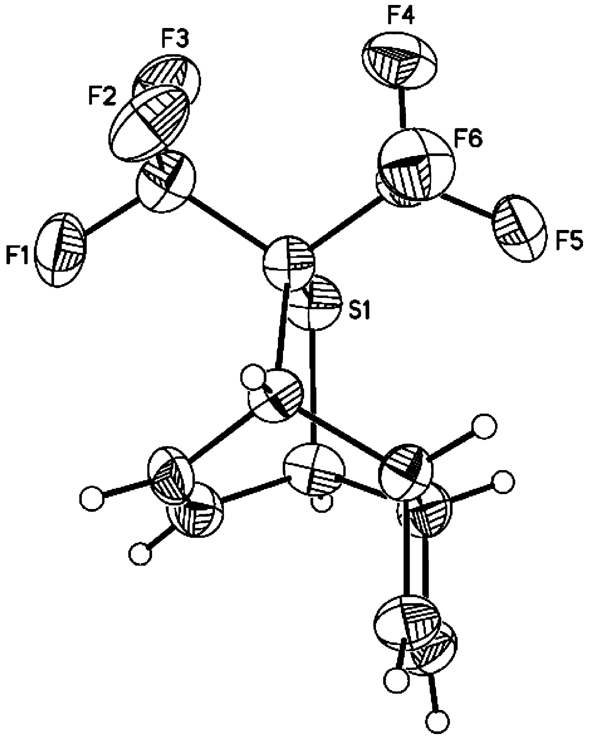
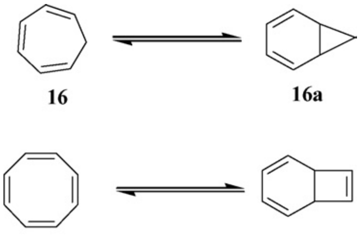


Fig. 4. ORTEP drawing of **19**. Thermal ellipsoids are drawn at the 50% probability level. The absolute configuration was determined in space group $P2_12_12_1$.

The reaction of **17** and **1** was significantly slower and required prolonged heating (5 days at 78 °C, Table 1, entry 8), but led to formation of cycloadduct **19** (Eq. (4)). Isolated **18** and **19** were thoroughly characterized by ^{1}H, ^{13}C, ^{19}F NMR spectroscopy and both suggested structures are in good agreement with spectroscopic data. Additional proof of correct structural assignment for **18** and **19** were obtained by single crystal X-ray diffraction (see Figs. 3 and 4) also confirming high stereoselectivity of HFTA cycloaddition leading to the products having *endo*-orientation of three- or four-membered rings, respectively.

The explanation of the formation compounds **18** and **19** is based on the fact that both (1*Z*,3*Z*,5*Z*)-cyclohepta-1,3,5-triene (**16**) and (1Z,3Z,5*Z*,7*Z*)-cycloocta-1,3,5,7-tetraene (**17**) exist in equilibrium with small amount of bicyclo[4.1.0]hepta-2,4-diene (**16a**) [21,22] or bicyclo[4.2.0]octa-2,4,7-triene (**17a**) [23], respectively. The highly efficient reaction of HTFA with either **16a** or **17a** leads to the corresponding cycloadducts **18** or **19**:



16 **16a**

17 **17a**

(5)

The significantly slower rate of cycloaddition HTFA to **17** correlates well with the substantially lower equilibrium concentration of bicyclic isomer **17a**, estimated to be 0.01% at 100 °C [21,22] versus 2% at 25 °C for isomer **16a** [23].

At present, there are several reported examples involving the cycloaddition to bicyclic cyclohexadienes **16a** [20,21,24–31] or **17a** [21,28,32]. The majority of these reactions however, have low selectivity, resulting in mixture of products. A few exceptions of highly selective processes include cycloaddition of **16a** [26,28,30] or **17a** [21,28] to highly reactive tetracyanoethylene and maleic anhydride, along with addition of fumaroyl chloride [29] and hexafluorobutyne [31] to **16a**. Thus, found in this study new reaction of HFTA with **16a** and **17a** is another example of process having exceptionally high selectivity towards compounds containing a cyclohexa-1,3-diene fragment.

Recently, we reported that 3-thia-4,4-bis(trifluoromethyl)-tricyclo[5.2.1.0^{2,5}]non-7-ene can be prepared by a direct reaction of sulfur/HFP and quadricyclane in the presence of KF [17]. In the present work this methodology was extended to other dienes. For example, the reaction of **3** or **6** with mixture of sulfur/KF and HFP at 35–45 °C in dry DMF solvent resulted in the formation of **4** and **7**, respectively (Eq. (6), Table 2):

$$\mathrm{KF + S + CF_3CF{=}CF_2} \xrightarrow{\mathrm{DMF}} \begin{cases} \xrightarrow[\text{35-45°C, 8h}]{\mathbf{3}} \mathbf{4}\text{, 87\%} \\ \xrightarrow[\text{35-45°C, 6h}]{\mathbf{6}} \mathbf{7}\text{, 80\%} \\ \xrightarrow[\text{35-45°C, 6h}]{\mathbf{10}} \mathbf{11a,b}\text{, 62\%} \\ \xrightarrow[\text{45-65°C, 4h}]{\mathbf{16}} \mathbf{18}\text{, 60\%} \end{cases} \tag{6}$$

Table 2
Preparation of HFTA cycloadducts using sulfur/HFP/KF—ratio of reactants and reaction conditions

Entry no.	Sulfur (mol)	Diene (mol)	DMF (mL)	KF (mol)	Temperature (°C)	Time (h)	Product (yield %)
1	0.2	**3** (0.2)	150	0.08	30–45	6	**5** (87)
2	0.2	**6** (0.1)	150	0.08	30–45	6	**7** (80)
3	0.2	**10** (0.1)	80	0.06	30–45	6, 4 days at 25 °C	**11a**,**b** (62)
4	0.2	**16** (0.2)	100	0.06	45–65	4	**18** (60)[a]

[a] Isolated product contained 5% of DMF and 10% of **16**.

Moderate yield of **18** in reaction of **16** with KF/S probably is the result of higher temperature of the reaction (45–65 °C), leading to the formation of noticeable amount of higher molecular weight by-products. Since the reaction of **10** and **1** was relatively slow at ambient temperature (Table 1, entry 5), in case of reaction of **10** with HFP/S/KF the reaction mixture obtained 35–45 °C was kept at ambient temperature for 4 days. Adducts **11a**,**b** in this case were isolated in 62% yield (Table 2, entry 3). Higher isolated yield of **11a**,**b** is also the reflection of proper ratio of HFTA to substrate **10** (1:2, based on amount of sulfur used in reaction, Table 2, entry). It should be pointed out, that the formation of ring opening by-products, observed in the reaction of quadricyclane with KF/S/HFP mixture [17,33] (as the result of attack of $(CF_3)_2CF^-$ on sulfur of highly reactive 3-thia-4,4-bis(trifluoromethyl)tricyclo[5.2.1.0^{2,5}]non-7-ene) were not detected in one-pot synthesis of cycloadducts **4**, **8**, **11a**,**b** and **18**. We believed that absence of by-products in this case is the result of significantly lower sensitivity of compounds **4**, **8**, **11a**,**b** and **18** towards nucleophilic reagents. Data on comparative reactivity of HFTA cycloadducts in nucleophilic and electrophilic reactions will be reported in a separate publication.

In conclusion, we would like to emphasize that high reactivity of HFTA as dienophile in cycloaddition reactions, along with its amazingly high affinity to conjugated cisoid systems [especially containing cyclohexa-1,3 unit, such as cyclohexa-1,3- (**6**) and -1,4- (**10**) dienes, and bicyclic isomers **16a** and **17a**] results in highly selective Diels–Alder cycloaddition of HTFA to these materials, despite the low equilibrium concentration of bicyclic isomers. It should be also mentioned that one-pot synthesis of the corresponding cycloadducts through the reaction of unsaturated diene with HFP/S/KF/**1** mixture can be also considered as simple alternative method of preparation of variety cycloadducts containing HFTA moiety.

3. Experimental

^{1}H NMR spectra were recorded on Bruker DRX-500 (499.87 MHz) and ^{19}F NMR spectra were recorded on Bruker DRX-400 (376.8485 MHz) instruments using $CFCl_3$ as an internal standard. $CDCl_3$ was used as a lock solvent, unless stated otherwise. IR spectra were recorded on a Perkin-Elmer 1600 FT spectrometer (KCl plates for liquids or in KBr for solid materials). Moisture sensitive materials were handled in a glove box. GC and GC/MS analysis were carried out on a HP-6890 instrument, using HP FFAP capillary column and either TCD (GC) or mass selective detector (GS/MS), respectively.

Compounds **1** was prepared according literature procedure [6]. Cyclopentadiene was made by pyrolysis of bicycpentadiene and stored refrigerated. Compounds **3**, **6**, **8**, **10**, **12**, **16** and **17** (Aldrich) were purchased and used after being died over $MgSO_4$. Sulfur, CsF, KF were dried at 80–120 °C (2–4 h) under dynamic vacuum prior to use. HFP (DuPont) was used without further purification. Compound **4** was identified by comparison of NMR and mass spectra data with previously reported [3]; adduct **5**—by IR spectroscopy [3]. NMR data of **5** not reported previously, are given in this section.

Due to high ratio of sulfur to fluorine, elemental analysis was not attempted for new materials. The purity of isolated compounds was established using NMR and GC and is reported here in this section.

Single crystal diffraction data. Data for compounds **11a**, **13**, **18** and **19** were collected at −100 °C using a Bruker APEXII diffractometer equipped with a graphite monochromator and Mo radiation. The structures were solved using direct methods (XS) and refined using full-matrix least squares calculations with the Shelxtl suite of programs. Crystallographic data (excluding structure factors) for all structures have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. 630851, 630852, 630985 and 630986. Copies of the data can be obtained, free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336033 or e-mail: deposit@ccdc.cam.ac.uk).

3.1. *Typical procedure for reaction of* ***1*** *with* ***2, 3, 6, 8, 10, 12, 16*** *and* ***17***

Into a flask charged with dry CsF inside of a dry-box the solvent was added under nitrogen blanket. Compound **1** was added in one portion to agitated reaction mixture, followed by the addition of the corresponding substrate at 0–25 °C. The reaction mixture was agitated for time specified in Table 1, diluted with 10% hydrochloric acid, extracted by dichloromethane (DCM, 50 mL ×2), combined organic layers were washed by 10% hydrochloric acid (200 mL ×2), dried over $MgSO_4$. Solvent was removed under reduced pressure and the residue distilled under vacuum. Ratio of reactants and reaction conditions are given in Table 1.

3.1.1. *2,2-Bis(trifluoromethyl)-3,6-dihydro-4,5-dimethyl-2H-thiopyran* (***5***)

bp 84–86/30 mm Hg, purity >99%. ^{1}H NMR ($CDCl_3$): 1.83 (3H, s), 1.86 (3H, s), 2.56 (2H, s), 3.09 (2H, s) ppm. ^{19}F NMR: −71.33 (s) ppm. ^{13}C NMR (neat): 17.62, 18.74, 30.43, 31.81, 59.95 (sept., $J = 26.2$ Hz), 125.25 (q, $J = 283.9$ Hz), 126.65, 129.47 ppm. MS (EI, *m/z*): 264 (M^+, $C_9H_{10}F_6S^+$).

*3.1.2. 5,5-Bis(trifluoromethyl)-6-thia-bicyclo[2.2.2]oct-2-ene (**7**)*

bp 80–82/1 mm Hg, purity 96%, contaminated by 4% of diglyme. ^{1}H NMR ($CDCl_3$): 1.31 (1H, m), 1.78 (1H, m), 2.15 (2H, m), 3.43 (1H, dm, $J = 7.2$ Hz), 3.60 (1H, m), 6.40 (1H, m), 6.62 (1H, t, $J = 7.2$ Hz) ppm. ^{19}F NMR: −65.40 (3F, q, $J = 12$ Hz), −69.08 (3F, dq, $J = 12.0$, 2.9 Hz) ppm. ^{13}C (neat): 20.98, 25.44, 31.79, 35.32, 62.59 (sept., $J = 26.2$ Hz), 124.62 (q, $J = 284.8$ Hz), 125.17 (q, $J = 284.8$ Hz), 133.39, 133.43 ppm. MS (EI, *m/z*): 262 (M^+, $C_9H_8F_6S^+$).

*3.1.3. 7,7-Bis(trifluoromethyl)-6-thia-bicyclo[3.2.2]non-8-ene (**9**)*

bp 71–72/0.1 mm Hg, purity >99%. ^{1}H NMR ($CDCl_3$): 1.60 (2H, m), 2.00 (3H, m), 2.22 (1H, m), 3.31 (1H, quint., $J = 4.1$ Hz), 3.65 (1H, quint., $J = 4.1$ Hz), 6.15 (1H, t, $J = 8.5$ Hz), 6.46 (1H, t, $J = 8.5$ Hz) ppm. ^{19}F: −64.61 (3F, q, $J = 12.7$ Hz), −67.68 (3F, qd, $J = 12.7$, 1.1 Hz) ppm. ^{13}C ($CDCl_3$): 21.85 (q, $J = 1.9$ Hz), 25.52 (q, $J = 1.9$ Hz), 31.57, 36.31, 39.78, 65.11 (sept., $J = 25.2$ Hz), 125.36 (q, $J = 284.8$ Hz), 131.08, 132.51 (q, $J = 2.9$ Hz) ppm. MS (EI, *m/z*): 276 (M^+, $C_{10}H_{10}F_6S^+$, 100%); 207 ($M - CF_3^+$, $C_9H_{10}F_3S^+$).

*3.1.4. Compounds **11a,b***

bp 89–91/0.04 mm Hg; mp 42–48 °C, mixture of two isomers ratio 53:47, purity 98%. ^{1}H NMR ($CDCl_3$), major: 1.98 (1H, ddd, $J = 14.7$, 4.3, 2.8 Hz), 2.90 (1H, ddd, $J = 14.7$, 8.9, 1.8 Hz), 3.70 (1H, sept., $J = 7.3$ Hz), 3.75 (3H, m), 6.40 (1H, m), 6.81 (1H, t, $J = 7.3$ Hz) ppm. ^{19}F: −65.30 (3F, q, $J = 12.0$ Hz), −66.86 (3F, dq, $J = 9.8$, 7.3 Hz), −66.37 (3F, dq, $J = 9.8$, 8.1 Hz), −68.24 (3F, m) ppm.

Minor: 1.13 (1H, ddd, $J = 15.0$, 5.5 Hz), 2.80 (1H, ddd, $J = 15.0$, 9 Hz), 3.55 (1H, dt, 7.3, 3.1 Hz), 3.70 (sept., $J = 7.3$ Hz) 3.75 (2H, m), 6.40 (1H, m), 6.81 (1H, t, $J = 7.3$ Hz) ppm. ^{19}F: −64.51 (3F, q, $J = 12.0$ Hz), −66.78 (3F, quint., $J = 9.2$ Hz), −66.99 (3F, quint., $J = 8.6$ Hz), −68.24 (3F, m) ppm.

^{13}C ($CDCl_3$, mixture of isomers): 31.20, 33.51, 35.76, 37.84, 38.35, 39.41, 41.78, 45.20, 51.90 (sept., $J = 32.0$ Hz), 121–127 (m), 130.74, 131.25, 134.52, 135.93 ppm. MS (EI, *m/z*): 293 [$(M - C_3F_6H)^+$, $C_9H_7F_6S_2^+$].

*3.1.5. (1Z,3Z)-5,8-Bis(1,1,1,3,3,3-hexafluoropropan-2-ylthio)cycloocta-1,3-diene (**13**)*

mp ~30 °C; purity ~95% (contains ~5% of isomeric material). ^{1}H NMR ($CDCl_3$): 2.00 (2H, m), 3.50 (1H, sept., $J = 7.5$ Hz), 3.89 (1H, br.s), 5.54 (1H, dd, $J = 11.0$, 6.0 Hz), 6.01 (1H, d, $J = 11.0$ Hz) ppm. ^{19}F: −66.62 (6F, sept., $J = 9.2$ Hz), −67.26 (6F, br.s) ppm. MS (EI, *m/z*): 321 [$(M - C_3F_6H)^+$, $C_{11}H_{11}F_6S_2^+$, 100%].

*3.1.6. Compound **18***

bp 46–47/0.026 mm Hg, mp 18–19 °C, purity 98%. ^{1}H NMR ($CDCl_3$): 0.25 (1H, m), 0.35 (1H, m), 1.33 (1H, m), 1.62 (1H, sept., $J = 4.0$ Hz), 3.85 (1H, dd, 7.3, 4.0 Hz), 4.00 (1H, t, $J = 5.4$ Hz), 5.80 (1H, m), 6.22 (1H, t, $J = 7.3$ Hz) ppm. ^{19}F: −62.44 (3F, q, $J = 12$ Hz), −66.55 (1F, qd, $J = 12$, 2.9 Hz) ppm. ^{13}C ($CDCl_3$): 4.83, 6.14 (q, $J = 3.9$), 34.67, 39.49, 65.31 (sept., $J = 24.2$ Hz), 124.63 (q, $J = 284.5$ Hz), 125.10 (q, $J = 284.5$ Hz) 126.18, 129.81 (q, $J = 6.9$ Hz) ppm. MS (EI, *m/z*): 274 (M^+, $C_{10}H_8F_6S^+$).

*3.1.7. Compound **19***

bp 71–72/0.1 mm Hg, mp 29–30 °C, purity 98%. ^{1}H NMR ($CDCl_3$): 3.26 (2H, m), 3.49 (1H, dd, $J = 7.5$, 2.8 Hz), 3.80 (1H, dd, $J = 7.5$, 2.3 Hz), 5.88 (1H, d, $J = 2.8$ Hz), 5.95 (2H, m), 6.30 (1H, t, $J = 7.5$ Hz) ppm. ^{19}F: −62.41 (3F, q, $J = 12.0$ Hz), −67.15 (3F, qd, $J = 12$, 2.9 Hz) ppm. ^{13}C ($CDCl_3$): 37.33, 38.60 (q, $J = 3.9$ Hz), 40.67, 45.43, 63.62 (sept., $J = 25.2$ Hz), 124.25 (q, $J = 285.8$ Hz), 124.78 (q, $J = 285.8$ Hz) 126.58, 129.65 (q, $J = 2.9$ Hz), 139.28, 139.42 ppm. IR (liq., KCl, major): 3058, 2952, 1715, 1365, 1331, 1236, 1183, 1154, 1020, 923, 7894, 779 cm^{-1}. MS (EI, *m/z*): 286 (M^+, $C_{11}H_8F_6S^+$), 217 ($C_{10}H_8F_3S^+$, 100%).

*3.2. Preparation of cycloadducts **5**, **7**, **11a,b** and **18** using reaction with mixture of sulfur/HFP/KF*

The corresponding substrate **3**, **6**, **10** or **16** (0.1–0.2 mol) was added to a mixture of dry KF and sulfur in dry DMF solvent. The required amount of HFP gas was added to reaction mixture at 30–65 °C. The reaction mixture was agitated at ambient temperature for 2–4 h (4 days in case of compound **10**), diluted with 10% hydrochloric acid, extracted by CH_2Cl_2 (100 mL ×2). Combined organic layer was washed by 10% hydrochloric acid (300 mL ×3) to remove DMF and dried over $MgSO_4$. Solvent was removed under reduced pressure and the residue distilled under vacuum to afford the final product Ratio of reagents and reaction conditions are given in Table 2.

References

[1] W.J. Middleton, E.G. Howard, W.H. Sharkey, J. Am. Chem. Soc. 83 (1961) 2589–2590.

[2] W.J. Middleton, E.G. Howard, W.H. Sharkey, J. Org. Chem. 30 (1965) 1375–1384.

[3] W.J. Middleton, J. Org. Chem. (1965) 1390–1394.

[4] W.J. Middleton, W.H. Sharkey, J. Org. Chem. (1965) 1384–1390.

[5] B.L. Dyatkin, S.R. Sterlin, L.G. Zhuravkova, I.L. Knunyants, Dokl. Akad. Nauk SSSR 183 (1968) 598–601.

[6] D.C. England, J. Org. Chem. 46 (1981) 153–157.

[7] Y. Inouye, D.J. Burton, J. Fluorine Chem. 14 (1979) 89–92.

[8] T. Kitazume, N. Ishikawa, Chem. Lett. 3 (1973) 267–268.

[9] T. Kitazume, N. Ishikawa, Bull. Chem. Soc. Jpn. 47 (1974) 785–786.

[10] T. Kitazume, T. Otaka, R. Takei, N. Ishikawa, Bull. Chem. Soc. Jpn. 49 (1976) 2491–2494.

[11] S.A. Postovoi, I.M. Vol'pin, N.I. Delyagina, M.V. Galakhov, Y.V. Zeifman, L.S. German, Izv. Akad. Nauk SSSR Ser. Khim. (1989) 1380–1383.

[12] V.A. Petrov, N.V. Vasil'ev, Cur. Org. Synth. 3 (2006) 215–259.

[13] V.A. Petrov, J. Fluorine Chem. 127 (2006) 529–538.

[14] V.A. Petrov, F. Davidson, P.J. Krusic, A.A. Marchione, W.J. Marshall, J. Fluorine Chem. 126 (2005) 601–610.

[15] V.A. Petrov, F. Davidson, W. Marshall, J. Fluorine Chem. 125 (2004) 1621–1628.

[16] V.A. Petrov, F. Davidson, B.E. Smart, J. Fluorine Chem. 125 (2004) 1543–1552.

[17] V.A. Petrov, C.G. Krespan, W. Marshall, J. Fluorine Chem. 126 (2005) 1332–1341.

[18] B.I. Martynov, L.T. Lantseva, B.L. Dyatkin, Zh. Org. Khim. 11 (1975) 2282–2285.

[19] S. Sankararaman, Pericyclic Reactions—A Textbook, Wiley–VCH VerlagGmbh & Co. KGaA, Germany, Weinheim, 2005, p. 109.

[20] M.S. Raasch, J. Org. Chem. 37 (1972) 1347–1356.

[21] R. Huisgen, F. Mietzsch, Ang. Chem. Int. Ed. Engl. 2 (1964) 83–85.

[22] M.E. Squillacote, A. Bergman, J. Org. Chem. 51 (1986) 3910–3911.

[23] A.A. Jarzecki, J. Gajewski, E.R. Davidson, J. Am. Chem. Soc. 121 (1999) 6928–6935.

[24] T. Gillmann, K. Hartke, Chem. Ber. 119 (1986) 2859–2867.

[25] G. Jenner, M. Papadopoulos, J. Org. Chem. 51 (1986) 585–589.

[26] N.W. Jordan, I.W. Elliott, J. Org. Chem. 27 (1962) 1445–1447.

[27] J. Leitich, G. Sprintschnik, Chem. Ber. 119 (1986) 1640–1660.

[28] P. Scheiner, W.R. Vaughan, J. Org. Chem. 26 (1961) 1923–1925.

[29] T. Tsuji, S. Teratake, H. Tanida, Bull. Chem. Soc. Jpn. 42 (1969) 2033–2037.

[30] G.H. Wahl Jr., J. Org. Chem. 33 (1968) 2158–2159.

[31] M.G. Barlow, N.N.E. Suliman, A.E. Tipping, J. Fluorine Chem. 70 (1995) 95–102.

[32] W. Reppe, O. Schichting, K. Klager, T. Toepel, Annal 560 (1948) 1–92.

[33] V.A. Petrov, Mendeleev Commun. (2006) 155–157.