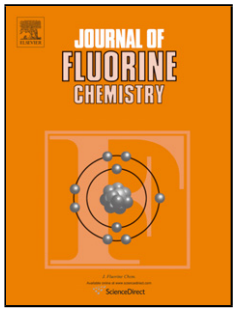

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Regiochemistry of Diels-Alder Reaction of Hexafluorothioacetone and Dienes.

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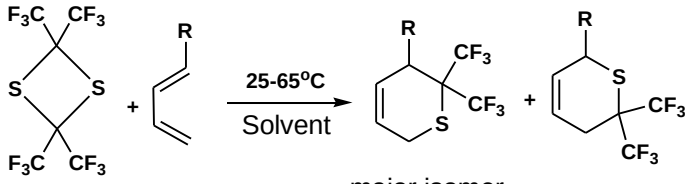
Keywords: Hexafluorothioacetone; 2,2-4,4-tetrakis(trifluoromethyl)dithietane-1,3; reaction with dienes.

Graphical abstract



major isomer

R=CH_3, OCH_3, $OSi(CH_3)_3$, $OC(O)CH_3$

Highlights:

- *Regiochemistry of Diels-Alder reaction*
- *Formation of two regio-isomers*
- *Structural assignment of isomers*

Abstract

*The reaction of 2,2,4,4-tetrakis(trifluoromethyl)-dithiethane-1,3 (**1**) with various hydrocarbon dienes is not regioselective and results in the formation of two isomeric Diels-Alder cycloadducts with the* ortho *isomer predominating. The reaction of non-conjugated dienes involves ene-insertion of hexafluorothioacetone (HFTA), followed by Diels-Alder reaction of the product of the ene- reaction with a second mole of HFTA, while the reaction of 1,1,4,4-tetramethylbutadiene-1,3 and 2,5-dimethylhexadiene-1,5 results exclusively in HFTA insertion into the allylic C-H bond.*

Keywords: 2,2,4,4-tetrakis(trifluoromethyl)-ditiethane-1-3; dienes; Diels-Alder reaction; ene-reaction; regioselectivity.

1. Introduction

Despite the fact that cycloaddition reactions of hexafluorothioacetone (HFTA) and its cyclic dimer (2,2,4,4-tetrakis(trifluoromethyl)-ditiethane-1-3, **1**) with conjugated dienes have been extensively studied in last 50 years, [1-4] the regioselectivity of the reaction of HFTA and unsymmetrical dienes is still not perfectly understood. While hexafluoroacetone (HFA) was reported to react with 2-methylbutadiene-1,3 in regiospecific fashion, producing only 5-methyl-

2,2-bis(trifluoromethyl)-3,6-dihydro-2H-pyran in high yield [5], the reaction of HFTA with 2-chloro-butadiene-1,3 and 1-methoxy-1,3-butadiene reportedly gives a mixture of regioisomers [6], but unfortunately the publication provides neither experimental details nor spectroscopic data for the cycloaddition products. The formation of two regioisomers in the Diels-Alder reaction of HFTA and unsymmetrical dienes seems to be consistent with known data on the reactivity of HFTA, since C=S in this compound is known to react through nucleophilic attack either on carbon or sulfur, depending on the character of the nucleophile [7].

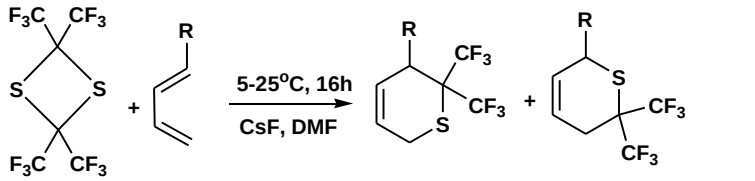
Fluorinated thioaldehydes $R_fCH=S$ ($R_f=H(CF_2)_2$-, $H(CF_2)_4$-) 3 were reported to react with 2-ethoxybutadiene-1 with the formation of two regioisomers [8], while the reaction of fluorinated aldehydes of similar structure with 2-ethoxybutadiene-1,3 led to highly selective formation of a single regioisomer [9].

These reports strongly suggest that in contrast to hexafluoroacetone, the monomeric $(CF_3)_2C=S$ reacts with unsymmetrical conjugated dienes, with the formation of a mixture of regioisomers. This hypothesis is consistent with data on the reactivity of hydrocarbon thiocarbonyls (these reactions usually lead to the mixture of two regioisomers [10] in Diels-Alder reactions) and also with data on the reactivity of fluorinated thioaldehydes towards 2-ethoxybutadiene-1,3 [8]. However, literature reports on this subject are contradictory. For example, the reaction of HFTA with styrenes (as originally discovered by W. Middleton [6] and lately studied in detail, the reaction of HFTA (or dimer **1** [2, 11, 12]), first step of this process (which involves a Diels-Alder reaction) proceeds in regiospecific fashion, typically resulting in selective formation of one regioisomer.

This study presents new data clarifying the regiochemistry of the Diels-Alder reaction of unsymmetrical dienes and HFTA, using readily available cyclic dimer **1** as a source of HFTA for cycloaddition reactions.

2. Results and Discussion.

Similar to the reaction of **1** and 2,3-dimethylbutadiene-1,3 [3], the CsF-catalyzed reaction of **1** with 1-substituted butadienes-1,3 (**2**, R=CH_3, **4**, R=OCH_3) proceeded under mild conditions and resulted in the formation of two regioisomers in each case. (Eq.1)

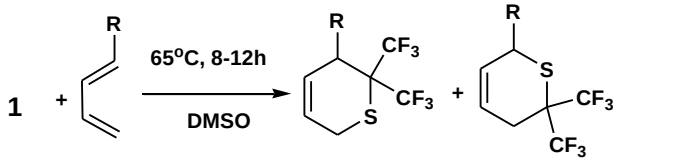


ratio **3a:3b** - 63:37
ratio **5a:5b** - 81:19

.

Eq.1

The reaction of diene **6** (R=$OSi(CH_3)_3$) in the presence of CsF led to the formation of complex mixture of products, but in the absence of the catalyst, in DMSO solvent [12] , it led to a mixture of cycloadducts **7a, b** isolated in high yield (Eq.2).



ratio **7a:7b** - 66:34
ratio **9a:9b** - 80:20

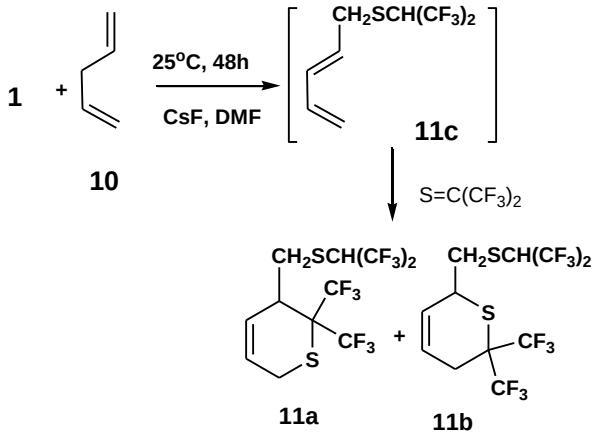
Eq.2

The reaction of diene **8** (R=OC(O)CH_3) with **1** was rather slow at ambient temperature (<10% conversion after 16 h), but at 65^{o}C it was completed after ~ 16 h, producing a mixture of isomers **9a,b**.

It should be pointed out, that regardless of the presence or absence of the catalyst, all these reactions resulted in the formation of a mixture of isomeric products, with predominance of more sterically hindered "ortho-like" isomer –(isomers **3a**, **5a, 7a** or **9a**, respectively), even in the case **of** diene **6** carrying the bulky –OSi$(CH_3)_3$, Typical isomeric ratios were 60:40, reaching 80:20 in case of dienes **4** (R=OCH_3) and **8** (R=OC(O)CH_3). The predominant formation of "ortho-like" isomers in the crude reaction mixture was observed in all of Diels-Alder reactions investigated in this work, with only one exception (diene **18,** Eq. 8,).

The structural assignment of regio- isomers formed in Diels-Alder involving dienes **2, 4, 6, 8** (and also **10, 18**) was based on assignment of structure of isomers **3a** and **3b** using NMR spectroscopy. The structures **3a** and **3b** were assigned to major and minor isomer based on a ^{13}C INADEQUATE spectrum, which established full carbon connectivity in the structures and permitted unambiguous structural determination. It should be pointed out that the chemical shifts of the CF_3 resonances in the ^{19}F NMR spectrum of major isomer **3a** evinced increased shielding due to steric interactions with the adjacent carbon. Since same trend was observed in ^{19}F NMR spectra for mixtures of compounds **5a,b, 7a,b** and **9a,b** (Table 2), the structure of "ortho-like" isomer was assigned to major isomers (compounds **5a, 7a** and **9a**). Because of the pronounced ability of HFTA to undergo ene- type reaction with olefins having allylic hydrogens [1, 3, 6, 12-14] it was also possible to involve unconjugated dienes into reaction with **1**. For

example, pentadiene-1,4 (**10**) underwent reaction with **1,** producing a mixture of two isomeric cycloadducts **11a,b** (ratio 80:20), derived from two sequential processes: – ene- insertion of HFTA leading to **11c,** followed by Diels-Alder reaction with a second mole of HFTA (Eq. 3)

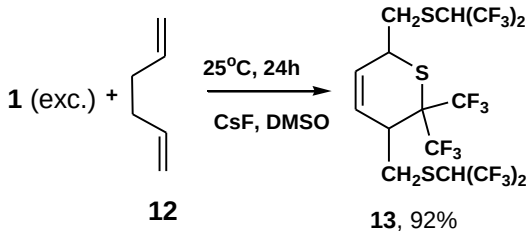


yield 56%, ratio **11a : 11b** - 80 : 20

Eq.3

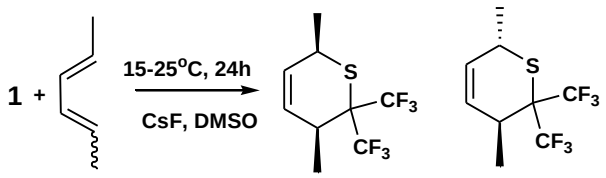
An interesting feature of this reaction was the predominant formation of "ortho-like" isomer **11a**, (ratio **11a:11b**= 80:20), despite of the presence of the bulky $–CH_2SCH(CF_3)_2$ substituent in the α-position to the carbon bearing two CF_3 groups.

The reaction of hexadiene-1,5 (**12**) with excess of **1** led to the formation of the 1: 3 adduct, with high predominance of one isomer. (Eq. 4). Compound **13,** comprising ~10 % of isomeric product, was isolated in 55 % yield, but the structural assignment of isomers was not carried out was in this case.



Eq.4

The CsF-catalyzed reaction of conjugated diene **14** (ratio *trans-, trans-* / *trans-,cis-* isomers – 77:23) with **1** was exothermic (the temperature of the reaction mixture was controlled using a cooling bath) and led to the formation of two isomers **15a** and **15b** (Eq. 5)



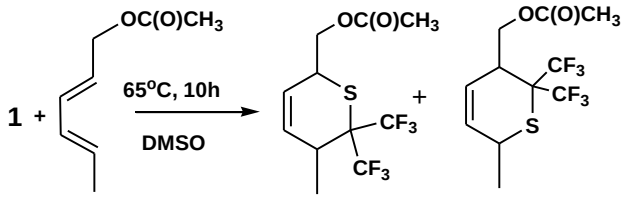
14
trans-, trans : trans-, cis - 77:23

15a **15b**

conv. of **14** - 96%,
yield **15a,b -** 86%
ratio **15a:15b** - 68:32

Eq. 5

By monitoring the reaction progress by NMR, it was confirmed that *trans-, trans-* isomer reacted faster than the *trans-, cis-* isomer; the ratio of **15a : 15b** was progressively changing over time from 91:9 (1 h), to 78: 22 (6h) and finally to 68:32 (24h, at 96% conversion of **14**). The reaction of diene **16** (*trans-, trans-* isomer) with **1** (carried out in the absence of CsF catalyst) led to high yield formation of two isomeric products (Eq. 6)



16
trans-, trans- >96%

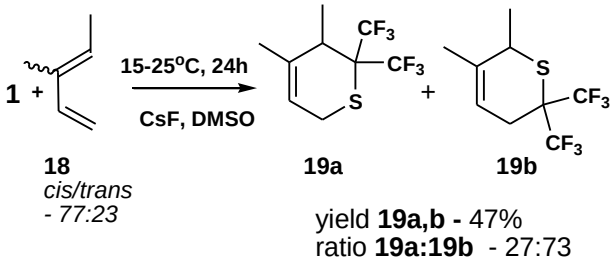
17a,b

yield **17a,b -** 80%
ratio isomers - 57:43

Eq.6

Based on the geometry of starting material **16** (*trans*-, *trans*- isomer, 96%) a *cis*- relationship of CH_3- and $–CH_2OC(O)CH_3$ was assumed for both regio- isomers **17a** and **17b**, since Diels-Alder reactions proceed through disrotatory cyclization process, leading to the *cis*- relationship of substituents in case of *trans*- *trans*- dienes [15], however the assignment of isomers was not carried out in this case.

The geometry of the diene component has a great effect on the regioselectivity of the Diels-Alder reaction with **1**. For example, the addition of **1** to a mixture of dienes **18** (a mixture of *cis*- and *trans*- isomers, ratio 77:23) and CsF catalyst in DMSO, resulted in exothermic reaction; all *cis*- isomer was reacted away within 6 h at ambient temperature (NMR). In this case, the reaction led to the formation of two regioisomers **19a** and **19b,** but this time with significant predominance of the "meta-like" isomer **19b** (Eq.7). It should be pointed out that "reversed" regioselectivity observed in this reaction is not well understood at this point.

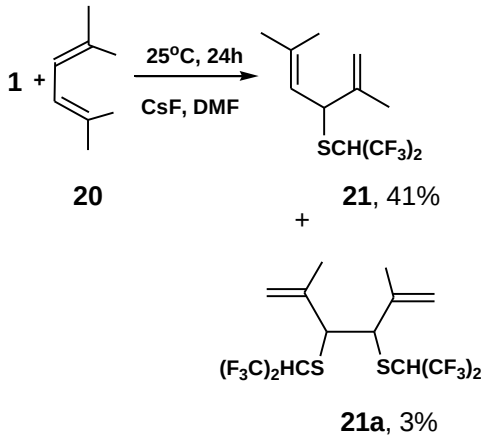


Eq. 7

Extension of the reaction time eventually resulted in full conversion of *trans*- isomer of **18.** However, it also led to formation of noticeable amounts of 1:2 adduct (up to 14%, mixture of

two isomers, ratio 95:5). Although these adducts were not characterized, experimental data suggest that they evolved from the reaction of *trans*- isomer with **1**, since only trace of these materials were observed in the reaction mixture in first 6 hours of reaction at 100% consumption of *cis*- isomer, but this amount of this fraction went up to 14% after 24 h at ambient temperature.

Dienes carrying several methyl substituents are known to be unreactive in Diels-Alder reaction due to steric destabilization of *cisoid* conformation, required for the cycloaddition process. For example, 1,1,4,4-(tetramethyl)butadiene -1,3 (**20**) in reaction with bezyne was reported to give exclusively ene- product. [16] A similar effect was noted in the reaction of 1,1,4,4-tetaramethylbutadiene-1,3 (**20**) with **1**, in which the diene **21** was formed selectively and was isolated in 41% yield, along with a small amount of double-insertion product **21a** (Eq.8).



Eq.8

Compound **21a** was isolated in low yield from the residue of distillation pot by recrystallization from hexane, and its structure was established by single crystal X-ray diffraction (Fig.1).

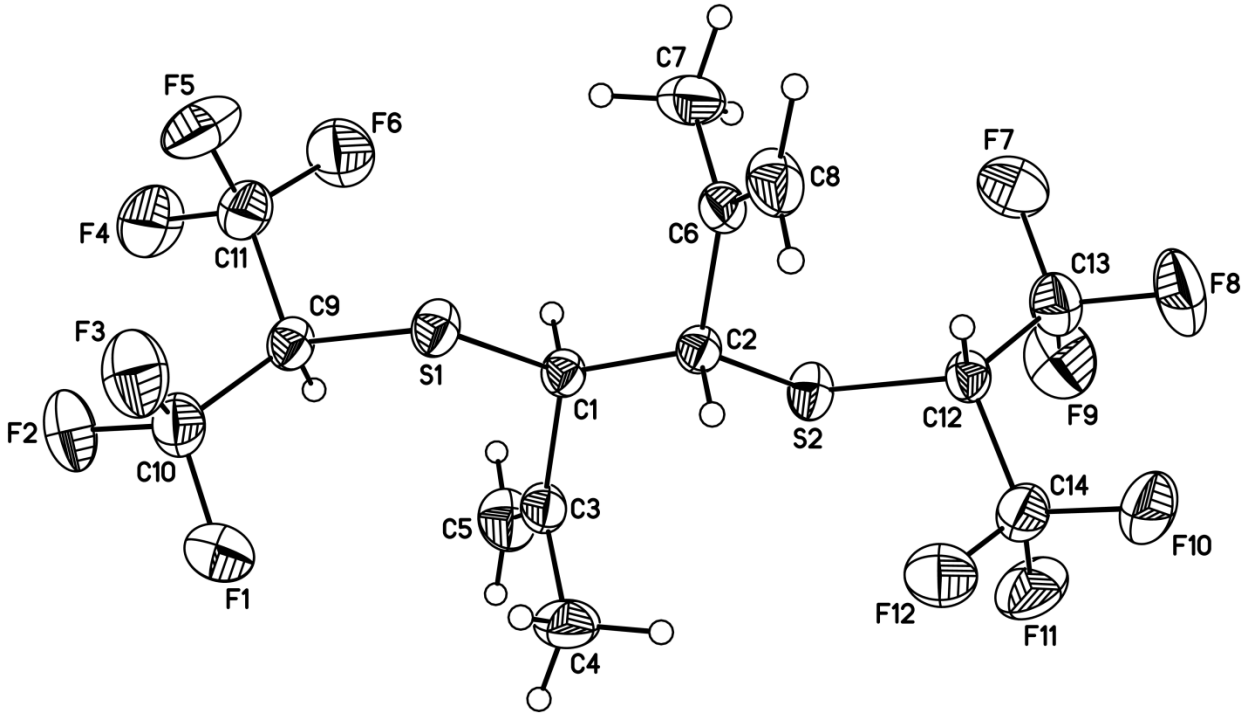
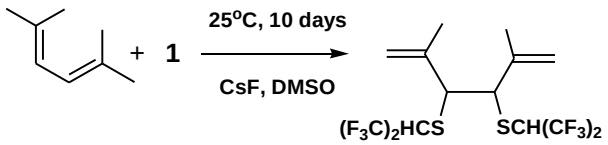


Fig. 1. Crystal structure of **21a** with thermal ellipsoids draw to the 30% probability level.

Extension of the reaction time up to 10 days (molar ratio **1** : **20** – 2:1, DMSO, CsF catalyst, 25 °C) led to an increase in the yield of **21a** (up to 17 %, Eq.9). According NMR, compound **21a** forms as a mixture of isomers (diastereomers) and the fact that only *anti*-isomer isolated, probably was related to its limited solubility in the hexane, which was used as a solvent for recrystallization.

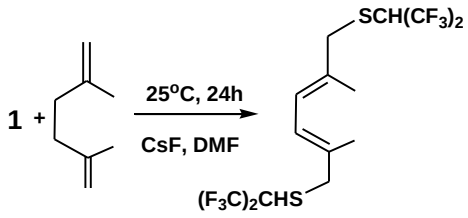


21 **21a**, 17%

Eq.9

The significantly longer reaction time (10 days *vs*. 24h) required to increase the yield of **21a,** attests to the difference in rates of insertion of the first and second molecule of HFTA. Since an ene- reactions proceed through a formation of highly ordered six-membered transition state [17], followed by migration of a double bond, the introduction of a bulky $–SCH(CF_3)_2$ into the α-position to the reaction center may significantly retard the rate of the second insertion of HFTA into **21**.

The reactivity of diene **22** towards **1** is consistent with this model, since the diene gave the product of double insertion of HFTA (diene **23**) after only 24 h (Eq.10). Compound **23** formed as a mixture of isomers, with a high predominance of *trans*-, *trans*- isomer, which was isolated in 38% yield (Eq. 10).



22 **23**, 38%

Eq.10

The structure of compound **23** was established by single crystal X-ray diffraction (Fig.2).

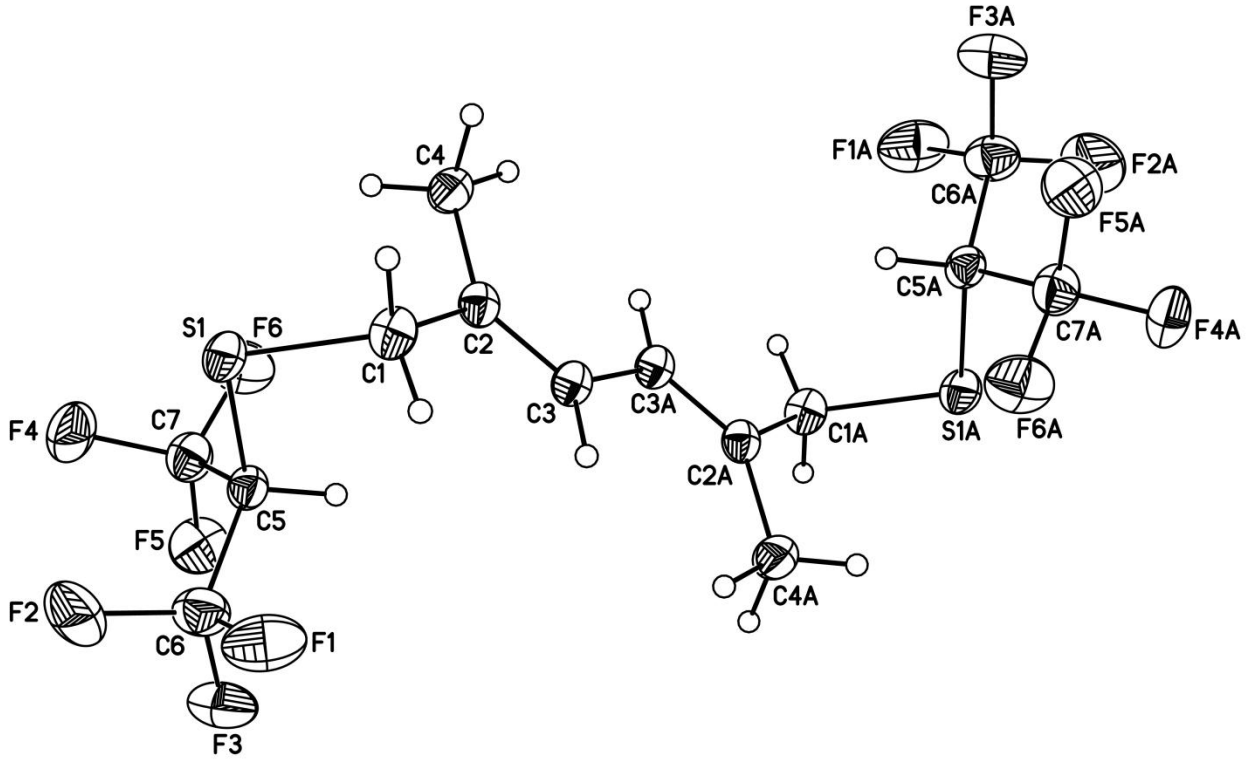


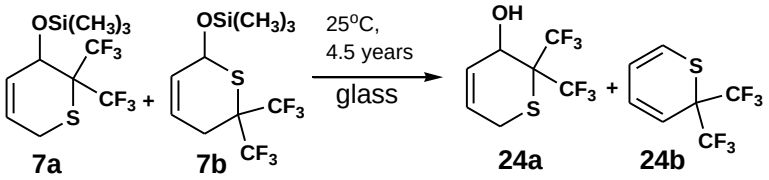
Fig. 2 Crystal structure of **23** with thermal ellipsoids draw to the 30% probability level.

Regio-Chemistry of Diels-Alder Reactions involving HFTA.

The results obtained in this study indicate that the Diels-Alder in the reaction of HFTA with dienes **2,4,6,8,** and **10** the more sterically hindered "ortho-like" isomers (**3a, 5a, 7a, 9a** and **11a**, Eq. 1-4) are formed preferentially. While the ratio of regioisomers fluctuated depending on the substituents at the terminal carbons of the diene, formation of the "ortho-like" isomer was

invariably favored in these reactions. The root cause of this phenomenon is not well understood at this point, but computational studies may shed some light on this problem.

Although the structural assignment of isomers was based on the difference in ^{19}F chemical shifts of CF_3 moieties in the various isomers (*vide supra*), an additional confirmation of the assignment was obtained in the case of cycloadducts **7a,b**. An isolated sample of isomers **7a,b** (ratio 1:1, isolated by distillation), underwent complete decomposition upon storage in a glass ampule under ambient conditions for 4.5 y. NMR analysis of this material confirmed the absence of either **7a** or **7b**, but instead, a mixture of alcohol **24a,** compound **24b** [6] and $[(CH_3)_3Si]_2O$ were observed in the mixture, in a ratio ~1:1:1.



Eq.11

A pure sample of alcohol **24a** was isolated by crystallization, and its structure was confirmed by single crystal X-ray diffraction (Fig.3) and compound **24b** was isolated as a mixture with $[(CH_3)_3Si]_2O$, but was fully characterized by NMR spectroscopy (Table 2).

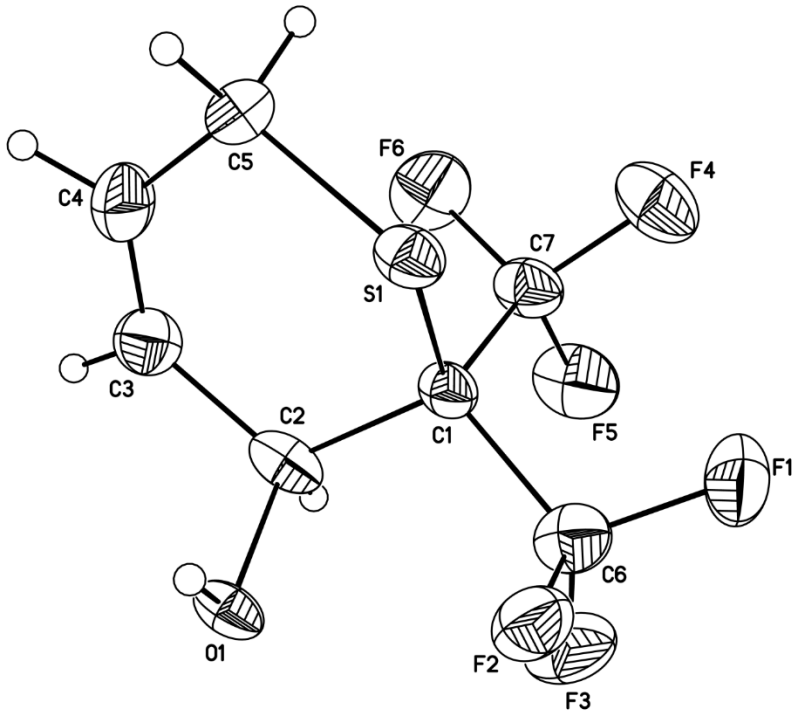
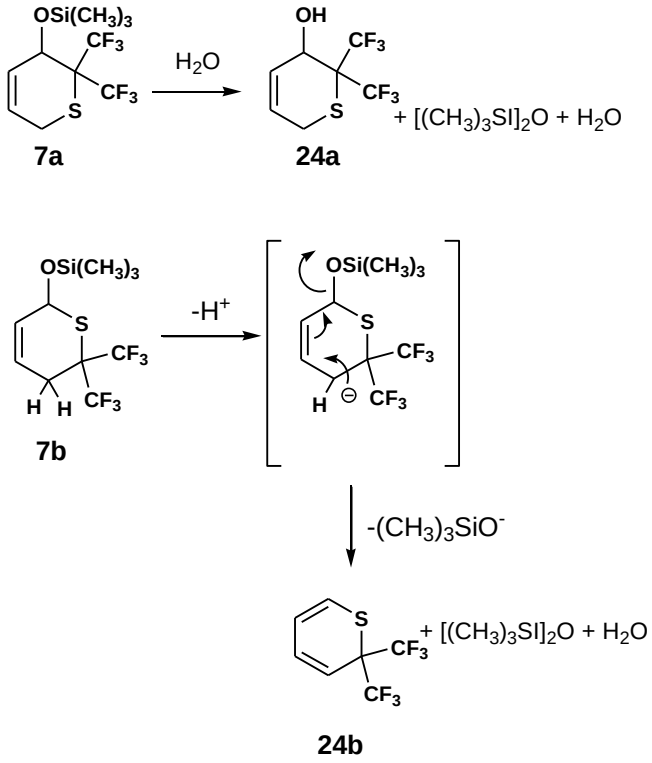


Fig. 3. Crystal structure of **24a** with thermal ellipsoids draw to the 30% probability level.

While the formation of compound **24a** can be rationalized as being a result of hydrolysis of isomer **7a** by moisture, the formation of **24b** can be explained as a result of 1,4-elimination of "$HOSi(CH_3)_3$", due to the presence of a relatively acidic proton in α-position to electron withdrawing CF_3-groups in isomer **7b** (Eq.12)



Eq.12

It should be pointed out that 2-*H*-thyopyranes, structurally similar to **24b,** were prepared by selective reaction of the "meta-like" isomer derived from the reaction of $R_fCH=S$ [R_f=$H(CF_2)_2$- and $H(CF_2)_4$-] and 1-EtO-butadiene-1,3 in a HCl/i-PrOH mixture [8]. Reported ^{1}H NMR data of these materials [8] are in good agreement with ^{1}H NMR data of **24b** obtained in this work (Table 2).

Both structures of **24a** and **24b** also agreed well with proposed structures of products derived from Diels-Alder reaction of **6** and **1.** The confirmation of the structure of **24a** by single crystal X-ray diffraction can be considered as another example of the predominate formation of the "ortho-like" isomer in Diels-Alder reactions of HFTA with conjugated dienes. It should be pointed out that in this respect HFTA resembles closely $S=C[C(O)OMe]_2$, reported to give

predominantly "ortho-like" isomer in reaction with pentadiene-1,3 (ratio of "ortho-"/"meta-" isomers was 5:1 [18]), while the regioselectivity in reaction of fluorinated thioaldehydes $R_fCH=S$ with 1-EtO-butadiene-1,3 was opposite – in this case "meta-like" isomer was formed preferentially (ratio "ortho-":"meta-" isomers was 1:2 [8]). It should be pointed out that this regioselectivity is unusual, since based on results reported in ref. [10], thioaldehydes RCH=S carrying electron withdrawing groups reported to give predominantly "ortho-like" isomers in reaction with Danishefsky diene. It is not clear at this point whence the differing preferences in regiochemistry stems between HFTA and fluorinated thioaldehydes $R_fCH=S$. Computational studies may elucidate this problem, since it was reported [10] that in the case of hydrocarbon thioaldehydes the regiochemistry of cycloaddition process correlates well with the LUMO coefficient of the C=S bond.

4. Experimental

^{1}H, $^{13}C\{H\}$ and ^{19}F NMR spectra were generally acquired on a Varian VNMRS 500 MHz spectrometer equipped with a 5 mm ^{13}C-^{31}P $\{^{1}H,^{19}F\}$ probe. The INADEQUATE spectrum was acquired on a Bruker Avance I 500 MHz spectrometer equipped with a 5 mm $^{13}C\{^{1}H\}$ helium cryoprobe. $CFCl_3$ or TMS were used as an internal chemical shift standards and $CDCl_3$ as a lock solvent. GC and GC/MS analyses were carried out on a HP-6890 instrument, using HP FFAP capillary column and either TCD (GC) and mass selective (GS/MS)

detectors, respectively. Anhydrous DMF, THF, ACN and DMSO, dienes **2,4,6,8,10,12,14,16,18,20** and **22** (Aldrich) were purchased and used without further purification; dienes **2, 4, 6, 8, 14, 16, 18** were analysed by NMR to determine ratio of isomers:

Comp. No	Ratio of isomers *trans-,trans- to trans/cis*
2	>96:4 *trans-*
4	>96:4 *trans-*
6	65:35 *trans-/cis-*
8	96:4 *trans/cis*
14	77:23 *(trans-,trans- : trans/cis*
16	96:4 *(trans-,trans- : trans/cis)*
18	23:77 *(trans/cis)*

Compound **1** was prepared according modified procedure [19] using CsF as a catalyst. For all experiments not purified compound **1** was used (purity ~96-98%, reminder cyclic trisulfide $C_6F_{12}S_3$ and a trace of DMF, GC/MS).

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%, unless it is stated otherwise.

4.1.Crystallography:

X-ray data for **21a, 23 and 24b** 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 [20] 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 structure in this paper has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC #1445792 - #1445794. 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. Reaction of Compound **1** with Dienes **2,4,6,8,10,12,14,16,18,20,22** (typical procedure).*

A mixture of 12-35 mmol of **1** (~10-20 mol % excess), 20-60 mmol of the corresponding substrate, in 12-15 mL of dry DMSO or DMF [optionally in the presence of 0.3-0.5 g (2-3 mmol) of dry CsF] was agitated at 25-65^{o}C for period of time specified in Table 1. The reaction progress was monitored by GC and NMR. The reaction mixture was diluted by water (20-300 mL) and extracted by hexane (2x 50-70mL). The organic layer was washed with water (2x100-200 mL), and dried over $MgSO_4$. The solvent was removed under vacuum and the residue was distilled under reduced pressure. Compounds **21a** and **23** were isolated by crystallization from hexane. Reaction conditions, ratio of reagents, conversions and mass-spectrometry data are given in Table 1 and NMR data for new materials and are given in Table 2.

*4.2. Isolation of products **24a** and **24b**.*

A sample (3g) of 1:1 mixture of **7a** and **7b**, which was stored in glass sample vial for 4.5 years, was analysed by NMR and GC/MS. It was found to be a mixture of **24a, 24b** and hexamethyldisiloxane (HMDS) in ratio ~ 1:1:1. Sample was placed under vacuum (1 mm Hg) and a mixture of **24b** and HMDS (1.9 g, mixture ~1:1) was collected in cold trap (-78^{o}C) and residue (~0.8 g) crystalized upon standing at ambient temperature. It was recrystallized from hexane to give 0.6 g of **24a**.

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References

[1] W.J. Middleton, J. Org. Chem. (1965) 1395-1398.

[2] T. Kitazume, N. Ishikawa, Chem. Lett. No. 3 (1973) 267-268.

[3] V. Petrov, W. Marshall, J. Fluor. Chemistry 128 (2007) 729-735.

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

[5] W.J. Linn, J. Org. Chem. 29 (1964) 3111.

[6] W.J. Middleton, J. Org. Chem. (1965) 1390-1394.

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

[8] L.N. Markovskii, Kornuta, P.P., Shermolovich, Yu.G., Zh. Org. Khim. 35 (1999) 1172-1174.

[9] Y.G. Shermolovich, Pazenok, S.V., Slyusarenko, E.I., Markovskii, L.N., Zh. Org. Khim. 26 (1990) 2213-2218.

[10] E. Vedejs, Perry, D.A.Houk, K.N., Rondan, N.G., J. Am. Chem. Soc. 105 (1983) 6999-7001.

[11] V.A. Petrov, W. Marshall, New data on the reaction of hexafluorothioacetone with styrenes, J. Fluorine Chem. 132 (2011) 783-791.

[12] V.A. Petrov, W. Marshall, J. Fluorine Chem. 179 (2015) 56-63.

[13] D.J. Burton, Y. Inouye, J. Fluorine Chem. 18 (1981) 459-473.

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

[15] S. Sankararaman, Pericyclcic Reactions - A Textbook, pp. 109-111 , Wiley-VCH, Weinheim, Germany 2005.

[16] E.M. Arnett, J. Org. Chem. 25 (1960) 324-327.

[17] S. Sankararaman, Pericyclcic Reactions -A Textbook, pp. 329-349, Wiley-VCH, Weinheim, Germany 2005.

[18] S. Perreault, M. Poirier, P. Leveille, O. Rene, P. Joly, Y. Dory, C., J. Org. Chem. 73 (2008) 7457-7466.

[19] V.A. Petrov, W. Marshall, J. Fluorine Chem. 131 (2010) 1144-1155.

[20] G. Sheldrick, (SHELXTL Sofware Suite, v. 6.0, Bruker Axes Corp., Madison WI, 1996.

Table 1. Reaction of compound 1 with dienes – reaction conditions, yields, ratio isomers, and mass-spectrometry data. [a]

Entry No	Comp. No	Temp. (^{o}C)	Time (h)	Scale (mmol) [b]	Solvent [c]	Catalyst (mmol)	Yield (%) [d]	Ratio isomers (in crude)	B.P. (^{o}, mm/Hg)	MS (*m/z*)
1	**3a,b**	5-25	16	70	DMF	CsF (3)	69	**3a:3b-** 63:37	81-84/30	250 (M^+, $C_8H_8F_6S^+$)
2	**5a,b**	5-25	16	60	DMF	CsF (2)	59	**5a:5b-** 81:19	117-119/50	266 (M^+, $C_8H_8F_6OS^+$)
3	**7a,b**	25-50 [e]	48	60	DMSO	---	91	**7a:7b-** 66:34	61-70/1.5	324 (M^+, $C_{10}H_{14}F_6OSSi^+$)
4	**9a,b**	65[e]	12	30	DMSO	---	73	**9a:9b-** 80:20	96-100/10	294 (M^+, $C_9H_8F_6O_2S^+$)
5	**11a,b**	25	48	20	DMF	CsF (2)	56	**11a:11b-** 80:20	101-103/1.2	431[$(M-H)^+$, $C_{11}H_7F_{12}S_2^+$]
6	**13**	25	16	20	DMF	CsF	92	**13**	99.5-	628 (M^+,

						(2)			105/0.2	$C_{15}H_{10}F_{18}S_3^+$)
7	**15a,b**	25	16	60	DMSO	CsF (3)	86 [f]	**15a:15b-** 68:32	99.5-105/0.2	264(M^+, $C_9H_{10}F_6S^+$)
8	**17a,b**	65	8	60	DMSO	---	80	**17a:17b-** 57:43	78-80/1.1	322 (M^+,$C_{11}H_{12}F_6O_2S^+$)
9	**19a,b**	15-25	24	60	DMSO	CsF (3)	47	**19a:19b-** 27:73	28-29/0.2	264(M^+, $C_9H_{10}F_6S^+$)
10	**21**	25	24	50	DMF	CsF (3)	34	---	105-109/50 [g]	292 (M^+, $C_{11}H_{14}F_6S^+$)
11	**21a**	25	10 d	25	DMSO	CsF (2)	17	---	(108-109)[i]	474(M^+, $C_{14}H_{14}F_{12}S_2^+$)
12	**23**	25	24	50	DMF	CsF (3)	38	Mixture of isomers	(103-104)[i]	474(M^+, $C_{14}H_{14}F_{12}S_2^+$)
13	**24a,b**	25	4.5 years	30	---	---	Quant.	**24a:24b:** HMDS[j] - 1:1:1	---	**24a**: 252(M^+, $C_7H_6F_6OS^+$) **24b**: 234(M^+,

										$C_7H_4F_6S^+$)

[a] see Sec. 4.2 for general procedure

[b] based on diene; 10-20 mol % excess of **1** was used in all experiments

[c] 50 mL

[d] isolated yields; conversion of diene at least 99%, unless stated otherwise

[e] delayed exotherm (up to 50^{o}C in 5 h)

[f] at 96%conversion of **14**

[g] distilled material crystallized in freezer at -20^{o}C; liquid at ambient temperature.

[i] melting point

[j] HMDS - hexamethyldisiloxane

Table 2. ^{1}H and ^{19}F NMR data for new materials.[a]

Entry No	Comp. No	^{1}H NMR (δ, ppm, J, Hz)	^{19}F NMR (δ, ppm, J, Hz)
1	**3a**[b]	1.36(3H, dm, 7.2), 2.86(1H,m), 3.21(1H, dd, 16.5, 5.0), 3.28(1H, d, 16.5), 5.68(1H, dm, 10.3), 5.96(1H, dm, 10.3)	-63.69(3F, q, 11.0), -67.53(3F, q, 11.0)
2	**3b**[c]	1.39(3H, dm, 7.1), 2.43(1H,dm,17.1),), 2.81(1H, dd, 17.1, 5.3), 3.64(1H, m), 5.87(1H, dm, 10.3), 6.00(1H, dm, 10.3)	-70.65(m)
3	**5a**	3.17(1H, d, 17.0), 3.35(1H,dd, 17.0, 4.8), 3.50(3H,s), 4.26(1H,s), 5.95(1H,d, 10.5), 6.15(1H,d, 10.5)	-63.22(3F, q, 9.5), -67.82(3F, q, 9.5)
4	**5b**	2.70(1H, dd, 16.6,5.4).), 2.81 (1H,d, 16.5), 3.45(3H,s), 5.04(1H,d, 5.4), 6.04(1H, m), 6.26(1H, m)	-70.27(3F, q, 10.5), -71.10(3F, q, 10.5)
5	**7a**	0.00(9H,s), 2.98(1H, d, 16.0), 3.16(1H,dd, 16.0, 5.0), 4.61(1H,s), 5.58(1H,d, 10.3), 5.89(1H,d, 10.3)	-62.90(3F, q, 10.0), -67.20(3F, q, 10.0)
	7b	0.04(9H,s), 2.32(1H, dm, 17.0), 2.71(1H,dd, 17.0, 5.8), 5.34(1H,s),	-70.11(3F, q, 10.8), -70.92(3F, q, 10.8)

		5.74(1H, dm, 9.6), 5.98(1H,dm, 9.6)	
6	**9a**	2.11(3H,s), 3.20(1H, d, 17.3), 3.42(1H,d, 18.2, 4.5), 6.09(2H,m), 6.24(1H,d, 4.8)	-63.51(3F, q, 10.0), -68.48(3F, q, 10.0)
7	**9b**	2.08(3H,s), 2.76(1H, dm, 18.2), 2.84(1H,dd, 17.3), 5.66(1H,dd, 10.7, 2.2), 6.01(1H,s), 6.13((1H,m)	-69.83(3F, q, 10.8), -70.73(3F, q, 10.8)
8	**11a**	2.89(2H,m), 3.16(2H,m), 3.44(1H,m), 3.61(1H. sept., 7.3), 5.95(1H,d, 10.2), 6.22(1H,d, 10.2)	-63.25(3F, q, 10.0), -66.04(3F, quint, 9.2), -66.54(3F, quint., 9.2), -67.02(3F,q, 10.0)
9	**11b**	2.60(1H,d, 18.0), 2.81(1H,d,18.0), 3.08(2h,m), 3.44(1H,m), 3.76(1H. sept., 7.3), 6.00(1H,dm, 11.0), 6.09(1H,dm, 11.0)	-66.17(3F,m), -66.25(3F, m), -70.46.02(6F, m)
10	**13**[d]	Major isomer: 2.80(1H,d, 11.4), 3.00(1H,t, 11.4), 3.11(2H,m), 3.63(1H, sept., 7.3), 3.74(1H, sept., 7.5), 3.82(1H,m), 6.01(1H, dt, 10.2, 3.0), 6.21)1H, dt, 10.2, 2.8)	Major Isomer: -63.30(3F,q, 10.0), -66.14(6F, m), -66.30(3F,m), -66.46(3F, m), -66.66(3F,q, 10.0 Minor isomer: -62.82(3F,quint., 8.9), -63.10(3F,quint., 8.9) -68.83(3F,q, 9.6), -69.78(3F, q, 9.6),

11	**15a**	1.38(3H,d, 7.0), 1.40(3H,dm, 6.7), 2.68(1H,m), 3.61(1H,m), 5.66(1H,dt, 9.8, 3.4), 5.88(1H, dt, 9.8, 2.7)	-64.17(3F, q, 10.3), -67.44(3F,q, 10.3)
12	**15b**	1.32(3H,dm, 7.0), 1.35 (3H,dm, 7.1), 3.09(1H,m), 3.75(1H,m), 5.54(1H,dt, 11.0, 2.7), 5.74(1H, dt, 11.0, 2.4)	-62.73(3F, q, 10.6), -67.57(3F,q, 10.6)
13	**17a**	1.40(3H,d, 7.0), 2.06(3H,s), 2.80(1H,dm, 5.6), 3.64(1H,q, 5.7), 4.23(1H,t, 10.4), 4.58(1H, dd, 10.4, 4.1), 5.84(1H, dt, 10.2, 2.3), 6.0(1H, 10.0, 2.9)	-64.60(3F, q, 10.6), -67.34(3F,q, 10.6)
14	**17b**	1.37(3H,dq, 7.0, 2.1), 2.08(3H,s), 2.78(1H, quint, 2.8), 3.88(1H,m),), 4.23(1H,t, 10.4), 4.14(1H, dd, 10.4, 8.1),4.30 (1H,dd, 10.4, 6.7), 5.76(1H, ddd, 9.7, 4.5, 2.0), 5.84(1H, dm, 9.7)	-63.89(3F, q, 10.7), -67.28(3F,q, 10.7)
15	**19a**	1.30(3H, dq, 6.7, 2.4), 1.80(3H,m), 2.71(1H,m), 3.21(1H, dq, 15.6, 3.4), 3.27 (1H, dd, 15.6, 3.9), 5.69(1H, tq, 4.9, 1.3)	-64.66(3F,qq, 12.2, 2.4), -67.99(3F, q, 12.2)
16	**19b**	1.41(3H, d, 7.3), 1.83(3H, m), 2.47(1H,dd, 16.3, 5.6), 2.71(1H,dd, 16.3, 5.5),3.54(1H, q, 7.5), 5.60(1H,	-70.80(3F,q, 10.0), -70.52(3F, q, 10.0)

		t, 5.3)	
17	**21**	1.73(3H,s), 1.79(3H,s), 1.82(1H,s), 3.52(1H, sept., 8.4), 4.43(1H, d,9.7), 4.93(1H,s), 5.02(1H, s), 5.19(1H,d, 9.7)	-65.84(3F, quint., 8.4), -66.73(3F, quint., 8.4)
18	**21a**[e]	1.82(3H,s), 1.79(3H,s), 3.61(1H, sept., 7.8), 3.63(1H,s), 4.93(1H,s), 5.02(1H, s), 5.28(1H,quint., 1.3)	-65.39(3F, quint., 8.9), -67.00(3F, quint., 8.9)
19	**23**	1.88(6H,s), 3.40(4H,m), 3.48(2H, sept, 7.4), 6.10(2H,s)	-66.39(d, 7.4)
20	**24a**	2.27(1H, br. s, OH), 3.l27(2H,m), 4.72(1H, m, 1.2), 5.93(1H, dm, 10.3), 6.12(1H, dd, 10.6, 6.5)	-63.40(3F,q, 10.3), -67.34(3F, q, 10.3)
	24b	5.40(1H,d, 10.6), 6.10(1H, dd, 9.8, 6.4), 6.24(1H,d, 9.8), 6.40(1H,dd, 10.6, 6.4)	-72.94(s)

[a] in $CDCl_3$ as lock solvent

[b] ^{13}C {^{1}H} NMR: 17.65, 24.98(sept., 25.4), 31.83,59.29, 123.99, 125.0(m, CF3), 132.66 ppm

[b] ^{13}C {^{1}H} NMR: 19.70, 24.73(sept., 1.8), 33.65, 58.10(sept., 26.9), 124.02, 125.0(m, CF3), 133.20 ppm

[d] sample contained 10 mol % of isomeric material

[e] ^{13}C {H} NMR: 14.73, 50.00(sept., 33.0), 54.41, 121.29, 122.98 (q, 280.0), 125.50(q, 282.0), 138.64 ppm