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2-Phenylthio-3,3,3-Trifluoropropene, its Sulfoxide or Sulfone in Diels-Alder Cycloadditions#

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#Dedicated to Ekkehard Winterfeld at the occasion of his 65th anniversary

Abstract : The Diels-Alder reaction of 2-phenylthio-3,3,3-trifluoropropene **1** and its derivatives sulfoxide **2** and sulfone **3**, respectively was carried out with cyclopentadiene, 2,3-dimethylbutadiene, butadiene and isoprene to give the [4+2] cycloadducts in good to excellent yields. The particular reactivity of 2-phenylsulfinyl-3,3,3-trifluoropropene **2** is revealed as an α,β-isomerisation *via* cycloaddition, sulfenic acid elimination, readdition followed by retro Diels-Alder. © 1997 Elsevier Science Ltd.

INTRODUCTION

3,3,3-Trifluoropropene and its derivatives can be regarded as trifluoromethyl carrier reagents on C_2. α-Substitution to the trifluoromethyl group by thioether or its oxidized derivatives results in compounds with tuned reactivity. We recently reported the reactivity of 2-phenylthio-3,3,3-trifluoropropene **1** and its S-oxides, *i.e.* sulfoxide **2** and sulfone **3** in 1,3-dipolar cycloaddition.[1] We describe now Diels-Alder reactions of **1-3** with various dienes.

The parent 3,3,3-trifluoropropene is known as a weak dienophile, towards cyclopentadiene only, because of a lack of π-electron delocalisation.[2] However, introduction of electron-withdrawing substituents in α or β position decreases the LUMO energy level and increases the dienophilicity.[3,4] Although trifluoropropenes **1-3** are expected to be good dienophiles, their reactivity in Diels-Alder cycloaddition has previously not been described in the literature.

RESULTS AND DISCUSSION

Our investigation consists of the Diels-Alder reaction of trifluoropropenes **1-3** with symmetrical dienes (cyclopentadiene, 2,3-dimethylbutadiene and butadiene) and isoprene as sole representative of a unsymmetrical diene. The results obtained are summarized in tables 1 and 2.

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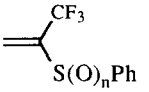


n = 0 **1**
n = 1 **2**
n = 2 **3**

Scheme 1

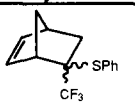
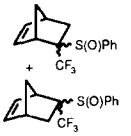
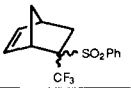
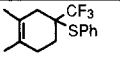
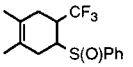
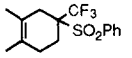
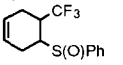
Diene	Reagent (n=)	Conditions	Cycloadducts		Yield (*endo/exo*)
	0 **1**	C_6H_6,110°C, 24h		**4**	72 (1/1)
	1 **2**	Et_2O, reflux, 5 d		**5**	98 (2/1)
	2 **3**	Et_2O, r.t., 24h		**6**	99 (4/1)
	0 **1**	reflux, 20 d		**7**	60
	1 **2**	reflux, 16 d		**12**	20
	2 **3**	Et_2O, reflux, 24 h		**9**	98
	0 **1**	150°C, 4 d	polymerisation		
	1 **2**	120°C, 2 d		**10**	26
	2 **3**	120°C, 2 d	polymerisation		

Table 1 - Reaction of S-substituted trifluoropropenes **1-3** with symmetrical dienes.

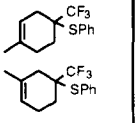
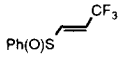
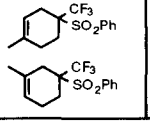
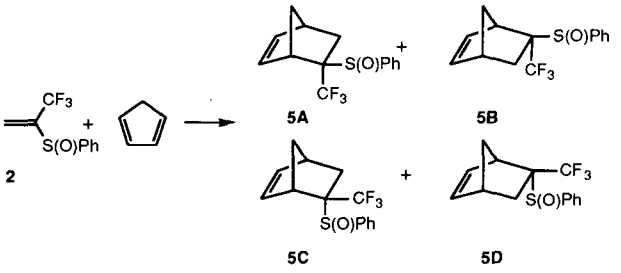
Diene	Reagent (n=)	Conditions	Cycloadducts		Yield (%)	*para/meta*
	0 **1**	C_6H_6, HQ 140°C, 2 d.		**18**	53	76:24
	1 **2**	reflux, 20 d.		**14**	54	
	2 **3**	CH_2Cl_2, reflux,4 d.		**19**	99	83:17

Table 2 - Reaction of S-substituted trifluoropropenes **1-3** with isoprene.

Analysis of our results shows that cycloadditions are promoted by sulfur substitution. Vinylthioether **1** is much more reactive than 3,3,3-trifluoropropene itself, whereas **3** reacts at room temperature in nearly quantitative yields. 2,3-Dimethylbutadiene and isoprene behave similarly well whereas butadiene is hampered by competing polymerisation.

Reaction of vinylthioether **1** with cyclopentadiene proceeds at 110°C (sealed tube) to give the bicyclo[2.2.1]heptene **4** in 72% yield as a mixture of stereoisomers *endo* CF_3/*exo* CF_3 (1:1 ratio) (Table 1). The lack of stereoselectivity indicates that the π stacking of CF_3 is as important as that of the thiophenyl group, but electronic effects and secondary orbital overlap may also be involved. After purification by column chromatography on silica gel (eluent : petroleum ether), *exo* CF_3 isomer is isolated as a pure product and clearly characterized by spectroscopic analysis (^1H NMR, $^3J_{HH}$=3.5 Hz).

Reaction of vinylsulfoxide **2** with cyclopentadiene leads, after 5 days in refluxing ether, to bicyclo[2.2.1]heptene **5** as a mixture of four diastereoisomers (Scheme 2).



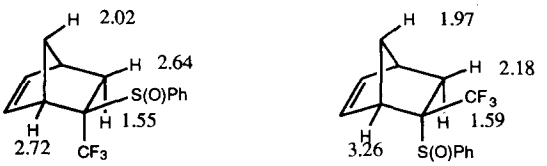
Scheme 2

Diastereoisomers **5A** and **5C** are isolated as crystals; thus, diastereoselectivity of the cycloaddition is easily deduced (^{19}F NMR; Table 3) showing a slight preference for *endo* CF_3 conformation (2:1 ratio).

	5A	**5B**		**5C**	**5D**
endo CF_3	38	28	*exo* CF_3	24	10
δ (^{19}F)	-59.92	-62.24	δ (^{19}F)	-60.87	-62.06

Table 3

Characterization of isomers *endo* CF_3 - *exo* CF_3 (**5A-5D**) is clearly established by spectroscopic analysis. Thus, it is shown that the CF_3 group had induced a shielding effect on neighbouring hydrogens,[2,4,5] as shown by the pair of diastereoisomers **5A** and **5C** (Scheme 3) :



5A *endo* CF_3 **5C** *exo* CF_3

Scheme 3

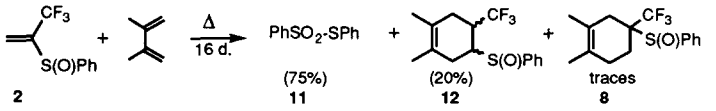
This behaviour, already observed for vinylthioether **1**, is however less noticeable due to the parallel effect of the thiophenyl function.

Bicyclo[2.2.1]heptene **6** is also obtained in 99% yield with vinylsulfone **3** as a mixture of *endo* / *exo* CF_3 diastereoisomers from which *endo* CF_3 is the major product (4:1 ratio). This result is in accordance with the literature since cycloaddition of 1-phenylsulfonyl-3,3,3-trifluoropropene (β isomer of vinylsulfone **3**) with cyclopentadiene proceeds with equal *endo* CF_3 diastereoselectivity (4:1 ratio).[6]

All these results show that the stereochemistry of the reaction of cyclopentadiene with S-substituted trifluoropropenes **1-3** is governed by the trifluoromethyl group, as *endo* CF_3 adducts are always preferentially formed. The *endo* orientating ability of CF_3 is due to secondary attractive forces between non-bonding centers. For vinylthioether **1**, the lack of diastereoselectivity could be rationalized by a possible stabilization by sulfur secondary orbitals in the *endo* transition state.

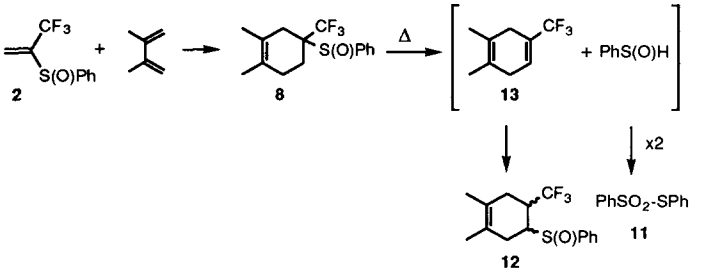
In comparison with the reaction performed with 3,3,3-trifluoropropene and cyclopentadiene, S-substituted trifluoropropenes **1-3** are better dienophiles than 3,3,3-trifluoropropene, due to the introduction of an electron-withdrawing group α to CF_3. This can be explained by a significant decrease in the LUMO energy level (strengthening the interaction with HOMO cyclopentadiene) by the thioether function and *a fortiori* by sulfoxide and sulfonyl functions, successively. This takes form as a noticeable increase in yields, under milder reaction conditions.

Whereas, with 2,3-dimethylbutadiene, the reactions usually result in the formation of the expected cycloadducts (Table 1); with vinylsulfoxide **2**, different behaviour is observed. Thus, cyclohexene **7** is prepared with 60% yield, from heating vinylthioether **1** in refluxing diene for 20 days. Equally, the reaction with vinylsulfone **3**, conducted in refluxing ether for 24 hours, affords cyclohexene **9** as a single pure product in 98% yield. However, vinylsulfoxide **2** gives rise to a mixture of products; the expected α-substituted cyclohexene **8** is only present as traces (discernable on ^{19}F NMR : 2 diastereoisomers : δ=-75.30 (s, 50%), δ=-75.35 (s, 50%)). In this case, the major product is the thiosulfonate **11** (75%) accompanied by a small quantity of trifluoromethyl β-sulfinyl cyclohexene **12** (20%) (Scheme 4).



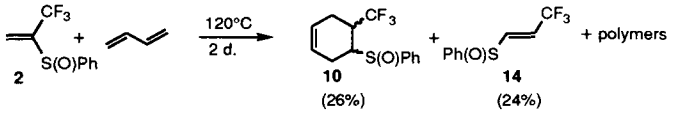
Scheme 4

Formation of compounds **11** and **12** can be explained by the initial formation of cycloadduct **8** which can eliminate sulfenic acid, PhS(O)H that either condenses to give thiosulfonate **11**, or adds to the intermediately formed olefin **13** to afford compound **12** (Scheme 5). Cyclohexene **12** is isolated as a single diastereoisomer (^{19}F NMR : δ=-70.89 (d), $^{3}J_{HF}$=10.1 Hz).



Scheme 5

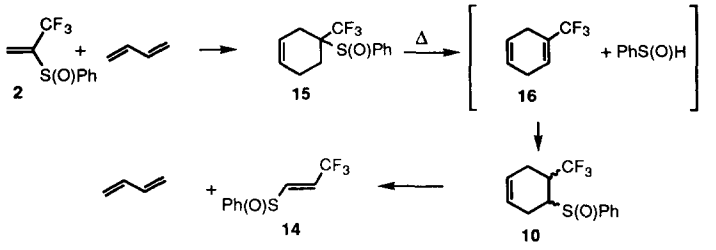
Similar behaviour is observed when vinylsulfoxide **2** reacts with butadiene. After heating at 120°C for 2 days, trifluoromethyl β-sulfinyl cyclohexene **10** is obtained, accompanied by equal quantity of 1-phenylsulfinyl-3,3,3-trifluoropropene **14** (β isomer of starting vinylsulfoxide **2**) (Scheme 6).



Scheme 6

In this case, compound **10** is isolated as two diastereoisomers (^{19}F NMR : δ=-70.83 (d), $^{3}J_{HF}$=10.2 Hz (50%); δ=-70.85 (d), $^{3}J_{HF}$=9.9 Hz (50%)). Olefin **14** is only obtained as its *trans*-conformer (^{1}H NMR, $^{3}J_{HH}$=14.7 Hz).

The mechanism involved again proceeds *via* the formation of the expected cycloadduct **15**, followed by elimination of sulfenic acid, PhS(O)H. This unstable compound adds directly to the diene, **16** intermediately formed, to give cyclohexene **10**. Under the relatively vigorous reaction conditions, **10** is able to undergo a retro Diels-Alder leading to α,β-substituted olefin **14** (Scheme 7).



Scheme 7

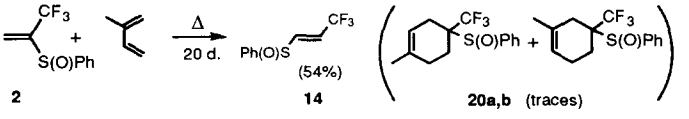
The structures of dienes **13** and **16** are confirmed by spectroscopic analysis (^1H and ^{13}C NMR). Experiments were performed to support the proposed mechanism and dismiss the one involving preliminary isomerisation of α-sulfinyl trifluoropropene **2** to β-sulfinyl trifluoropropene **14** followed by the reaction of **14** in cycloaddition.

The ability to easily eliminate sulfenic acid from the initial cycloadducts is not surprising : such behaviour has already been reported in the literature.[7,8]

Finally, the regioselectivity of cycloaddition was examined, reacting S-substituted trifluoropropenes 1-3 with isoprene (Table 2).

Cycloaddition of vinylthioether **1** with isoprene is performed in a sealed tube at 140°C for 2 days. Corresponding [4+2] cycloadducts are obtained in 53% yield as a mixture of *para/meta* isomers of which *para* isomer is major (*para/meta* : 76/24 ratio). Reaction with vinylsulfone **3** gives the same results. After heating in refluxing dichloromethane for 4 days, cycloadducts **19a-b** are obtained in 99% yield. *Para* isomer (**19a**) is again predominant (*para/meta* : 83/17 ratio). The regioselectivity can be rationalized in terms of frontier-orbital models. Diels-Alder reaction of trifluoropropenes **1** and **3** with isoprene proceeds *via* HOMO diene-LUMO dienophile interaction to give the *para* cycloadduct as major product. This suggests that the geminal presence of CF_3, σ electron-withdrawing group, and respectively thioether and sulfonyl functions, gives rise to a remarkable decrease in the LUMO energy level (strengthening its interaction with HOMO isoprene), and an increase in the LUMO coefficient of C-2. This effect is of course more noticeable for vinylsulfone **3** than for its thioether analog **1**. However, it is not sufficient to generate complete regioselectivity with isoprene.

Concerning the vinylsulfoxide **2**, we only isolated the β-sulfinylated trifluoropropene **14** (54%). The presence, as traces, of expected cycloadducts **20a-b** could be detected by ^{19}F NMR (Scheme 8).



Scheme 8

The formation of trifluoropropene **14** can be again explained by desulfenylation of cycloadducts **20a-b**, followed by the addition of sulfenic acid to the intermediately formed diene. Finally, under the conditions involved, a retro Diels-Alder is observed leading to compound **14**. This result constitutes a new synthesis of **14** and shows, at the same time, that cycloaddition of β-isomer **14** is less favorable than the one of the α-compound **2**.

CONCLUSION

The work described herein shows the remarkable increase in reactivity induced by introduction of thioether, sulfoxide or sulfonyl group α to CF_3 in 3,3,3-trifluoropropene in Diels-Alder reactions. Thus, cycloadditions of S-substituted trifluoropropenes **1-3** with different dienes give rise to various cyclohexenes bearing CF_3, with high regio- and stereoselectivities. We have shown that it was possible to tune the reactivity of the trifluoropropenic double bond depending on the oxidation state of S-substituent. These sulfur functions promise to be useful starting materials for further transformations.

ACKNOWLEDGEMENTS

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EXPERIMENTAL

Melting points were taken in sealed capillaries using a Dr. Tottoli apparatus and are uncorrected. IR (ν_{max} in cm^{-1}) and mass spectra were measured on a Perkin Elmer 1710 and Finnigan Mat TSQ 70 apparatus, respectively. ^1H, ^{19}F and ^{13}C-NMR spectra were recorded in $CDCl_3$ solutions on a Varian VXR or Gemini 200 spectrometers using TMS as the internal reference for ^1H and ^{13}C spectra and $CFCl_3$ for ^{19}F spectra. Chemical shifts are expressed in ppm on the δ scale and coupling constants J are given in Hz. The following abbreviations are used : s singlet, d doublet, t triplet, q quartet, quint quintuplet and m multiplet; δ' indicates the chemical shifts of the other diastereoisomer.

Reactions of S-substituted trifluoropropenes 1-3[9] with cyclopentadiene. a) from sulfide 1 : A Carius tube was charged with 0.50g (0.0024 mole) of sulfide 1, 5 ml of cyclopentadiene, hydroquinone and 1 ml of dry benzene. The tube was sealed under vacuum and heated at 110°C for 24 hours. After evaporation, the residue was purified by column chromatography on silica gel (EP) to provide 0.48g (72%) of 4 as a mixture of *endo/exo* conformers (1/1 ratio) from which *exo* CF_3 isomer was isolated as a pure product. **Rf** = 0.30 (*exo* CF_3, 50%); Rf' = 0.40 (*endo* CF_3, 50%); **IR** (neat) : 2900, 1500,

1285-1120, 1250-1015, 700, 600; **MS** : 270, 204, 160, 135, 109, 91, 77, 69, 66; **^{1}H-NMR** : δ (*exo* CF_3) = 1.27 (dd, J=13.4-2.9, 1H), 1.57 (ddd, J=9.3-2.9-1.5, 1H), 1.89 (dd, J=9.3-1.5, 1H), 2.06 (dd, J=13.3-3.5, 1H), 2.97 (s br, 1H), 3.22 (s br, 1H), 6.31 (dd, J=5.6-3.0, 1H), 6.39 (dd, J=5.4-3.4, 1H), 7.25-7.55 (m, 5H); δ' (*endo* CF_3) = 1.56 (d, J=8.1, 1H), 1.59 (d, J=12.4, 1H), 1.89 (d, J=12.4, 1H), 2.46 (d, J=8.1, 1H), 2.88 (s br, 1H), 3.00 (s br, 1H), 5.93 (dd, J=5.5-2.7, 1H), 6.25 (dd, J=5.8-3.0, 1H), 7.26-7.64 (m, 5H); **^{19}F-NMR** : δ = -66.08 (s, 3F); δ' = -63.57 (s, 3F); **^{13}C-NMR** : δ = 34.38 (td, J=139.0), 41.97 (dd, J=147.5-6.4), 47.83 (tdd, J=134.4-7.0-4.0), 47.90 (q, $^2J_{CF}$=26.1), 48.77 (dd, J=158.7-8.5), 128.15 (q, $^1J_{CF}$=286.0), 128.70 (dd, J=161.0-6.9), 128.94 (dt, J=161.1-7.9), 136.09 (d, J=164.9), 137.07 (d, J=173.4), 137.15 (d, J=163.2), 140.20 (s); δ' = 36.62 (td, J=136.5-6.7), 43.31 (dd, J=148.2-6.8), 47.87 (q, $^2J_{CF}$=26.1), 49.38 (tdd, J=151.0-16.0-8.5), 49.68 (d, J=135.4), 127.68 (q, $^1J_{CF}$=280.1), 128.70 (dd, J=161.1-6.3), 129.08 (dt, J=161.2-7.9), 129.52 (dt, J=161.0-7.5), 167.07 (s), 137.04 (d, J=163.6), 139.21 (d, J=164.2); **Analysis** : calculated for $C_{14}H_{13}SF_3$: C (62.21), H (4.85), S (11.86) - found C (61.76), H (5.05), S (12.54) %. **b) from sulfoxide 2** : To a solution of sulfoxide 2 (0.50g; 0.0023 mole) in 5 ml of dry ether was added cyclopentadiene (0.30g; 0.0045 mole) at room temperature and the mixture was stirred in refluxing solvent for 5 days. After evaporation, the residue was purified by column chromatography on silica gel (EP/AE : 7/3) to provide 0.64g (98%) of bicycloheptene 5 as a mixture of four diastereoisomers (2/1 ratio *endo* CF_3/*exo* CF_3). Cycloadducts **5A** and **5C** were isolated as pure yellow crystals. **5A** (*endo* CF_3) : Yield : 37%; **Rf** = 0.67; **Mp** = 51°C; **IR** (KBr) : 2900, 1570, 1390-1180, 1165-1080, 1050, 790; **MS** : 286, 177, 161, 141, 126, 109, 91, 77; **^{1}H-NMR** : δ = 1.22 (m, 1H), 1.55 (dd, J=13.5-2.9, 1H), 2.02 (d, J=9.2, 1H), 2.65 (dd, J=13.5-3.7, 1H), 2.72 (dd, J=3.0-1.5, 1H), 3.05 (s br, 1H), 5.95 (dt, J=5.5-2.8, 1H), 6.42 (dd, J=5.5-2.9, 1H), 7.53-7.75 (m, 5H); **^{19}F-NMR** : δ = -59.92 (s, 3F); **^{13}C-NMR** : δ = 30.77 (td, J=142.8-7.8), 42.19 (dd, J=148.3-5.1), 46.38 (t, J=132.8), 48.29 (ddd, J=153.0-16.2-8.2), 74.81 (q, $^2J_{CF}$=15.8), 126.00 (d, J=164.1), 126.33 (q, $^1J_{CF}$=286.0), 128.80 (dd, J=163.6-8.3), 131.64 (dt, J=161.7-7.2), 133.77 (d, J=175.0), 136.05 (s), 142.04 (d, J=169.8); **Analysis** : calculated for $C_{14}H_{13}OSF_3$: C (58.73), H (4.58) - found C (58.86), H (4.52) %. **5C** (*exo* CF_3) : **Yield** : 24%; Rf = 0.51; **Mp** = 53°C; **IR** (KBr) : 2900, 1590, 1450-1170, 1220-1060, 1080, 750; MS : 286, 177, 161, 141, 126, 109, 91, 77; **^{1}H-NMR** : δ = 1.59 (d, J=13.5, 1H), 1.64 (m, 1H), 1.97 (d, J=8.9, 1H), 2.17 (dd, J=13.9-3.7, 1H), 3.00 (s br, 1H), 3.26 (dd, J=2.9-1.5, 1H), 6.04 (dt, J=5.2-2.6, 1H), 6.40 (dd, J=5.5-3.0, 1H), 7.27-7.73 (m, 5H); **^{19}F-NMR** : δ = -60.87 (s, 3F); **^{13}C-NMR** : δ = 33.25 (td, J=141.5-9.2), 42.13 (dd, J=148.9-9.2), 47.85 (ddd, J=153.1-16.3-9.0), 48.81 (t, J=133.7), 74.98 (q, $^2J_{CF}$=15.3), 125.82 (d, J=160.1), 126.19 (q, $^1J_{CF}$=285.9), 129.08 (dt, J=161.7-3.2), 131.72 (dt, J=161.6-7.3), 132.75 (dt, J=174.9-6.0), 140.96 (s), 141.59 (d, J=170.6); **Analysis** : calculated for $C_{14}H_{13}OSF_3$: C (58.73), H (4.58) - found C (58.74), H (4.57) %. **5B** (*endo* CF_3; 75%) - **5D** (*exo* CF_3; 25%) : **Yield** : 37%; **Rf** = 0.45; **Mp** = 59.5°C; **IR** (KBr) : 2900, 1590, 1390-1150, 1200-1000, 1060, 750; **MS** : 286, 258, 177, 161, 142, 126, 109, 91, 77; **^{1}H-NMR** : δ (*endo* CF_3) = 1.68 (d, J=13.5, 1H), 1.69 (d, J=13.5, 1H), 1.85 (d, J=13.3, 1H), 2.00 (dd, J=14.3-3.6, 1H), 3.12 (s br, 1H), 3.56 (s br, 1H), 6.49 (dd, J=5.5-3.0, 1H), 6.60 (dd, J=5.5-2.9, 1H), 7.46-7.71 (m, 5H); δ' (*exo* CF_3) = 1.68 (d, J=13.5, 1H), 1.69 (d, J=13.5, 1H), 1.85 (d, J=13.3, 1H), 2.31 (dd, J=14.2-3.4,

1H), 3.12 (s br, 1H), 3.56 (s br, 1H), 6.43 (m, 1H), 6.60 (dd, J=5.5-2.9, 1H), 7.46-7.71 (m, 5H); **^{19}F-NMR** : δ = -62.24 (s, 3F); δ' = -62.06 (s, 3F); **^{13}C-NMR** : δ = 29.47 (td, J=135.9-7.8), 41.86 (dd, J=148.6-6.8), 48.29 (tdd, J=135.1-6.6-3.3), 48.78 (ddd, J=154.1-16.0-7.9), 74.90 (q, $^{2}J_{CF}$=26.2), 125.74 (d, J=163.7), 126.45 (q, $^{1}J_{CF}$=283.1), 128.74 (dd, J=162.7-8.3), 131.36 (dt, J=161.6-7.4), 134.89 (s), 135.64 (d, J=175.5), 139.79 (d, J=170.2); δ' = 30.36 (t, J=135.9), 41.86 (dd, J=148.6-6.8), 48.34 (tdd, J=135.1-6.6-3.3), 48.78 (ddd, J=154.1-16.0-7.9), 74.90 (q, $^{2}J_{CF}$=26.2), 125.37 (d, J=163.7), 126.45 (q, $^{1}J_{CF}$=283.1), 128.82 (dd, J=162.7-8.3), 131.36 (dt, J=161.6-7.4), 134.89 (s), 135.64 (d, J=175.5), 139.79 (d, J=170.2); **Analysis** : calculated for $C_{14}H_{13}OSF_3$: C (58.73), H (4.58) - found C (58.67), H (4.72) %. **c) from sulfone 3** : To a solution of sulfone **3** (0.50g; 0.0021 mole) in 5 ml of dry ether was added cyclopentadiene (0.28g; 0.0042 mole) and the mixture was stirred at room temperature for 24 hours. After evaporation, the residue was purified by recrystallization from ether to provide 0.63g (99%) of bicycloheptene **6** as a mixture of *endo* CF_3/*exo* CF_3 conformers (4/1 *endo* CF_3/*exo* CF_3 ratio). **Mp** = 83.8-84.6°C; **IR** (KBr) : 2900, 1560, 1350-1150, 1320-1200, 1150-1110, 1180, 715; **MS** : 302, 216, 177, 161, 142, 141, 126, 95, 91, 77, 69, 66; **^{1}H-NMR** : δ = 1.56 (d, J=7.6, 1H), 1.70 (dd, J=13.5-2.7, 1H), 2.60 (d, J=7.2, 1H), 2.64 (m, 1H), 3.08 (s br, 1H), 3.47 (s br, 1H), 6.02 (m, 1H), 6.41 (m, 1H), 7.26-7.99 (m, 5H); **^{19}F-NMR** : δ (*endo* CF_3, 80%) = -58.23 (s, 3F); δ' (*exo* CF_3, 20%) = -62.53 (s, 3F); **^{13}C-NMR** : δ = 32.07 (td, J=134.9-8.3), 41.82 (dd, J=148.7-6.4), 48.56 (ddd, J=138.6-17.1-8.6), 49.40 (t, J=135.1), 78.61 (q, $^{2}J_{CF}$=26.1), 124.49 (q, $^{1}J_{CF}$=283.5), 128.66 (dd, J=163.9-6.8), 129.76 (dt, J=169.8-6.4), 133.36 (dt, J=162.7-7.2), 133.88 (d, J=173.2), 138.49 (s), 141.54 (d, J=170.9); δ' = 32.87, 42.09, 49.13, 49.40, 78.61, 124.49, 128.48, 129.35, 133.11, 133 .65, 138.49, 140.20; **Analysis** : calculated for $C_{14}H_{13}O_2SF_3$: C (55.62), H (4.34), S (10.60) - found C (55.04), H (4.58), S (10.34) %.

Reactions of S-substituted trifluoropropenes 1-3 with 2,3-dimethylbutadiene. a) from sulfide 1 : A mixture of sulfide **1** (0.50g; 0.0024 mole) in 5 ml of 2,3-dimethylbutadiene was stirred in refluxing solvent for 20 days. After evaporation, the residue was purified by column chromatography on silica gel (EP/EE : 95/5) to provide 0.42g (60%) of cyclohexene 7. **Rf** = 0.8; **IR** (neat) : 3020, 2930, 1675, 1475, 1270, 1240-1060, 705, 595; **MS** : 286, 177, 176, 161, 110, 109, 107, 91, 77, 69; **^{1}H-NMR** : δ = 1.45 (s, 3H), 1.55-1.61 (m, 2H), 1.70 (s, 3H), 1.80-2.01 (m, 2H), 2.28-2.54 (m, 2H), 7.30-7.53 (m, 5H); **^{19}F-NMR** : δ = -76.24 (s, 3F); **^{13}C-NMR** : δ = 18.44 (q, J=125.6), 18.46 (q, J=124.0), 25.44 (t, J=128.6), 27.87 (t, J=126.4), 33.50 (t, J=128.6), 54.57 (q, $^{2}J_{CF}$=25.6), 120.39 (s), 125.23 (s), 127.86 (q, $^{1}J_{CF}$=280.9), 128.34 (dd, J=161.0-7.6), 129.47 (dt, J=160.7-7.6), 129.88 (t, J=7.8), 138.04 (dt, J=164.4-6.1); **Analysis** : calculated for $C_{15}H_{17}SF_3$: C (62.92), H(5.98) - found C (62.78), H (6.02) %. **b) from sulfoxide 2** : A mixture of sulfoxide **2** (0.50g; 0.0023 mole) in 5 ml of 2,3-dimethylbutadiene was stirred in refluxing solvent for 16 days. After evaporation, the residue was purified by column chromatography on silica gel (CH_2Cl_2) to provide a complex mixture from which 0.14g (20%) of cyclohexene **12** was isolated. **Rf** = 0.62; **Mp** : 48°C; **IR** (KBr) : 2900, 1650, 1430, 1320-1150, 1080, 1275-1130, 750; **MS** : 302, 220, 176, 125, 111, 107, 97, 77, 69; **^{1}H-NMR** : δ = 1.46 (s, 3H), 1.52 (s, 3H), 2.08-2.10 (m, 2H), 2.32 (s br, 2H), 3.11 (m, 1H), 3.47 (m, 1H), 7.19-

7.84 (m, 5H); **^{19}F-NMR** : δ = -70.89 (d, $^{3}J_{HF}$=10.1, 3F); **^{13}C-NMR** : δ = 18.63 (q, J=125.5), 18.79 (q, J=126.1), 26.61 (t, J=130.0), 27.30 (t, J=129.6), 35.94 (dq, J=135.0, $^{2}J_{CF}$=27.8), 58.03 (d, J=137.2), 125.00 (q, $^{1}J_{CF}$=282.0), 128.72 (dt, J=167.0-7.0), 129.23 (dd, J=165.3-7.3), 134.05 (dt, J=162.5-7.5), 137.69 (t, J=7.2). **c) from sulfone 3** : To a solution of sulfone **3** (0.50g; 0.0021 mole) in 5 ml of dry ether was added dropwise 1 ml of 2,3-dimethylbutadiene diluted in 2 ml of dry ether. The reaction mixture was heated in refluxing ether for 24 hours. After evaporation, the solid residue was purified by recrystallization from ether to provide 0.66g (98%) of cyclohexene **9** as white crystals. **Mp** = 48.3-48.9°C; **IR** (KBr) : 3020, 2945, 1660, 1450, 1300, 1265-1150, 1255-1140, 710; **MS** : 318, 278, 220, 205, 176, 161, 141, 125, 111, 107, 97, 77, 69; **^{1}H-NMR** : δ = 1.64 (s, 6H), 2.13-2.34 (m, 4H), 2.83 (d, J=18.1, 2H), 7.53-7.95 (m, 5H); **^{19}F-NMR** : δ = -68.32 (s, 3F); **^{13}C-NMR** : δ = 18.41 (q, J=125.6), 22.83 (t, J=134.0), 27.65 (t, J=127.0), 30.05 (t, J=129.3), 69.54 (q, $^{2}J_{CF}$=24.9), 120.39 (s), 124.92 (q, $^{1}J_{CF}$=285.2), 125.14 (s), 128.70 (dd, J=165.9-6.8), 130.21 (dt, J=169.1-6.1), 134.19 (dt, J=162.7-7.4), 136.37 (t, J=8.2); **Analysis** : calculated for $C_{15}H_{17}O_2SF_3$: C (56.59), H (5.38), S (10.07) - found C (55.73), H (5.41), S (9.74) %.

Reaction of sulfoxide 2 with butadiene : A Carius tube was charged with sulfoxide **2** (0.5g; 0.0023 mole). The tube was cooled in dry ice/acetone bath, evacuated and charged with 5 ml of butadiene. The tube was sealed under vacuum and placed in oven at 120°C for 2 days. The tube was then opened and vented to atmospheric pressure. The residue was purified by column chromatography on silica gel (CH_2Cl_2) to provide a complex mixture from which cyclohexene **10** was the major product. **10** : **Yield** : 26%; **Rf** = 0.55; **Mp** = 47-50°C; **IR** (KBr) : 2900, 1650, 320-1215, 1090, 790, 690; MS : 274, 148, 143, 125, 109, 79, 77, 69; **^{1}H-NMR** : δ = 2.28-2.37 (m, 2H), 2.54-2.62 (m, 2H), 3.23 (d, J=8.7, 1H), 3.56 (d, J=6.6, 1H), 5.41 (s br, 1H), 5.69 (s br, 1H), 7.57-7.95 (m, 5H); **^{19}F-NMR** : δ = -70.83 (d, $^{3}J_{HF}$=10.2, 50%); δ' = -70.85 (d, $^{3}J_{HF}$=9.9, 50%); **^{13}C-NMR** : δ = 20.91 (t, J=131.9), 30.08 (t, J=131.9), 34.57 (dq, J=133.2, $^{2}J_{CF}$=27.6), 56.48 (d, J=139.5), 121.97 (ddt, J=76.2-12.2-5.9), 123.61 (ddt, J=81.2-12.2-6.6), 124.50 (q, $^{1}J_{CF}$=285.4), 128.82 (dt, J=166.7-6.4), 129.45 (dd, J=165.2-7.2), 134.15 (dt, J=162.5-7.2), 137.45 (t, J=7.2). **14** : **Yield** : 24%; **Rf** = 0.33; **^{1}H-NMR** : δ = 6.65 (dq, J=14.9, $^{3}J_{HF}$=6.6, 1H), 7.14 (dq, J=14.9, $^{4}J_{HF}$=1.8, 1H), 7.47-7.77 (m, 5H); **^{19}F-NMR** : δ = -64.17 (d, $^{3}J_{HF}$=6.6, 3F).

Reactions of S-substituted trifluoropropenes 1-3 with isoprene. a) from sulfide 1 : A mixture of sulfide **1** (0.30g; 0.0015 mole), isoprene (4 ml), hydroquinone and dry benzene (1 ml) was placed in a Carius tube. The tube was sealed under vacuum and heated to 140°C for 2 days. After evaporation, the residue was purified by column chromatography on silice gel (EP) to provide 0.21g (53%) of a mixture of regioisomeric cyclohexenes **18** (*para*/*meta* ratio : 76/24) from which *para* isomer was isolated as a pure product. **18a** (*para* isomer; 76%) : **Rf** = 0.3; **IR** (neat) : 3000, 2900, 1450, 1300, 1280-1150, 750, 690; **MS** : 272, 162, 109, 77, 69; **^{1}H-NMR** : δ = 1.56 (m, 2H), 1.76 (s, 3H), 1.87-2.40 (m, 4H), 5.23 (s, 1H), 7.22-7.57 (m, 5H); **^{19}F-NMR** : δ = -75.54 (s, 3F); **^{13}C-NMR** : δ = 23.20 (q, J=125.8), 25.17 (t, J=129.8), 26.25 (t, J=125.9), 28.07 (t, J=126.6), 53.60 (q, $^{2}J_{CF}$=24.9),

115.67 (d, J=156.6), 128.00 (q, $^1J_{CF}$=276.5), 128.47 (dd, J=161.2-7.5), 129.52 (dt, J=161.3-7.6), 130.80 (s), 133.40 (t, J=7.1), 137.94 (dt, J=164.1-6.1); **Analysis** : calculated for $C_{14}H_{15}F_3S$: C (61.75), H (5.55), S (11.77) - found C (62.09), H (5.66), S (11.82) %. **18b** (*meta* isomer; 24%) : **Rf** = 0.4; **IR** (neat) : 3000, 2900, 1450, 1300, 1280-1140, 750, 690; **MS** : 272, 203, 162, 110, 93, 77, 69; **^{1}H-NMR** : δ = 1.76 (s, 3H), 1.80-1.98 (m, 4H), 2.31-2.39 (m, 2H), 5.53 (s br, 1H), 7.25-7.57 (m, 5H); **^{19}F-NMR** : δ = -75.98 (s, 3F); **^{13}C-NMR** : δ = 23.00 (q, J=126.2), 25.38, 26.40 (t, J=125.9), 32.37 (t, J=129.6), 53.57 (q, $^2J_{CF}$=24.9), 120.62 (d, J=155.7), 128.00 (q, $^1J_{CF}$=276.3), 128.46 (dd, J=161.6-7.5), 129.49 (dt, J=161.0-7.5), 130.80 (s), 133.40 (t, J=7.2), 137.91 (dt, J=164.4-6.5). **b) from sulfoxide 2** : A mixture of sulfoxide **2** (0.50g; 0.0023 mole) and isoprene (5ml) was heated under reflux for 20 days. After evaporation, the residue was purified by column chromatography on silica gel (CH_2Cl_2) to provide 0.27g (54%) of 1-phenylsulfinyl-3,3,3-trifluoropropene **14**. **c) from sulfone 3** : To a solution of sulfone **3** (0.50g; 0.0021 mole) in 5 ml of dry dichloromethane was added dropwise isoprene (1 ml) in 2 ml of dry dichloromethane. The rection mixture was heated under refluxing solvent for 4 days. After evaporation, the residue was purified by column chromatography on silica gel (CH_2Cl_2) to provide 0.64g (99%) of cyclohexene **19** as a mixture of regioisomers (*para*/*meta* ratio : 83/17). **19** : **Rf** = 0.64; **IR** (neat) : 3020, 2960, 1675, 1450, 1315, 1280-1180, 1220-1060, 720; MS : 305, 265, 236, 163, 143, 141, 125, 97, 78, 77, 69; **^{1}H-NMR** : δ (*para* isomer) = 1.69 (s, 3H), 2.00-2.30 (m, 2H), 2.43 (d, J=18.0, 2H), 2.90 (d, J=18.0, 2H), 5.31 (s br, 1H), 7.58-7.96 (m, 5H); δ' (*meta* isomer) = 1.57 (s, 3H), 2.00-2.30 (m, 2H), 2.43 (d, J=18.0, 2H), 2.90 (d, J=18.0, 2H), 5.51 (s br, 1H), 7.58-7.96 (m, 5H); **^{19}F-NMR** : δ = -68.27 (s, 3F, 83%); δ' = -68.38 (s, 3F, 17%); **^{13}C-NMR** : δ = 22.44 (t, J=126.3), 22.53 (q, J=132.0), 24.68 (t, J=132.0), 25.80 (t, J=129.7), 67.79 (q, $^2J_{CF}$=24.8), 115.31 (d, J=158.6), 124.85 (q, $^1J_{CF}$=285.1), 128.62 (dd, J=166.4-7.3), 130.09 (dt, J=168.9-6.3), 133.02 (s), 134.12 (dt, J=162.7-7.3), 136.21 (t, J=8.0); δ' = 21.36, 21.90, 22.53 (q, J=132.0), 28.43, 69.16 (q, $^2J_{CF}$=25.1), 120.02 (d, J=158.3), 124.85 (q, $^1J_{CF}$=285.1), 128.62 (dd, J=166.4-7.3), 130.09 (dt, J=168.9-6.3), 133.05 (s), 134.12 (dt, J=162.7-7.3), 136.21 (t, J=8.0); **Analysis** : calculated for $C_{14}H_{15}O_2SF_3$: C (55.25), H (4.97), S (10.53) - found C (54.87), H (4.96), S (10.53) %.

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9. For the synthesis of S-substituted trifluoropropenes **1-3** see reference (1).

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