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Remarkable effect of metal fluoride catalyst on reaction of hexafluoropropene, sulfur and vinyl ethers. Convenient synthesis of 2,2-bis(trifluoromethyl)-4-R-thietanes, 3,3-bis(trifluoromethyl)-5-R-1,2-dithiolanes and 2,2-bis(trifluoromethyl)-4-R-1,3-dithiolanes

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SC_2H_5)
2,2,4,4-Tetrakis(trifluoromethyl)thietane
3,3-Bis(trifluoromethyl)-5-alkoxy-1,2-dithiolanes
2,2-Bis(trifluoromethyl)-4-alkoxy-1,3-dithiolanes
2,2-Bis(trifluoromethyl)-4-alkoxy-1,3-dithiolene

ABSTRACT

It was demonstrated that the outcome of the reaction of hexafluoropropene, sulfur and vinyl ether strongly depends on the catalyst and reaction conditions. The reaction of HFP and S_x leading to the formation of 2,2,4,4-tetrakis(trifluoromethyl)-1,3-dithietane (**1**) when it is catalyzed by CsF, proceeds under milder conditions and is easier to control compared to KF catalyzed process. The order of addition of reagents plays a crucial role on the outcome of the reaction. For example, the addition of vinyl ether to pregenerated solution of **1** in DMF solvent results in slow reaction, leading to the corresponding 2,2-bis(trifluoromethyl)-4-R-thietanes in 8–91% yield, and it is catalyzed by either by KF or CsF. The addition of second mole of sulfur to the solution of 2,2-bis(trifluoromethyl)-4-R-thietanes in the presence MF catalyst leads to insertion of sulfur into thietane ring with the formation of the corresponding cyclic disulfides—3,3-bis(trifluoromethyl)-5-R-1,2-dithietanes. On the other hand, the addition of second mole of sulfur to the solution of **1** in DMF in the presence of CsF catalyst, followed by addition of vinyl ether results in exothermic reaction, and it produces the corresponding 2,2-bis(trifluoromethyl)-4-alkoxy-1,3-dithiolanes in good yield.

It was also demonstrated that 2,2-bis(trifluoromethyl)-4-R-thietanes can undergo disproportionation under action of fluoride anion, producing a mixture of the corresponding 1,2-dithiolane and $CF_2{=}C(CF_3)CH_2CFHOR$. The nucleophilic attack of fluoride anion in this case proceeds selectively on the carbon of the thietane ring, bearing alkoxy group.

The structure of 2,2-bis(trifluoromethyl)-4-R-thietanes forming as the result of 2 + 2 cycloaddition reaction between hexafluorothioacetone generated “in situ” from dimer **1** and vinyl ether was firmly supported by single crystal X-ray diffraction data, obtained for thietane bearing *t*-BuO-group.

1. Introduction

Due to presence of sulfur in strained four-membered ring, fluorinated thietanes possess an interesting reactivity and were used as starting materials for the preparation of fluorinated sulfur containing materials [1,2]. For example, 2,2-bis(trifluoromethyl)-4-R-thietanes (R = –OR) were converted to fluorinated 1,2-dithiolanes [3]; a number of unsaturated products, were prepared as the result of ring opening processes [3,4], along with the corresponding S-oxides [5], and 5-R-2-fluoro-3-trifluoromethyl-2,3-dihydrothiophenes [5].

2,2-Bis(trifluoromethyl)-4-alkoxythietanes originally were prepared by the reaction of monomeric hexafluorothioacetone (HFTA) with vinyl ethers [6], but the development of simpler synthesis [3], which does not involve handling monomeric, gaseous HFTA made this materials readily available. It is based on the reaction of, stable at ambient temperature, 2,2,4,4-tetrakis(trifluoromethyl)-1,3-dithietane (**1**, cyclic dimer of HFTA, prepared by reaction of sulfur and hexafluoropropene (HFP) in the presence of KF catalyst [7,8]) with methyl- or ethyl-vinyl ethers [3]. Recently we reported, a “one-pot” process for preparation of 5-alkoxy-2-fluoro-3-trifluoromethyldihydrothiophenes starting with sulfur, HFP and vinyl ether [5]. In course of that work we discovered an interesting effect of the catalyst on the reaction of sulfur, HFP and vinyl ethers, which is reported in this publication. This study was also focused on the optimization of the synthesis of 2,2-bis(trifluoromethyl)-4-R-thietanes and the corresponding 1,2- and 1,3-dithiolanes.

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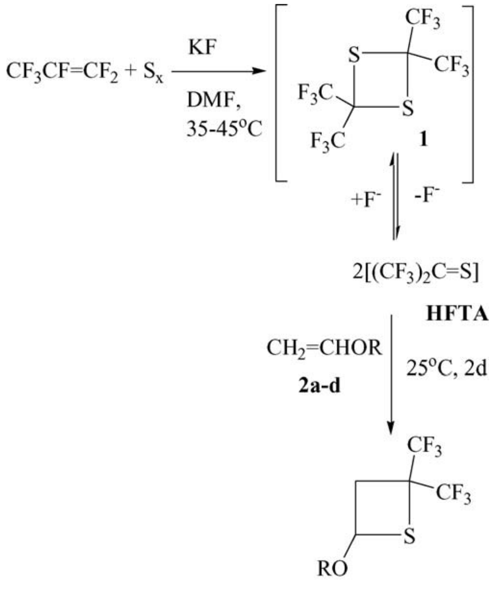
2. Results and discussion

2.1. Effect of metal fluoride catalyst on reaction of HFP, S_x and vinyl ethers. One-pot synthesis of polyfluorinated thietanes

The Ishikawa group reported the synthesis of 2,2-bis(trifluoromethyl)-4-R-thietanes (R = OCH_3, OC_2H_5) using reaction of **1** and vinyl ethers in the presence of KF catalyst [3]. Since in the synthesis of **1** same catalyst was employed [8] we decided to combine both steps in one-pot synthesis to simplify the preparation of fluorinated thietanes by eliminating step involving isolation of **1**. Indeed, it was found that thietanes **3a**–**d** can be prepared without isolation of **1**, by KF catalyzed reaction of HFP/S_x/vinyl ether in DMF solvent (Eq. (1)):



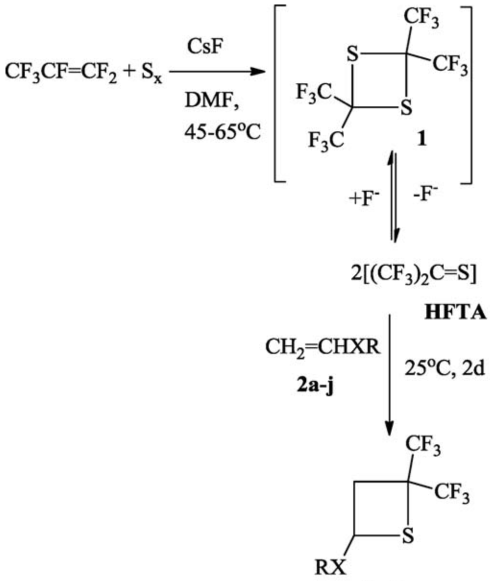
(1)

3a, R=C_2H_5, 86 %
3b, R=n-C_3H_7, 72%
3c, R=i-C_3H_7, 82%
3d, R=n-C_4H_9, 91 %

In a typical experiment gaseous HFP was continuously added into preheated (to 35–50 °C), well agitated mixture of sulfur and dry KF catalyst (5–10 mol%) suspended in anhydrous DMF and placed in a reaction vessel equipped with dry-ice condenser and thermocouple. The reaction of HFP with sulfur is relatively fast, however this step requires careful adjustment of the rate of addition of HFP, in order to avoid the condensation of HFP on the dry-ice condenser on one hand, and the overheating of the reaction mixture leading to the formation of byproducts [8], on the other hand. Vinyl ether was usually added to the reaction mixture after all the sulfur was dissolved, at 25–50 °C. Although the formation of thietanes is a slow process (~2 days at ambient temperature) the reaction is clean, producing thietanes **3a**–**d** in high yield (Eq. (1)). The KF catalyzed thietane synthesis was incorporated in a recently reported "one-pot" type synthesis of various 5-R-2-fluoro-3-trifluoromethyl-2,3-dihydrothiophenes [5].

Interestingly, the replacement of KF catalyst by CsF has a drastic effect on the reaction of HFP with sulfur. When CsF is used as catalyst, the addition of HFP (started at ambient temperature) results in exothermic reaction. Due to quicker HFP uptake and higher exothermicity, the reaction is faster and easier to control, compared to the KF catalyzed process. The end of the reaction can be judged, by the disappearance of sulfur and the formation of yellow or orange-yellow, slightly hazy, homogenous solution. Typically this step is carried out at 45–65 °C and the temperature can be easily controlled by adjusting the rate of addition of HFP or by applying external cooling. In order to ensure full consumption of sulfur, typically ~5–10% excess HFP was employed. The reaction can be stopped at this stage and compound **1** can be isolated in 80–90% yield after distillation (crude product after water quench typically contained ~5% of $(CF_3)_2CFSCH(CF_3)_2$ as major impurity), or it can be used without isolation for further reactions. It should be also pointed out that this process is sensitive to the amount of CsF catalyst and highest yields of **1** were obtained when ~2–5 mol% of CsF was used. In sharp contrast to KF catalyzed process, which can lead to the formation of higher molecular weight byproducts [8], the CsF catalyzed process does not suffer this disadvantage and it stops once one mole of HFP is consumed. The detailed study of the reaction of HFP and sulfur and CsF will be the subject of the forthcoming publication.

The addition of dry vinyl ethers **2a**–**i** or vinyl sulfide **2j** to the reaction mixture containing **1** (generated in CsF catalyzed reaction) results in the formation of the corresponding thietanes **3a**–**j** (Eq. (2)):



3a-j

(2)

3a,X=O, R=C_2H_5, 81 %
3b, X=O, R=n-C_3H_7, 69%
3c, X=O, R=i-C_3H_7, 85%
3d, X=O, R=n-C_4H_9, 76 %
3e, X=O, R=$(CH_3)_2CHCH_2$,75%
3f, X=O, R=t-C_4H_9, 72%
3g,X=O, R=c-C_6H_{11}, 86 %
3h, X=O, R=$Cl(CH_2)_2$, 62%
3i, X=O, R=CF_3CH_2, 8%
3j, X=S, R=C_2H_5, 68 %

Vinyl ethers **2a**–**h** could be added to the reaction mixture rapidly, since the formation of the corresponding thietanes is slow at ambient temperature. Longer reaction time (up to 8 days) leads to the formation of other byproducts, derived from disproportionation of thietanes under action of F^- (see Section 2.2).

It should be pointed out that isolated yields of thietanes prepared in the CsF catalyzed process involving vinyl ethers are slightly lower compared to the KF catalyzed process, due to the formation ~5–15% of the corresponding 1,3-dithiolane byproduct (see Section 2.2 for additional discussion). Although the formation of byproducts lowers the yield, it does not affect the purity of the isolated thietanes, due to substantial difference in boiling points of thietanes and 1,3-dithiolanes. Compounds **3a**–**j** (typical purity

Table 1
Yields, boiling points and mass spectrometry data for new materials.

Entr. no.	Compound no.	Yield (%)	Boiling point (°C/mm Hg) (melting point, °C)	MS (*m*/*z*)
1	**3a**	71[a]–86[b]	45/12[c]	254(M^+, $C_7H_8F_6OS^+$)
2	**3b**	69[a]–72[b]	78–79/50	268(M^+, $C_8H_{10}F_6OS^+$)
3	**3c**	82[a]–85[b]	70–72/25	268(M^+, $C_8H_{10}F_6OS^+$)
4	**3d**	72[a]–91[b]	94–96/30	282(M^+, $C_9H_{12}F_6OS^+$)
5	**3e**	75	88–89/30	282(M^+, $C_9H_{12}F_6OS^+$)
6	**3f**	72	55–57/5	282(M^+, $C_9H_{12}F_6OS^+$)
7	**3g**	86	60/0.1	308(M^+, $C_{11}H_{14}F_6OS^+$)
8	**3h**	62	100–101/20	288(M^+, $C_7H_7ClF_6OS^+$)
9	**3i**	8[d]	80–83/50	308((M^+, $C_7H_5F_9OS^+$)
10	**3j**	68	30–32/0.7	270(M^+, $C_7H_8F_6S_2^+$)
11	**3k**	45[e]	29–30/0.1	252(M^+, $C_7H_6F_6OS^+$)
12	**3l**	75	112–113	346(M^+, $C_7H_2F_{12}S^+$)
13	**4a**	63[a]–73[b]	44/2[f]	286(M^+, $C_7H_8F_6OS_2^+$)
14	**4b**	53[a]–83 [b]	108/25	300(M^+, $C_8H_{10}F_6OS_2^+$)
15	**4c**	87	46–48/1	300(M^+, $C_8H_{10}F_6OS_2^+$)
16	**4d**	82	84–85/2	314(M^+, $C_9H_{12}F_6OS_2^+$)
17	**4e**	–	–	250(M^+, $C_9H_{12}F_6O^+$)
18	**4f**	–	–	302($C_9H_{13}F_7OS^+$)
19	**4g**	–	–	288($C_8H_{11}F_7OS^+$)
20	**5a**	66	52–54/0.7 (38–39)	286(M^+, $C_7H_8F_6OS_2^+$)
21	**5b**	83	63–64	300(M^+, $C_8H_{10}F_6OS_2^+$)
22	**5c**	20	102–104/25 (46–47)	300(M^+, $C_8H_{10}F_6OS_2^+$)
23	**5d**	51	60–62/0.5	314(M^+, $C_9H_{12}F_6OS_2^+$)
24	**5e**	64	68–69/1	314(M^+, $C_9H_{12}F_6OS_2^+$)
25	**5f**	40	81–84/1	320(M^+, $C_7H_7ClF_6OS_2^+$)
26	**5g**	15	99–105/50	340(M^+, $C_7H_5F_9OS_2^+$)
27	**5h**	58	81–87/3[g]	284($C_7H_6F_6OS_2^+$)
29	**7**	50	(60–61)	356(M^+, $C_9H_6F_6O_4S_2^+$)

[a] Yield in KF catalyzed reaction.
[b] Yield in CsF catalyzed reaction.
[c] Reported b.p. 78–80 °C/70 mm Hg [3]; 43 °C/10 mm Hg [6].
[d] Crude product contained 35% of **5g**.
[e] Mixture of *cis*- and *trans*-isomers, ratio 98:2.
[f] Reported for **4a** b.p. 73–75 °C/11 mm Hg [3].
[g] Mixture of *cis*- and *trans*-isomers, ratio 65:35.

>98%,) were obtained after fractionational distillation of crude reaction mixture under reduced pressure (see Table 1).

Electron deficient vinyl ethers **2h** and **2i** (R = CH_2CH_2Cl and CH_2CF_3, respectively) have lower reactivity towards HFTA, which results in longer reaction times, lower isolated yields of thietanes **3h** and **3i** and the formation of substantial amount of the corresponding of 1,3-dithiolane byproducts (see Table 1 and Section 2.2 for discussion on formation of 1,3-dithiolanes).

Ethyl vinyl sulfide **2j** has the highest reactivity towards **1** and should be added to the reaction mixture slowly, due to

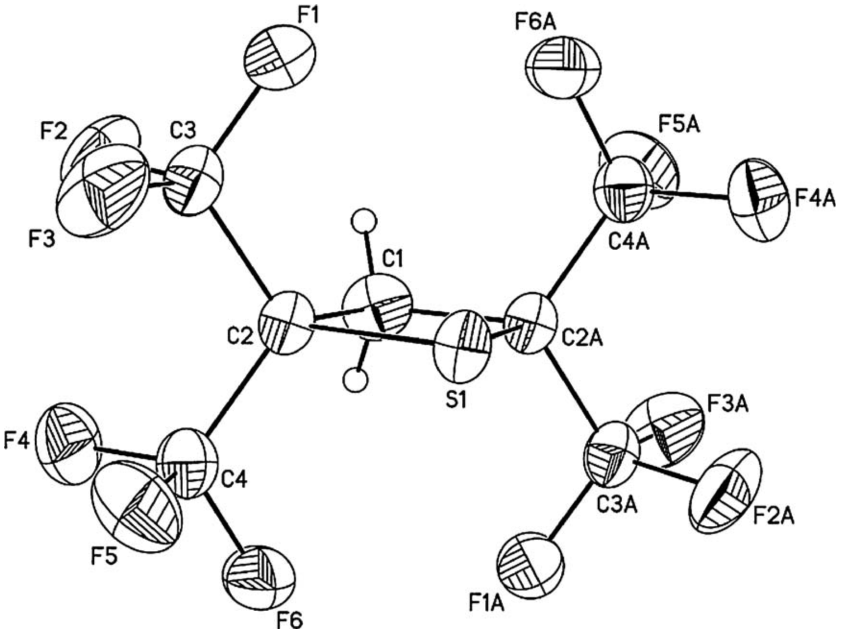
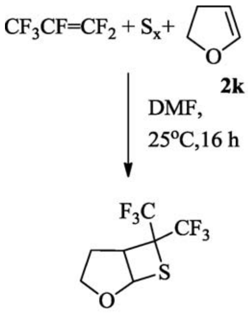


Fig. 1. Crystal structure of **3l**. Thermal ellipsoids drawn to the 50% probability level. Disordered positions are omitted for clarity.

exothermicity of the reaction, which in this case was completed in a few hours, leading to thietane **3j**.

The one-pot process was tested in the lab on up to 0.5 mol scale (using both KF or CsF catalysts), and the corresponding fluorinated thietanes **3a**–**h**, were prepared in 62–91% yield.

The CsF catalyzed reaction of 2,3-dihydrofurane (**2k**) with **1** resulted in formation of bicyclic thietane **3k** in moderate yield:



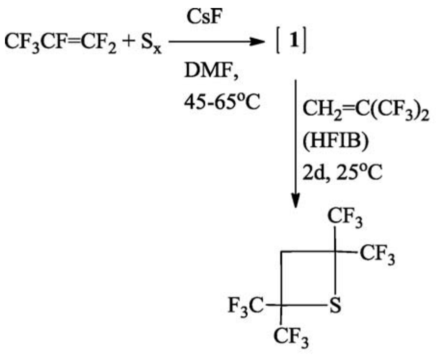
3k, 45%,
cis : trans - 98 : 2

(3)

It is interesting that, the cycloaddition step is stereoselective, leading to predominant formation of *cis*-isomer **3k** (Eq. (3)).

2,3-Dihydropyran, containing a less strained double bond has significantly lower reactivity towards **1**. The reaction at ambient temperature was very slow, but at elevated temperature (50–65 °C) it led to a mixture of equal amount of the corresponding thietane and unsaturated product containing the $-SCH(CF_3)_2$ group (NMR data). Later probably derives from the well-known *ene*-reaction of HFTA [6,9] involving the allylic hydrogen of 2,3-dihydropyran. It should be also mentioned that monomeric HFTA seems to have higher reactivity, since it was reported to react with 2,3-dihydropyran giving the corresponding cycloadduct in 40% yield under mild conditions [6].

Zeifman and Postovoii reported that electrondeficient $CF_2{=}C(CF_3)_2$ (perfluoroisobutene, PFIB) can undergo cycloaddition in CsF catalyzed reaction with **1**, producing perfluoro-(2,2,4,4-tetramethyl)thietane [10]. We found that less electrophilic $CH_2{=}C(CF_3)_2$ (hexafluoroisobutene, HFIB), also gives the corresponding thietane **3l** in one-pot reaction with HFP/S_x/CsF mixture in DMF solvent (Eq. (4)):



3l, 75%

(4)

The thietane **3l** is a liquid at ambient temperature, however, in contrast to compounds **3a**–**e**, **g**–**j** it readily crystallizes being placed in ice. We were able to confirm symmetrical structure of **3l** by single crystal X-ray diffraction data (Fig. 1, see also Section 2.3 for the discussion on the mechanism of cyclization).

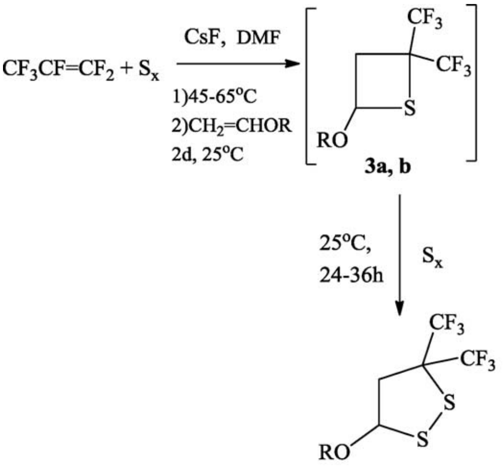
On the other hand, attempt to involve in the reaction with **1** electron deficient dimethylmaleate was not successful (**7d**, 25 °C, CsF, DMF solvent), despite the fact that the formation of the corresponding cycloadduct was previously mentioned in Ref. [11] for the KF catalyzed reaction of dimethylmaleate and **1**.

2.2. Effect of order of reagents addition. Preparation of 1,2- and 1,3-dithiolanes

2.2.1. Preparation of 3,3-bis(trifluoromethyl)-5-alkoxy-1,2-dithiolanes

Another interesting feature of the reaction between sulfur, HFP and vinyl ethers is a surprising sensitivity of the process to the order of reagents addition.

We found, that, the addition of a second mole of sulfur to the reaction mixture containing thietane **3a** and **b** prepared in the CsF catalyzed "one-pot" reaction of HPF/S_x/vinyl ether (see Section 2.1), leads to the formation of the corresponding 1,2-dithiolane **4a** or **4b** (Eq. (5)):



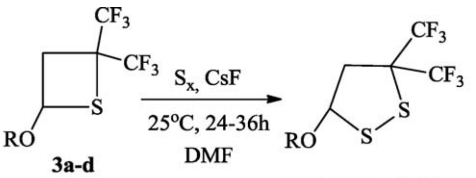
4a,R=C_2H_5, 63 %
4b, R=*n*-C_3H_7, 53%

(5)

The reaction is relatively slow and takes 24–36 h (GC, NMR).

Values of chemical shifts and coupling constants of ^{19}F NMR spectra for compound 1,2-dithiolane **4a** are in reasonable agreement with reported values, for the material synthesized in the reaction of **3a** with sulfur and diethylamine [3].

It should be pointed out, that the crude products **4a** and **4b** isolated in "one-pot" process (Eq. (5)), were contaminated by the corresponding 1,3-dithiolanes (forming at the stage of preparation of thietane, see Section 2.1), and isolated by thiolanes **4a** and **4b** contained 2–4% 1,3-isomers. This problem was resolved by reacting pure, isolated thietanes **3** with sulfur in the presence of CsF catalyst. Using this protocol 1,2-dithiolanes **4a**–**d** were isolated in 73–87% yield and fully characterized (Eq. (6), Tables 1 and 2).



4a,R=C_2H_5, 73 %
4b, R=*n*-C_3H_7, 83%
4c, R=*i*-C_3H_7, 87%
4d, R=*n*-C_4H_9, 82 %

(6)

It should by pointed out, that potassium fluoride can also be used as the catalyst for this process, however, the reaction was found to be significantly slower (typical conversion ~20% after 5

Table 2
^{1}H, ^{19}F and ^{13}C NMR data for new materials.

Entr. no.	Comp. no.	^{1}H NMR (δ, ppm, J, Hz)[a]	^{19}F NMR (δ, ppm, J, Hz)[a]	^{13}C NMR (δ, ppm, J,Hz)[a,b]
1	**3a**	1.27(3H, t, 7.3), 3.24(1H, ddq, 14.3, 5.1, 1.1), 3.36(1H, dd, 14.3, 7.2), 3.45(1H, m), 3.56(1H, m), 5.36(1H, dd, 7.2, 5.1)	−73.73(m)[c]	12.92, 36.48, 46.08(sept., 32.0), 64.20, 74.51, 122.98(q, 279), 124.28(q, 280.5)
2	**3b**	0.98(3H, t, 7.7 Hz), 1.66(2H, m, 7.7), 3.25(1H, ddq, 14.3, 5.2, 1.5), 3.40(3H, m), 5.35(1H, dd, 7.2, 4.9)	−73.72(m)	8.87, 21.42, 36.34, 46.01 (sept., 32.0), 70.28, 74.29, 122.93(q, 280), 124.23(q, 280)
3	**3c**	1.18(3H, d, 4.0), 1.19(3H, d, 3.8), 3.22(1H, ddq, 14.1, 5.6, 0.8), 3.33(1H, dd, 14.1, 7.2), 3.68(1H, sept., 6.1), 5.4(1H, dd, 6.9, 5.8)	−73.61(m)	20.13, 20.69, 37.44, 46.33 (sept. 32.0), 72.42, 72.97, 122.94(q, 280), 124.40(q, 280)
4	**3d**	0.95(3H, t, 7.5), 1.42(2H, m), 1.61(2H, m), 3.23(1H, ddq, 14.3, 5.1, 1.2), 3.37(1H, dd, 14.3, 7.2), 3.40(1H, m), 3.48(1H, m), 5.35(1H, dd, 7.2, 5.1)	−74.14(m)	21.31, 18.35, 30.35, 36.40, 46.09(sept., 32.0), 68.42, 74.87, 122.95(q, 276), 124.23(q, 276)
5	**3e**	0.92(3H, d, 1.5), 0.93(3H, d, 1.5), 1.88(1H, sept., 7.0), 3.13(1H, m), 3.21(2H, m), 3.35(1H, m), 5.30, 1H, dd, 7.1, 4.9)	−73.63(3F, q, 9.6), −73.77(3F, q, 9.6)	15.70, 15.72, 25.42, 34.32, 44.11(sept., 33), 73.02, 121.05(q, 280), 122.30(q, 280)
6	**3f**	0.2(9H, s), 2.22(1H, ddq, 14.3, 6.0, 1.3), 2.32(1H, dd, 14.3, 7.2), 4.53(1H, t, 6.6)	−74.70(m)	–
7	**3g**	1.34(5H, m), 1.55(1H, m), 1.80(4H, m), 3.27(1H, dd, 14.1, 5.5), 3.35(1H, dd, 14.1, 7.1), 5.48(1H, t, 6.9)	−74.00(m)	–
8	**3h**	3.25(1H, ddq, 13.9, 5.0, 1.2), 3.40(1H, dd, 14.0, 7.1), 3.66(3H, m), 5.79(1H, m), 5.38(1H, dd, 7.3, 5.0)	−73.64(m)	34.28, 39.02, 43.74(sept., 32.5), 66.87, 72.79, 12079(q, 282), 121.98(q, 282)
9	**3i**	3.27(1H, dddq, 14.8, 4.5, 1.0), 3.43(1H, dd, 14.8, 7.2), 3.82(1H, m), 3.92(1H, m), 5.40(1H, dd, 7.3, 4.7)	−73.62(3F, q, 9.8), −73.67(3F, q, 8.4), −73.73(3F, q, 9.8)	36.83, 46.41(sept., 33.5), 66.06(q, 34.4), 76.34, 122.99(q, 286), 124.35(q, 280)
10	**3j**	1.29(3H, t, 7.7), 2.75(2H, m), 3.29(2H, m), 4.90(1H, t, 8.3)	−73.25(3F, q, 9.9), −74.45(3F, q, 9.9)	14.40(m), 24.48, 36.00, 42.20, 47.83(sept., 32), 123.31(q, 282), 124.72(q, 282)
11	**3k**[d]	*Cis*-isomer: 1.92(1H, m, 14.7), 2.39(1Hdd, 14.7, 4.9), 3.95(1H, dd, 10.1, 5.8), 4.32(1H, t, 8.9), 4.50(1H, ddd, 11.6, 10.5, 4.4), 5.92(1H, d, 5.8)	*Cis*-isomer: −68.60(3F, q, 10.0), −74.88(3F, q, 10.0) *trans*-isomer: −71.02(3F, q, 10.6), −73.23(3F, q, 10.3)	–
12	**3l**	3.49(s)	−72.54	27.85(s), 45.54(br s), 122.48(q, 284.3)
13	**4a**	1.3.1(3H, t, 7.2), 2.76(1H, ddq, 14.3, 4.7, 1.6), 2.82(1H, dd, 14.3, 3.7), 3.61(1H, m), 3.84(1H, m), 5.56(1H, t, 4.2)	−68.75(3F, q, 10.4), −71.05(3F, q, 10.4)[e]	10.98, 40.59, 63.78, 65.58 (sept., 27.9), 92.59, 121.11 (q, 282), 121.90(q, 282)
14	**4b**	0.94(3H, t, 7.6 Hz), 1.66(2H, m), 2.68(1H, dd, 14.6, 3.3), 2.79 (1H, dd, 14.6, 3.1), 3.45(1H, m), 3.68(1H, m), 5.51(1H, t, 3.8)	−68.52(3F, q, $J = 10.0$) −71.15(3F, q, $J = 10.0$)	7.28, 19.57, 40.72, 65.58 (sept., 27.6), 69.95, 92.78, 121.05(q, 283.5), 122.00(q, 283.5)
15	**4c**	1.21(3H, d, 6.2), 1.23(3H, d, 6.2), 2.67(1H, ddq, 14.4, 5.2, 1.2), 2.72(1H, ddq, 14.4, 4.6, 1.0), 3.91(1H, sept., 6.3), 5.56(1H, t, 4.7)	−69.43(3F, q, 9.5), −70.74(3F, q, 9.5)	17.37, 19.29, 40.48, 64.32(sept., 27.3), 70.19, 91.60, 121.28 (q, 282), 121.86(q, 282)
16	**4d**	0.94(3H, t, 7.5), 1.40(2H, m), 1.61(2H, m), 2.69(1H, dd, 14.4, 4.6), 2.81(1H, dd, 14.4, 3.8), 3.49(1H, m), 3.75(1H, m), 5.50(1H, t, 4.0)	−68.61(3F, q, 10.4), −71.21(3F, q, 10.4)	10.32, 16.31, 28.32, 40.74, 65.91(sept., 29.0), 68.00, 92.91, 121.10 (q, 282.5), 122.05(q, 282.5)
17	**4e**	–	−60.96(3F, ddd), 20.2, 11.3, 2.3), −74.39(1F, dm, $J_d = 20.2$), −78.24(1F, m), −124.00(1F, dt, 66.0, 14.0)	–
18	**4f**	–	−67.75(3F, q, 8.8), −67.82(3F, q, 8.8), −124.61(1F, dm, $J_{H-F} = 67.0$)	–
19	**4g**	1.25(3H, t, 7.2), 2.34(3H, sept., 1.0), 2.40(2H, m), 3.65(1H, m), 3.90(1H, m), 5.60(1H, dt, 65.8, 12.2)	−66.91(3F, q, 10.4), −67.32(3F, qd), 10.4, 4), −115.82(1F, dtd, 66.0, 12.0)	–
20	**5a**	1.03(3H, t, 7.0), 3.22(1H, m), 3.33(11H, d, 13.1), 3.38(1H, dd, 13.1, 3.0), 3.55(1H, m), 5.49(1H, br.s)	−67.98(3F, q, 9.8), −70.58(3F, q, 9.8)	14.83, 46.25, 65.77, 72.72(sept., 30), 95.28, 123.90(q, 282), 14.65(q, 282)
21	**5b**	0.96(3H, t, $J = 7.3$ Hz), 1.66(2H, m, $J = 7.5$), 3.34(1H, m), 3.56(1H, d, 12.2), 3.61(1H, dd, 12.2, 3.2), 3.68(1H, m), 5.71(1H, s)	−67.63(3F, q, 10.7) −70.45(3F, q, 10.7)	10.41, 22.17, 46.55, 71.17, 72.34(sept., 30), 95.19, 123.55(q, 282), 124.72(q, 282)
22	**5c**	1.17(3H, d, $J = 6.0$), 1.21(1H, d, 6.3), 3.47(1H, d, 11.7), 3.58(1H, dd, 11.7, 3.1), 3.85(1H, sept., 6.1), 5.83(1H, br.s)	−67.67(3F, q, 9.8), −70.58(3F, q, 9.8)	20.17, 22.26, 46.69, 71.71, 72.14(sept., 32), 92.48, 123.38(q, 280), 124.20(q, 282)
23	**5d**	0.92(3H, d, 2.5), 0.94(3H, d, 2.5), 1.91(1H, m), 3.11(1H, dd, 8.7, 3.8), 3.45(1H, dd, 8.7, 7.0), 3.58(2H, m), 5.69(1H, br.s)	−67.51(3F, q, 10.1), −70.52(3F, q, 10.1)	14.02, 19.05, 27.89, 43.57, 72.28(sept., 31.0), 76.12, 95.43, 123.50(3F, q, 280), 124.27(3F, q, 280)

Table 2 (*Continued*)

Entr. no.	Comp. no.	^1H NMR (δ, ppm, J, Hz)[a]	^{19}F NMR (δ, ppm, J, Hz)[a]	^{13}C NMR (δ, ppm, J,Hz)[a,b]
24	**5e**	0.94(3H, t, 7.5), 1.40(2H, m), 1.61(2H, m), 2.69(1H, dd, 14.4, 4.6), 2.81(1H, dd, 14.4, 3.8), 3.49(1H, m), 3.75(1H, m), 5.50(1H, t, 4.0)	−67.65(3F, q, 10.7), −70.48(3F, q, 10.7)	14.02, 19.58, 31.53, 46.92, 69.60, 72.75(sept., 31), 95.34, 123.910(q, 280), 124.60(q, 282)
25	**5f**	3.65(5H, m), 3.99(1H, m), 5.79(1H, br.s)	−67.64(3F, q, 10.3), −70.42(3F, q, 10.3)	39.06, 43.58, 66.18, 69.47(sept. 31), 92.29, 120.70(q, 281), 121.37(q, 281)
26	**5g**	3.67(2H, m), 3.86(1H, m), 4.05(1H, m), 5.85(1H, br.s)	−67.75(3F, q, 10.0), −70.37(3F, q, 10.1), −73.08(3F, t, 8.8)	46.50, 65.19(q, 36.0), 72.60(q, 31.0), 94.47, 123.33(q, 280), 123.47(q, 280), 124.00(q, 280)
27	*cis*-**5h**	2.15(1H, ddt, 13.5, 6.2, 2.3), 2.33(1H, dm, 13.5), 4.14(td, 8.6, 2.3), 4.47(1H, m), 4.60(1H, t, 5.3), 6.25(1H, d, 4.8)	−76.41(q, 10.6), −71.01(q, 10.6)	–
28	*trans*-**5h**	2.10(1H, m), 2.33(1H, m), 3.85(1H, m), 4.58(1H, m), 4.64(1H, m), 5.21(1H, d, 9.3)	−70.21(3F, q, 10.3), −70.82(3F, q, 10.3)	–
29	**7**	3.87(s)	−70.74(s)	53.42, 70.50(sept. 31.0), 122.45(q, 286), 128.10, 158.69
30	**1**	–	−72.63(s)	40.79(br.s), 122.38(q, 284)
31	**8**[f]	–	–	63.35(br.s), 112.06(t, 303.0), 121.08(q, 286.0)

[a] In $CDCl_3$.

[b] {H}^{13}C NMR spectra.

[c] Reported for **3a** [3]: ^{19}F NMR: −73.4(m) ppm.

[d] **3k** ratio *cis*/*trans*-98: 2.

[e] Reported for **4a** [3]: ^{19}F NMR: −67.9(q), −70.1(q), ppm, J = 10.4 Hz.

[f] Reported for compound **8** [10]: ^{19}F NMR: −67.0(t, 10.0), −91.8(m, 10.0); ^{13}C NMR: 70.0(m), 118.4(t, 284.7), 127.1(q, 300.8) ppm.

days at ambient temperature), which can be attributed to lower solubility of KF in DMF solvent.

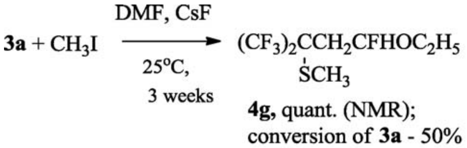
It should be pointed out that formation of neither 1,2- or 1,3-dithiolanes was not observed in the case of thietane **3l**, even when a large excess of sulfur was employed in the reaction of **1** and HFIB (DMF, 25 °C, 3 days).

It was also demonstrated, that thietanes **3** can undergo disproportionation in the presence of CsF catalyst. For example, 90% conversion of **3d** in the reaction with CsF was achieved after 2 weeks at 25 °C (DMF), leading to a mixture of 1,2-dithiolane **4d**, olefin **4e** and thiol **4f** (Eq. (7); compound **4f** probably formed as the result of quench of the reaction mixture by water, see Section 4.7). It should be pointed out, that his process is significantly slower compared to the formation of the corresponding thietanes and the formation of significant amount of compounds similar to **4e** and **4f** was not observed in typical reaction of **1** with vinyl ethers:

$$\mathbf{3d} \xrightarrow[25^{\circ}C,\ 2\ weeks]{CsF,\ DMF} \mathbf{4d} + \underset{\mathbf{4e}}{CF_2{=}C(CF_3)CH_2CFHOC_4H_9} + \underset{\mathbf{4f}}{(CF_3)_2C(SH)CH_2CFHOC_4H_9} \qquad (7)$$

ratio **4d**:**4e**:**4f**:**3d** = 50:30:10:10,
conversion **3d** - 90%

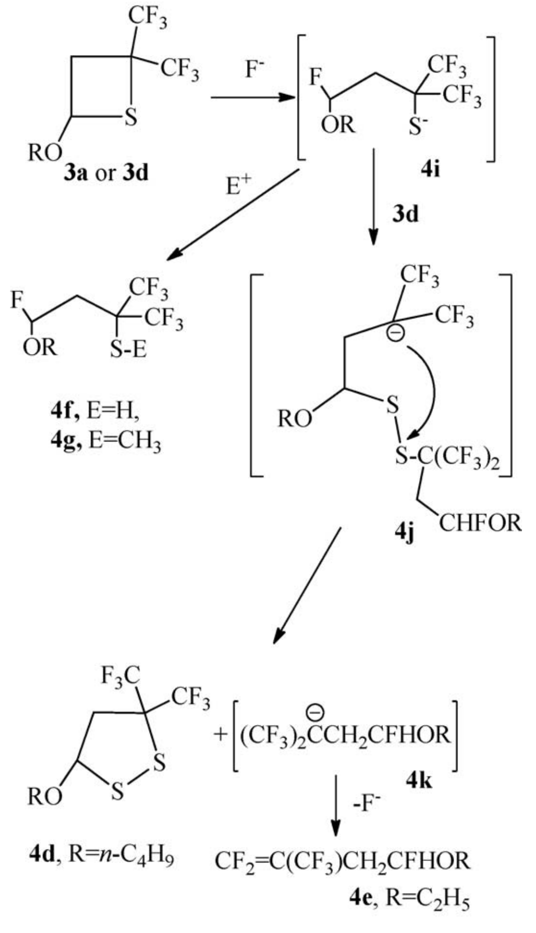
In the reaction of thietane **3a** with excess CsF and CH_3I 1,2-dithiolane **4a** did not form, but instead it resulted in clean formation of compound **4g** (Eq. (8)):



$$\mathbf{3a} + CH_3I \xrightarrow[25^{\circ}C,\ 3\ weeks]{DMF,\ CsF} \underset{SCH_3}{(CF_3)_2CCH_2CFHOC_2H_5} \qquad (8)$$

4g, quant. (NMR);
conversion of **3a** - 50%

Mechanistically the formation of compounds **4d**–**g** upon treatment of thietane **3a** or **3d** with CsF can be the result of thietane ring opening by fluoride anion (Scheme 1). Since F^- is a hard nucleophile, it attacks on carbon carrying an alkoxy group,

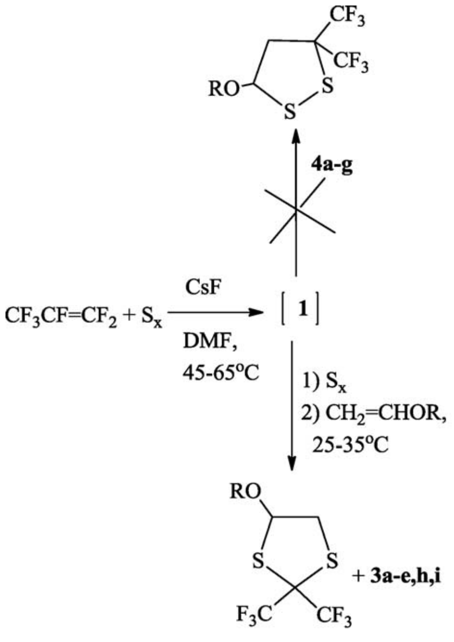


Scheme 1.

rather than on sulfur of the thietane ring. The intermediate thiolate anion **4i** can be trapped by either reaction with CH_3I or water leading to **4g** or **4f**, respectively. The formation of 1,2-dithiolanes **4a**–**d**, in this process is the result of nucleophilic attack of soft thiolate **4i** on the sulfur of second molecule of thietane, leading to the intermediate **4j**. Intramolecular cyclization in intermediate **4j** through the attack of carbanion center on sulfur results in formation of 1,2-dithiolanes (**4a**–**d**) and elimination of anion **4k**, which gives olefin **4e** after elimination of fluoride anion.

2.2.2. Preparation of 2,2-bis(trifluoromethyl)-4-alkoxy-1,3-dithiolanes

As it was mentioned in Section 2.2.1, a small change in order of addition of sulfur to the reaction mixture has significant impact on the outcome of the reaction of **1**, sulfur and vinyl ethers. Indeed, when a second mole of sulfur is added right after generation of **1** and is followed by the addition of vinyl ether, the reaction becomes *exothermic*, and it results in fast formation of the corresponding 1,3-dithiolanes **5** as major product (Eq. (9)). In this case, the addition of vinyl ethers **2a**–**e**, **h**, should be carried out slowly, in order to control the heat evolution. In sharp contrast to the reaction of sulfur with thietanes **3a**–**d** (Eqs. (5) and (6)), which is relatively slow, this process is fast and typically is completed within 1–3 h after the addition of vinyl ether. It does not produce expected 1,2-dithiolanes, but results in the formation of the corresponding 1,3-dithiolane **5a**–**f**, as principal product, along with smaller amount (5–15%) of the corresponding thietanes **3a**–**e**, **h**. In the case of vinyl ether **2b** it was demonstrated that dry KF is also catalyzes the reaction. The process is less exothermic, but it also results in the formation of 1,3-dithiolane **5b**, along with smaller amount of thietane **3b** (ratio **5b**:**3b**—84:16, calculated yield **5b**—86%):

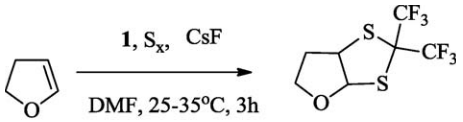


(9)

5a, R=C_2H_5, 66 %
5b, R=*n*-C_3H_7, 83%
5c, R=*i*-C_3H_7, 20%
5d, R=*n*-C_4H_9, 51%
5e, R=$(CH_3)_2CHCH_2$, 64%
5f, R=$Cl(CH_2)_2$, 51%
5g, R=CF_3CH_2, 15%

The structure of compound **5c** (crystallized from hexane) was confirmed by single crystal X-ray diffraction data.

2,3-Dihydrofurane **2k** under similar conditions gave 1,3-dithiolane **5h** as a mixture of *cis*- and *trans*-isomers (Eq. (10), ratio 65:35, NMR).



2k

5h, 58%
ratio *cis:trans* -
65 :35

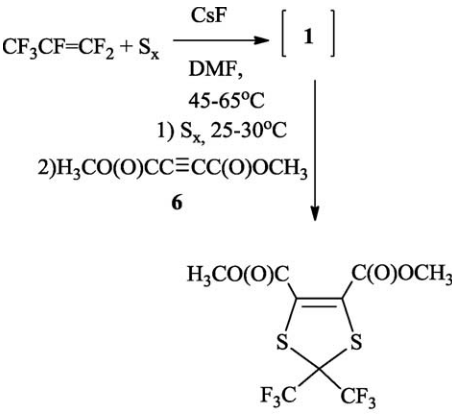
(10)

Since *trans*-isomer **5h** has higher solubility, relatively pure (96%, NMR) sample of *cis*-**5h** was obtained by crystallization of distilled product from hexane and its structure confirmed by single crystal X-ray diffraction (see Fig. 2).

It should be pointed out that the interaction of 2,3-dihydrofurane (**2k**) with a mixture of **1** and sulfur seems to have a high selectivity for the *cis*-cycloadduct, since the reaction which carried out at lower conversion and shorter time resulted in selective formation of *cis*-**5h** (95% selectivity at 50% conversion, NMR). This data suggest, that the *cis*-isomer forms first, but under reaction conditions it undergoes base catalyzed *cis*/*trans*-isomerization. It is probably initiated by the abstraction of relatively acidic proton from carbon connected to oxygen and sulfur, resulting in the generation of carbanion **A** (Scheme 2). Since the addition of H^+ to intermediate **A** can proceed from either "top" or "bottom", this process leads to the formation of both *cis*- and *trans*-isomers of **5h**.

The formation of approximately equal amount of *cis*- and *trans*-isomers in this reaction is indicative of small difference in energy between two isomers of **5h**. It is interesting, that the bicyclic compound **3k** (containing thietane, rather, 13-dithiolane ring) forms predominantly as *cis*-isomer under similar conditions (see Eq. (3)). This difference can be attributed to higher flexibility of compound **5h**, containing five-membered ring with two sulfur atoms.

The reaction of a mixture of **1**/S_x/CsF with electron deficient olefins, such as dimethylmaleate or HFIB failed to produce the corresponding 1,3-dithiolanes (2 and 7 days at 25 °C, respectively, DMF solvent, NMR). Surprisingly, acetylene **6** was found to be highly reactivity towards the mixture of **1** and sulfur, rapidly producing the corresponding 1,3-dithiolene **7**, along with some polymeric material. The structure of **7** was confirmed by single crystal X-ray diffraction.



(11)

7, 70%

2.3. Structure of thietanes and NMR spectra of 1,2- and 1,3-dithiolanes

Although products of the cycloaddition reaction HFTA with vinyl ethers/vinyl sulfides are known for over 40 years, analysis of

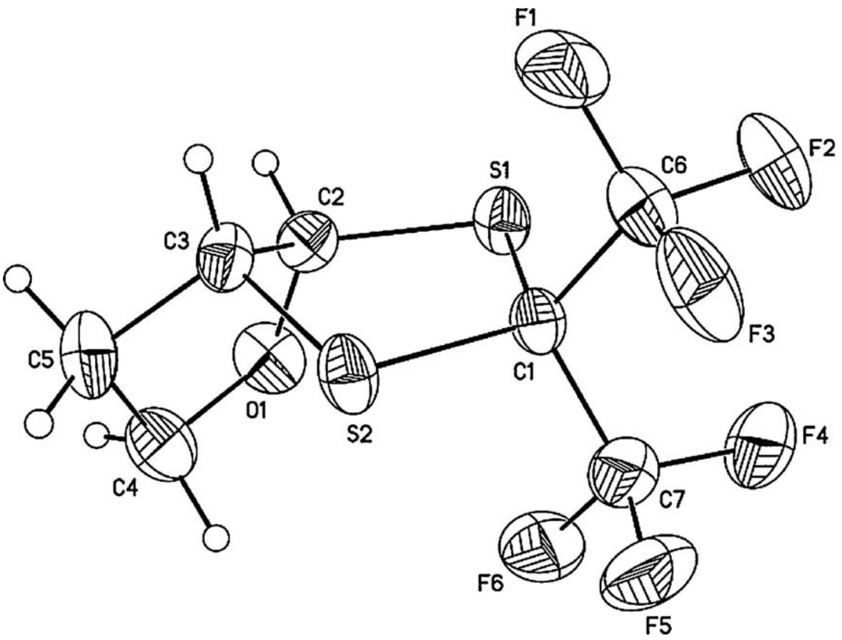


Fig. 2. X-ray crystal structure of *cis*-**5h**. Thermal ellipsoids drawn to the 50% probability level. Disordered positions are omitted for clarity.

literature data shows that actual structure of these cycloadducts was not firmly established. In the original paper [6], the structure of 2,2-bis(trifluoromethyl)-4-R-thietane (*vs.* 2,2-bis(trifluoromethyl)-3-R-thietane) was assigned based on data of mass spectrometry and low resolution ^{1}H and ^{19}F NMR spectroscopy [3,6]. It should be pointed out that the absence of significant coupling constants between CH_2- and CF_3-groups in thietanes **3** (see discussion below) makes standard of ^{1}H and ^{19}F NMR techniques insufficient for assigning the structure of the regioisomers. In addition, well-known dual reactivity of HFTA may be responsible for the formation of different regioisomers depending on the nature of nucleophile. For example, in reactions of HFTA, the attack of soft nucleophiles such as RS^- may proceed on sulfur [12], while hard RO^- or F^- [12,13], are known to attack the carbon of C=S fragment of HFTA. That brings the question—what is the actual orientation of HFTA cycloaddition with vinyl ethers or fluorinated olefins? Single crystal X-ray diffraction data reported recently for 2,2-bis(trifluoromethyl)-4-$SO_2C_2H_5$-thietane [5], suggested that structural assignment of cycloadducts of HFTA and vinyl ethers by Middleton is correct. However, 2,2-bis(trifluoromethyl)-4-$SO_2C_2H_5$-thietane did not derived from direct cycloaddition reaction, but was synthesizes by selective oxidation of the corresponding thietane **3j**.

In this study we were able unambiguously establish the structure of thietane **3f** (R = O–Bu–t) using single crystal X-ray diffraction and confirm that the cycloadduct indeed has the structure of 2,2-bis(trifluoromethyl)-4-(*t*-butoxy)-thietane (Fig. 3), rather than isomeric 2,2-bis(trifluoromethyl)-3-(*t*-butoxy)thietane. The structures of **3f** and **3j** suggest that in the reaction with vinyl ethers and vinyl sulfides, HFTA acts as if the negative charge is localized on sulfur of C=S fragment.

We also were able to confirm the structure of perfluoro(2,2,4,4-tetramethyl)thietane (**8**, PFIB/HFTA cycloadduct, sample was prepared in this laboratories by Dr. D. England). According to a single crystal X-ray structure the thietane **8** indeed has a symmetrical structure, similar to the structure of **3l** (see Fig. 1), with all four CF_3-groups located in the α-position to sulfur, as it

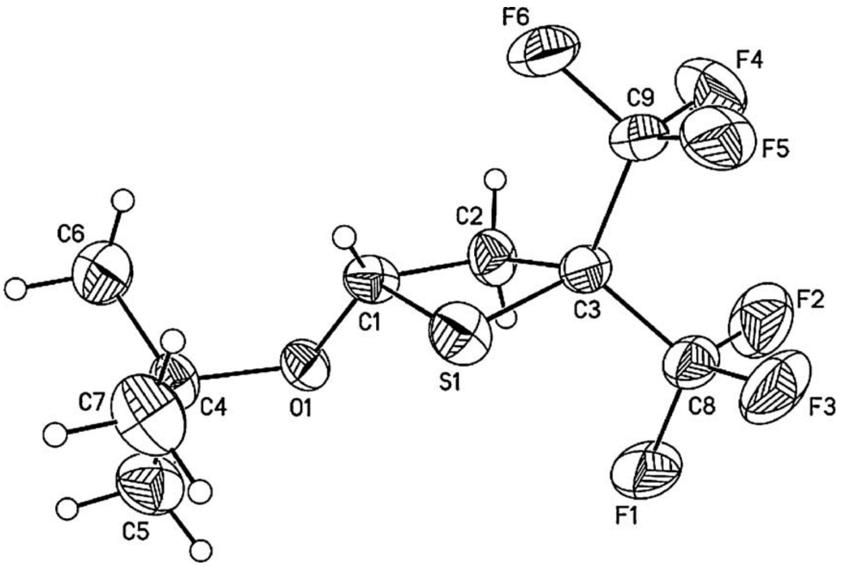


Fig. 3. X-ray crystal structure of **3f**. Thermal ellipsoids drawn to the 50% probability level. Disordered positions are omitted for clarity.

was suggested earlier by Zeifman and Postovoii [10], based on data of ^{19}F and ^{13}C NMR spectroscopy. An interesting feature of thietanes **3l** and **8** is flattening of the thietane ring as reflected in small values of torsion angle S–C2–C3–C4 (3.1° and 0.1°, respectively) *vs.* value 26° reported for the parent thietane [14].

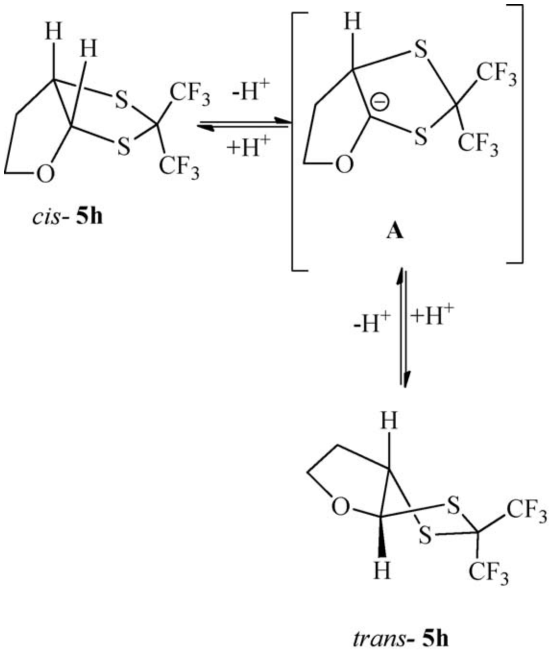
While ^{1}H and ^{19}F spectra of thietanes **3a–l** and **8**, 1,2-dithiolanes **4** and 1,3-dithiolanes are typical for this type of materials and differ only slightly, all the spectra share one common feature—the absence of observable coupling constant between CF_3-groups and CH_2 hydrogens of the thietane or 1,2- or 1,3-dithiolane ring, which makes impossible the identification of regioisomers using ^{1}H and ^{19}F NMR spectroscopy.

While in ^{19}F NMR spectra of thietanes **3**, the resonances of CF_3-groups usually appear between −73 and −74 ppm as either overlapped or not well separated quartets, the corresponding resonances in 1,2- and 1,3-dithiolanes are well separated by ~2–3 ppm. The resonances of trifluoromethyl groups in 1,3-dithiolanes **5a–g** are shifted upfield by ~0.5 ppm compared to 1,2-dithiolanes **4a–d**.

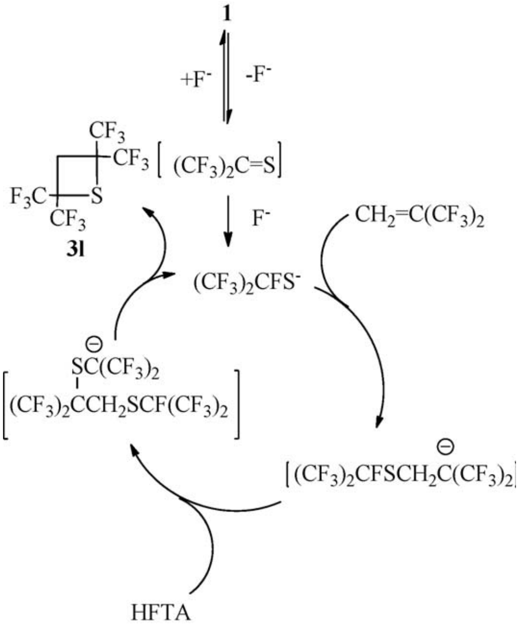
On the other hand, in the ^{13}C NMR spectra a significant difference in chemical shifts of the carbon carrying two trifluoromethyl groups was observed for thietanes, 1,2- and 1,3-dithiolanes (see Table 2). Indeed, resonances of C-2 in ^{13}C NMR spectra of thietanes **3a–l**, all appear within the narrow range of 43–47 ppm (*cf.* $\delta = 40.79$ ppm for compound **1** and $\delta = 26.1$ ppm for parent thietane [15]), with deviation of the chemical shift for perfluorinated thietane **8** ($\delta = 63.35$ ppm). While in 4-alkoxy thietanes **3** this signal is well resolved (septet, $J = 32–33$ Hz), in compounds **1**, **3l** and **8** it is broadened ($\Delta\upsilon_{1/2} = 70–80$ Hz) and does not have fine structure ($CDCl_3$, 25 °C). The resonance of the same carbon in 1,2-dithiolanes **4** is shifted downfield and located in the range of $\delta = 64–66$ ppm, while in 1,3-isomers **5** the septet of the carbon carrying two CF_3-groups is shifted even further and appears within the narrow range of $\delta = 69–72$ ppm.

2.4. Mechanistic considerations

While the regiochemistry of cycloaddition of HFTA to vinyl ethers is now reliably confirmed, the mechanism of formation of thietanes **3a–j** is still not clear. Both HFTA and hexafluoroacetone (HFA), react with vinyl ethers selectively forming 4-alkoxy-thietanes [6] or -oxetanes [16], respectively. On the other hand, in *ene*-reaction different regiochemistries of insertion into allylic C–H bond was observed for HFA and HFTA. For example the reaction propylene with HFA gives allylhexafluoroisopropanol [17], however, similar process involving HFTA results in selective formation of $CH_2{=}CHCH_2SCH(CF_3)_2$ [6].

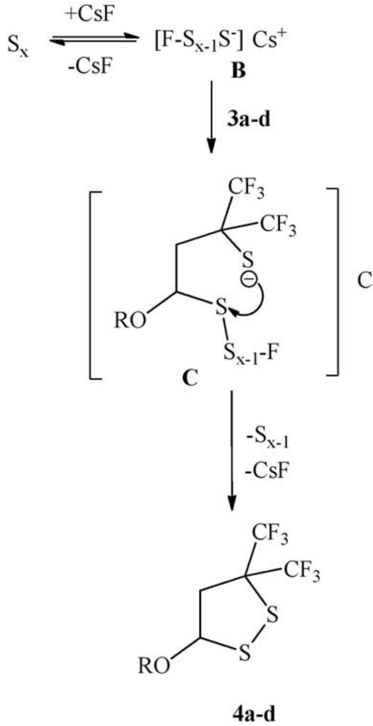


Scheme 2.



Scheme 3.

One of the explanations of unusual charge distribution in the C=S moiety of HFTA was suggested by Fukui [18] involves the participation of *d*-orbitals of sulfur, leading to higher electron density on sulfur. The observed regiochemistry of cycloaddition



Scheme 4.

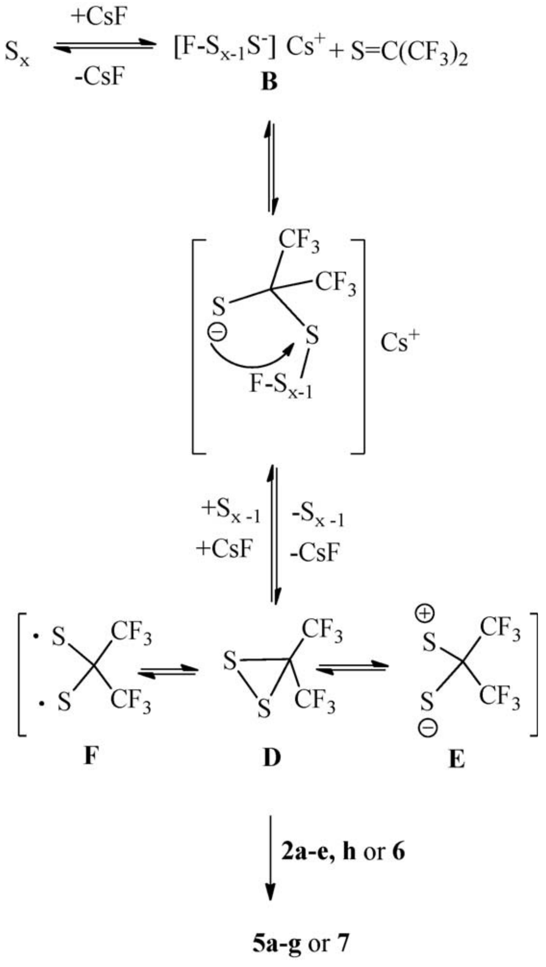
vinyl ethers and HFTA can be explained using three-centered coordination mechanism suggested for 2 + 2 cycloaddition reactions by Fukui [19].

The formation of thietane **3l** in the reaction of **1** and HFIB (Eq. (4)) can be explained by mechanism postulated by Zeifman and Postovoii for the reaction of PFIB and **1** [10]. It includes attack of $(CF_3)_2CFS^-$ on positively charged carbon of CH_2 group of HFIB and further reaction of the intermediate carbanion with HFTA and intermolecular cyclization with the formation of **3l** and release of $(CF_3)_2CFS^-$, which can be involved in the cyclization process again (Scheme 3).

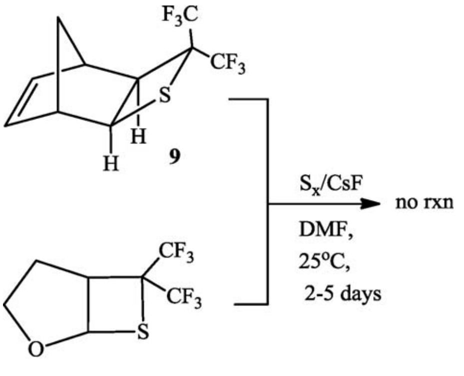
It should be pointed out, that at this point an alternative mechanism involving an single electron transfer step and the formation of intermediate zwitter-ion $^-C(CF_3)_2CH_2C(CF_3)_2S^+$ cannot be completely ruled out.

The formation of 1,2-dithiolanes **4a**–**d** in the reaction of thietanes **3** with sulfur (Eq. (4)) can be explained by the mechanism presented in Scheme 4. Sulfur anion **B** (formed as the result of the reaction of S_x with CsF in polar solvent) attacks the carbon carrying alkoxy group of the thietanes ring. The ring opening process leads to the generation of intermediate **C**. Intramolecular nucleophilic attack on a sulfur atom, followed by elimination of the sulfur anion results in the formation of 1,2-dithiolanes **4a**–**d**.

It should be mentioned that the mechanism depicted in Scheme 4 is preferred over an alternative one involving attack on sulfur anion on *sulfur* atom of the thietane ring, since it agrees with transformation of thietanes **3a** and **d** under action of CsF (Eqs. (5) and (6)). We also found that both norbonenthietane **9** [20] and thietane **3k** are inert towards the action of CsF or the mixture of S_x\CsF or (25 °C, DMF, 2–5 days, NMR, Eq. (12)). That fact is considered as an argument in favor of the mechanism involving nucleophilic attack on carbon, since in compounds **9** and **3l** α-carbon of thietane ring is sterically hindered and is not susceptible to nucleophilic attack.



Scheme 5.



(12)

3k

The mechanism of the formation of 1,3-dithiolanes **5a**–**g** and 1,3-dithiolene **7** is not quite clear at this point. One of several possible mechanisms is depicted by Scheme 5 is based on the assumption that HFTA generated from **1** under action of fluoride anion can react with sulfur anion **B** forming dithiirane **D**. Intermediate **D** can further undergo cycloaddition to vinyl ethers giving the corresponding 1,3-dithiolanes. The formation of the corresponding cyloadducts with both electron rich and electron deficient substrates (acetylene **6**) may suggest that the reactive intermediate involved in this process has zwitter-ionic structure **E**, however, the participation in this process intermediates such as dithiirane **D** or biradical **F** also cannot be excluded either.

3. Conclusion

Described in this paper one-pot procedure for the preparation of 2,2-bis(trifluoromethyl)-4-R-thietanes simplifies the synthesis of fluorinated thietanes. It is applicable for the preparation of a wide variety of thietanes **3**, including 2,2-bis(trifluoromethyl)-4-S-Et-thietane (**3j**) and 2,2,4,4-tetrakis(trifluoromethyl) thietane (**3l**). The structures of 2,2-bis(trifluoromethyl)-4-*t*-BuO-thietane (**3f**), along with structures of thietanes **3l** and **8** was confirmed by single crystal X-ray diffraction data.

Metal fluoride catalyzed reaction of thietanes **3a**–**d** with second mole of sulfur provided an easy access to 3,3-bis(trifluoromethyl)-5-alkoxy-1,2-dithiolanes **4a**–**d**. Thietanes **3** under the action of fluoride anion can undergo disproportionation, forming a mixture of the corresponding 1,2-dithiolane (**4**) and $CF_2{=}C(CF_3)CH_2CHF(OR)$. This reaction is significantly slower and doesn't compete with formation of thietanes or thiolanes. Preliminary mechanistic studies indicate that ring opening of thietanes **3** proceeds through attack of nucleophile on C-4 carbon of thietanes ring.

A simple modification of the synthetic protocol, by reversing an order of reagent addition leads to predominant formation of the 2,2-bis(trifluoromethyl)-4-alkoxy-1,3-dithiolanes **5a**–**h**, providing an access to new group of fluorinated sulfur containing heterocycles.

4. Experimental

^1H NMR and ^{19}F NMR spectra were recorded on a Bruker DRX-500 (499.87 MHz) instrument using $CFCl_3$ or TMS as internal standards. $CDCl_3$ was used as a lock solvent, unless stated otherwise. IR spectra were recorded on a Perkin-Elmer 1600 FT spectrometer (KCl plates, liquid film or in KBr for solids). Moisture sensitive materials were handled in a glove box, under nitrogen. GC and GC/MS analysis were carried out on a HP-6890 instrument, using HP FFAP capillary column and either TCD (GC) and mass selective (GS/MS) detectors, respectively. Dry DMF (anhydrous, water content 0.005%), dimethylacetylene carboxylate (**6**) (Aldrich), sulfur (sublimed, 99.5%, ~100 mesh, Alfa Aesar), hexafluoropropene, HFIB (DuPont), vinyl ethers **2a**–**k** (Aldrich, TCI), were obtained from commercial sources and used without further purification. CsF and KF (Aldrich) were dried at 100–120 °C under dynamic vacuum for 4–8 h and were stored and handled inside of the dry box.

Caution: All reactions described in the paper are affected by trace amounts of water, so using anhydrous solvents and reagents and proper drying and handling of CsF and KF is essential. Trace amount of water may significantly reduce the yield or completely inhibit the reaction, due to deactivation of metal fluoride catalyst.

Due to a high ratio of sulfur to fluorine, elemental analysis was not attempted for new materials. The purity of all isolated compounds established by GC and NMR spectroscopy was at least 98%.

4.1. *Crystallography*

X-ray data for **3l**, **3f**, **5c**, **5h**, **7** and **8** were collected at −100 °C using a Bruker 1K CCD system equipped with a sealed tube molybdenum source and a graphite monochromator.

The structures were solved and refined using the Shelxtl [21] software package, refinement by full-matrix least squares on F^2, scattering factors from Int. Tab. Vol C Tables 4.2.6.8 and 6.1.1.4. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC #769157 to #769162. 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).

4.2. *Preparation of thietanes* 3a–d *catalyzed by KF (typical procedure)*

Inside of dry box 250–500 mL three-neck, round bottom flask was charged with 1–2 g of dry KF. The flask was taken out, brought into a fume hood, and under flow of nitrogen was equipped with thermocouple, dry-ice condenser, gas inlet tube and magnetic stir bar. Dry DMF (50–100 mL) was added using syringe and sublimed sulfur (3.2–6.4 g, 0.1–0.2 mol) was added to agitated reaction mixture. The addition of sulfur resulted in the appearance of green or blue color, which quickly disappeared after addition of HFP was started. The reaction mixture was brought up to ~30–35 °C and gaseous hexafluoropropene (HFP) was fed into reaction mixture at a rate, which allowed to maintain internal temperature between 35 and 45 °C, but at same time avoid the condensation of an excessive amount of HFP on dry-ice condenser. After the required amount of HFP (0.11–0.22 mol, measured by weight difference of the HFP cylinder) was added and all sulfur went into solution, the reaction mixture was allowed to cool down to ambient temperature. Required amount (0.1–0.2 mol) of vinyl ether **2** was added to the reaction mixture and it was agitated at ambient temperature for 24–48 h. The reaction was monitored by GC and when the conversion of starting materials exceed 90% the reaction mixture was diluted by 200–300 mL of water, extracted by hexane (50–75 mL ×2), combined organic layer was washed by water (100 mL ×3), dried over $MgSO_4$. Solvent was removed under reduced pressure and the residue was distilled under vacuum to give thietanes **3a**–**d**. Data for compound **3a**–**d** are given in Tables 1 and 2.

4.3. *One-pot preparation of thietanes* 3a–k *catalyzed by CsF (typical procedure)*

Inside of dry box 250–500 mL three-neck, round bottom flask was charged with 1–2 g of dry CsF. The flask was taken out, brought into a fume hood, and under flow of nitrogen was equipped with thermocouple, dry-ice condenser, gas inlet tube and magnetic stir bar. Dry DMF (50–250 mL) was added using syringe and sublimed sulfur (3.2–16 g, 0.1–0.5 mol) was added to agitated reaction mixture. The addition of sulfur resulted in the appearance of green or blue color, which quickly disappeared after addition of HFP was started. The addition of gaseous hexafluoropropene (HFP) was started at ambient temperature and resulted in rapid raise of internal temperature to 45–50 °C. HFP was fed into reaction mixture at a rate, which allowed to maintain internal temperature between 50 and 65 °C, but at same time avoid the condensation of an excessive amount of HFP on dry-ice condenser. After the required amount of HFP (0.1–0.5 mol, measured by weight difference of the HFP cylinder) was added and all sulfur went into solution, the reaction mixture was allowed to cool down to ambient temperature. Required amount (0.1–0.5 mol) of vinyl ether **2** was added to the reaction mixture and it was agitated at ambient temperature for 24–48 h. The reaction was monitored by GC and when the conversion of starting materials would exceed 90%, the reaction mixture was diluted with 200–300 mL of water, extracted with hexane (50–75 mL ×2), combined organic layer was washed by water (100 mL ×3), dried over $MgSO_4$. Solvent was removed under reduced pressure and the residue was distilled under vacuum to give thietanes **3a**–**k**. Yields, boiling points and data of mass spectrometry for **3a**–**k** are given in Table 1 and NMR data in Table 2.

4.4. *Preparation of thietane* 3l

To a DMF solution of **1** (0.1 mol; prepared from 6.4 g of sulfur and 33 g HPF, 1.0 g of CsF in 100 mL of DMF, as describe in Section 4.3) placed in 250 mL three-neck flask equipped with thermocouple, dry-ice condenser and gas inlet tube, it was slowly added 33 g (0.2 mol) of gaseous $CH_2{=}C(CF_3)_2$ at 25–35 °C. The reaction mixture was agitated at ambient temperature for 48 h, diluted by 300 mL of water, organic layer was separated, washed by water (100 mL) dried over $MgSO_4$ and distilled to give 52 g (75%) of **3l**, b.p. 112–113 °C. Data for compound **3l** are given in Tables 1 and 2.

4.5. *Preparation of 1,2-dithiolanes* 4a–d *(typical procedure)*

Dry three-neck flask was charged with 0.5–1.0 g of dry CsF inside of dry box. The flask was taken out, brought into a fume hood, and under flow of nitrogen was equipped with thermocouple, reflux condenser and magnetic stir bar. Under nitrogen blanket via syringe it was added 30 mL of dry DMF, 1.0–1.6 g (0.03–0.05 mol) of sulfur and 2.5–7.5 g (0.01–0.03 mol) of thietane **4**. The reaction mixture was agitated at ambient temperature for 24–36 h and the progress was monitored by GC. After all starting thietane was consumed the reaction mixture was poured into 300 mL of water, extracted with hexane (50 mL ×3), organic layer was washed by water (100 mL ×3), dried over $MgSO_4$ and solvent was removed under reduced pressure. The residue was distilled under vacuum. Yields, boiling points and data of mass spectrometry for **4a**–**d** are given in Table 1 and NMR data can be found in Table 2.

4.6. *Preparation of 1,3-dithiolanes* 5a–h *and 1,3-dithiolene* 7

Dry three-neck flask was charged with 1.0–2.0 g of dry CsF inside of dry box. The flask was taken out, brought into a fume hood, and under flow of nitrogen was equipped with thermocouple, dry-ice condenser and inlet tube and magnetic stir bar. Under nitrogen blanket via syringe was added 50 mL of dry DMF and 3.2 g (0.1 mol) of sublimed sulfur. The addition of gaseous hexafluoropropene (HFP) was started at ambient temperature and resulted in exothermic reaction and rapid absorption of HFP. The HFP addition was maintained at a rate which allowed internal temperature to remain between at 45–65 °C, but at same time avoid the condensation of excessive amount of HFP on the dry-ice condenser. After required amount of HFP (~0.11–0.12 mol) was added and all sulfur went into solution, the reaction mixture was allowed to cool down to ambient temperature. Another portion of sulfur (3.2 g) was added to the agitated reaction mixture and was followed by drop-wise addition of the corresponding vinyl ether (0.1 mol) at a rate, which kept the internal temperature of the reaction mixture <35 °C. The reaction mixture was agitated at ambient temperature for 2–4 h. It was then diluted by 200–300 mL of water, extracted by hexane (50–75 mL ×2), organic layer was washed by water (100 mL ×3), dried over $MgSO_4$. Solvent was removed under reduced pressure. According to NMR and GC/MS, the crude product contained a mixture of 1,3-dithiolane and the corresponding thietane in ratios between 85:15 and 90:10. Pure **5a**–**h**, **7** (purity $>98\%$) were isolated by vacuum distillation. Yields, boiling points and data of mass spectrometry for **5a**–**h** and **7** are given in Table 1 and NMR data in Table 2.

4.7. Disproportionation of thietane 3d

A mixture of 0.3 g dry CsF, 2.8 g (0.01 mol) of **3g** and 15 mL of dry DMF was agitated at 25 °C under nitrogen. The progress of the reaction was monitored by NMR. After 14 days, when the conversion of **3d** reached 90%. At this point the reaction mixture was diluted with 75 mL of water, organic layer was separated, dried over $MgSO_4$ and filtered. Isolated crude product (2.5 g) contained based on ^1H and ^{19}F NMR compounds **4d**, **4e**, **4f** and **3d** in ratio = 50:30:10:10. Compounds **4d**–**f** were identified, in the reaction mixture by ^{19}F NMR and mass spectrometry (see Tables 1 and 2).

4.8. Reaction of thietane 3a with CH_3I

A mixture of 2.5 g (0.01 mol) of **3a**, 1.6 g of dry CsF, 2.8 g (0.02 mol) of CH_3I and 20 mL of dry DMF was agitated under nitrogen for 18 days at 25 °C. The progress of the reaction was monitored by GC/MS and NMR. The reaction mixture was worked up as described above, using hexane extraction. 2.6 g of crude product was isolated. The crude reaction mixture, according to ^1H and ^{19}F NMR contained compounds **3a** and **4g** in a ratio of 1:1. Sulfide **4g** was characterized in reaction mixture and NMR data are given in Tables 1 and 2.

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