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Trifluoroethyl Sulfenylation or Sulfinylation with 2,2,2-Trifluoroethyl *t*-Butyl Sulfoxide[#]

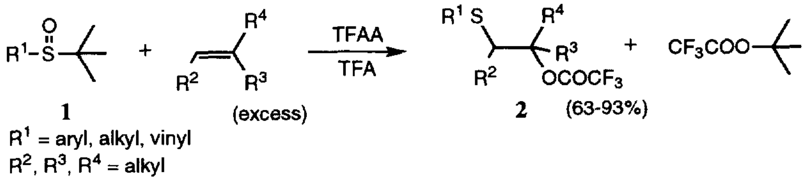
Martine REDON, Zdenek JANOUSEK[†], Heinz G. VIEHE*
Laboratoire de Chimie Organique, Université Catholique de Louvain, Place L. Pasteur, 1, B-1348 Louvain-la-Neuve (Belgium)

[#]Dedicated to Dietrich Doepp at the occasion of his 60th anniversary

Abstract : Treatment of 2,2,2-trifluoroethyl *t*-butyl sulfoxide **8** under acylating conditions, in the presence of various alkenes or 1-hexyne gives β-trifluoroacetoxy trifluoroethyl thioethers in good yields. Activated aromatic compounds furnish *ortho* and mainly *para*-substitution. In contrast, under thermal conditions **8** reacts with dimethyl acetylene dicarboxylate as a *cis*-trifluoroethyl sulfinylating agent. © 1997 Elsevier Science Ltd.

INTRODUCTION

Under acylating conditions, tertiary sulfoxides can become sulfenylating agents, able to react with nucleophiles present in the reaction medium.[1] This particular behaviour was extensively studied in our laboratory. It was shown that *t*-butyl sulfoxides such as **1** react intermolecularly with alkenes in the presence of trifluoroacetic acid (TFA) and anhydride (TFAA), to produce β-trifluoroacetoxythioethers **2** in good yields[2] (Scheme 1).



Scheme 1

The reaction is general and can be extended to numerous types of unsaturation including conjugated dienes, alkynes or allenes, for example.[2] Recently, the intramolecular version of this reaction was demonstrated[3] (Scheme 2).

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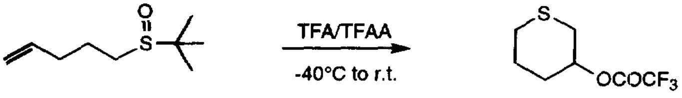
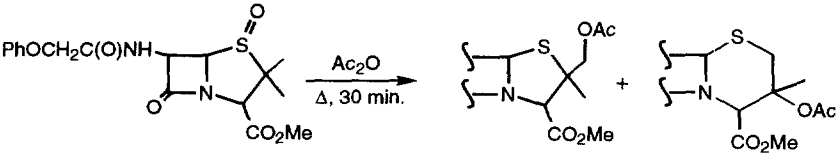
*Fax : 32(10)47 27 88



3 **4** 82%

Scheme 2

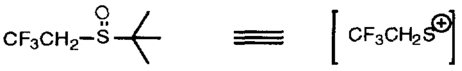
This reactivity is to rely to the well known transformation of penicillin S-oxide **5** into β-cephalosporin **7**[4] (Scheme 3).



5 **6** (49%) **7** (49%)

Scheme 3

In this paper, we report the reactivity of 2,2,2-trifluoroethyl *t*-butyl sulfoxide **8** as an electrophilic trifluoroethyl sulfenylating agent **9** (Scheme 4), allowing the facile synthesis of β-trifluoroacetoxy trifluoroethyl thioethers. The reactivity of **8** as sulfinylating agent under thermal conditions is also evocated within an example later in this report.

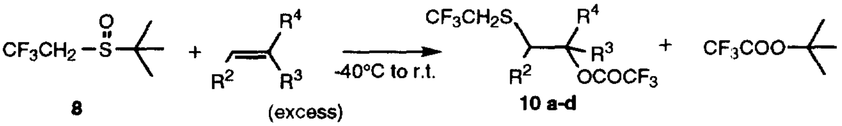


8 **9**

Scheme 4

RESULTS AND DISCUSSION

Our investigations begin with an examination of the addition reaction of *t*-butyl sulfoxide **8** with various alkenes, following the experimental conditions previously established for other non fluorinated sulfoxides in our laboratory, *i.e.* sulfoxide (1 eq.)/alkene (excess)/trifluoroacetic acid (2 eq.) and trifluoroacetic anhydride (1.5 eq.), leading to the new β-trifluoroacetoxy sulfenylation of the alkene (Scheme 5).



8 **10 a-d**

Scheme 5

The results obtained are summarized in table 1.

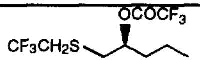
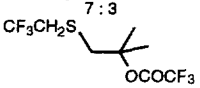
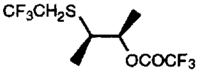
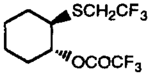
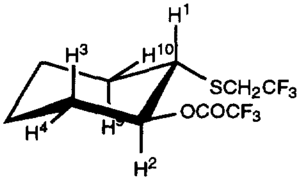
Entry	Alkene	Products	Yield (%)
a		 + regioisomer 7 : 3	**10a** 83
b			**10b** 85
c			**10c** 70
d			**10d** 82

Table 1 . Addition reactions of **8** to alkenes in the presence of TFAA and TFA.

The reaction is rapid and proceeds with high yields. All the products are purified by distillation under reduced pressure, and isolated as colourless oils.

The reaction is highly regioselective : in the case of isobutene (entry b, Table 1), we obtain exclusively the Markovnikov adduct (M); with pentene (entry a, Table 1), a mixture of predominantly Markovnikov adduct is isolated.

Stereochemically, the addition to cyclohexene (entry d, Table 1) is exclusively *trans*. This is clearly demonstrated by spectroscopic analysis (^{1}H NMR) which confirms the substituents ($-SCH_2CF_3$) and ($-OCOCF_3$) both to be in the equatorial position (Figure 1).

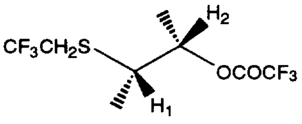


10d

Figure 1

The axial hydrogens H^1 and H^2 both give triplet of doublet signals, from which two equal and high axial-axial coupling constants (for example, H^1 : $^3J_{1\text{-}2}$ = $^3J_{1\text{-}9}$ = 10 Hz) and a single and low axial-equatorial coupling constant ($^3J_{1\text{-}10}$ = 4 Hz) are easily deduced. This data allows us to assert without ambiguïty the *trans* conformation of the adduct **10d**.

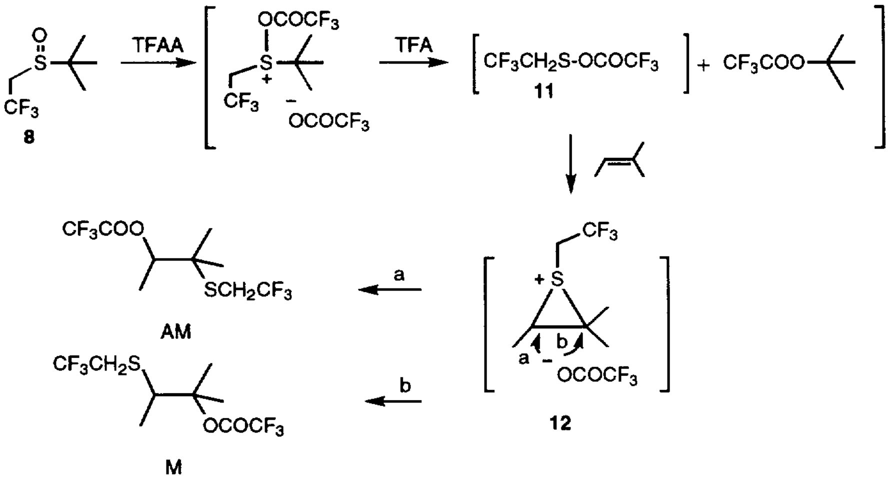
The stereospecificity of the reaction is, in turn, shown by the addition of **8** to *cis* butene (entry c, Table 1). The *threo* adduct is exclusively obtained (Figure 2). ^{1}H NMR Spectroscopy gives a coupling constant $^3J_{1-2}$=7Hz. This data is not enough to conclude without doubt the *threo* configuration; but, precedent studies carried on in our laboratory are largely in its favour.[5]



10c

Figure 2

A proposed mechanism based on previous studies is given in scheme **6**.[2]



Scheme 6

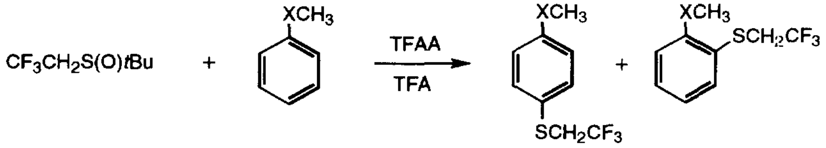
The reaction begins, as in the Pummerer rearrangement, by the acylation of the oxygen of the sulfoxide to give the sulfenyl trifluoroacetate intermediate **11**. Then, **11** adds to the alkene, creating an episulfonium ion **12**. The trifluoroacetate anion then opens the ring by attacking preferentially the most procationic carbon (adduct M major).[6]

This trifluoroethyl sulfenylating reaction, proceeding with a starting material stable and facile to handle, is rapid, highly regioselective and stereospecific. The easy introduction of trifluoroethyl thioether moiety into organic molecules offers considerable interest. Thus, this new trifluoroethyl sulfenylation promises to be useful, particularly in view of the comparison with trifluoromethyl sulfenylation which is of biological interest.

This methodology was extended to other unsaturated compounds.

reaction with aromatic compounds [7]

Aromatic substitution starting from *t*-butyl sulfoxide **8** was examined. In the presence of activated aromatic compounds, *i.e.* methoxybenzene or thiomethoxybenzene, the reaction leads to the formation of a mixture of *ortho/para* substituted products **13** and **14**, of which the *para* isomer is always predominant (Scheme 7).



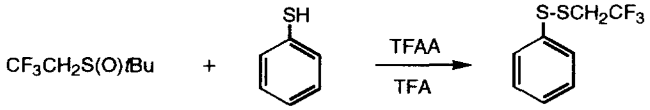
8

X = O
X = S

13 75 : 25 (32%)
14 70 : 30 (49%)

Scheme 7

With thiophenol, a different result is observed by formation of the disulfide **15** (Scheme 8).



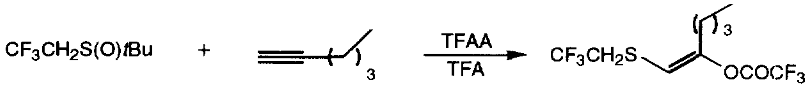
8

15 (59%)

Scheme 8

addition to alkyne

An example of trifluoroethyl sulfenylation of alkyne was also examined. The addition of *t*-butyl sulfoxide **8** to 1-hexyne produces compound **16** in excellent yield (Scheme 9).



8

16 (94%)

Scheme 9

The *trans*-stereochemistry of the only adduct **16** suggests the passage of the reaction *via* a thiirenium ring **17**, as postulated in the case of addition of sulfenyl chloride to alkynes.[8] Thus **17** would be opened by nucleophilic attack of trifluoroacetate anion on sp^2 carbon (Figure 3).

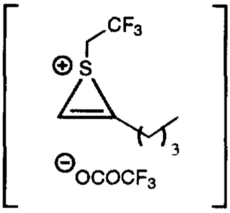
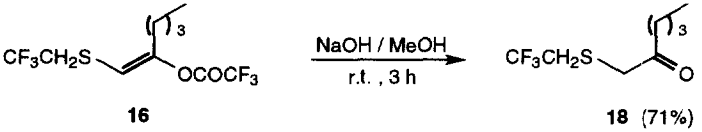

17

Figure 3

However, in contrast with sulfenyl chlorides that give preferentially AM adducts, even in acetic acid, we obtain exclusive formation of M adduct[8,9]. These regio- and stereoselectivities have been clearly shown by spectroscopic analysis (^{19}F-NMR : a single isomer : δ = -66.85 (t); $^3J_{HF}$ = 9.8 Hz (SCH_2CF_3) and δ = 76.33 (s) ($OCOCF_3$)) and the following transformation.

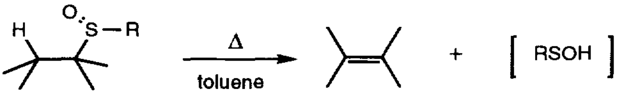
Treatment of compound **16** with basic methanol (NaOH/MeOH) leads to β-ketothioether **18** in high yield (Scheme 10).



Scheme 10

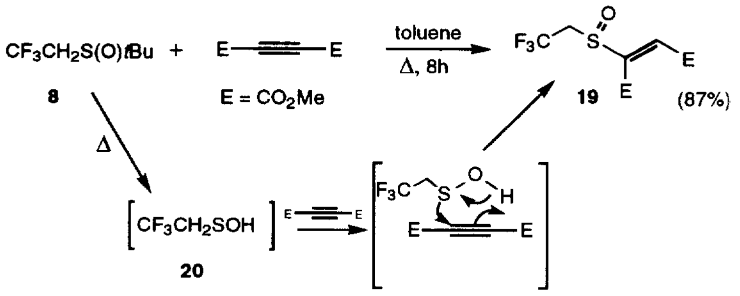
Thus, we report here a new synthesis of β-ketothioethers having a particular substitution on sulfur.

To complement the work dealing with the reactivity of 2,2,2-trifluoroethyl *t*-butyl sulfoxide **8** as sulfenylating agent, we were interested in studying its behaviour under thermolytic conditions.[10] Indeed, it is known that pyrolysis of sulfoxides generates *in situ* the corresponding sulfenic acid and olefin[8] (Scheme 11). *t*-Butyl sulfoxides are ideal compounds for this kind of reaction since they easily lose gaseous isobutene.



Scheme 11

This is observed when compound **8** in refluxing toluene reacts with dimethyl acetylene dicarboxylate (DMAD) for a period of 8 hours. The *cis* adduct **19** is produced with 87% yield as single pure product (Scheme 12).



Scheme 12

The *cis*-stereoselectivity of the adduct is in accordance with the addition of sulfenic acid, created by thermolysis of **8**, *via* a six electron *syn*-concerted rearrangement (Scheme 12). This result constitutes the first example of alkyne sulfinylation from fluoro substituted *t*-butyl sulfoxyde. This new trifluoroethyl sulfinylation would deserve more attention.[11]

CONCLUSIONS

The work described herein demonstrates the remarkable reactivity of 2,2,2-trifluoroethyl *t*-butyl sulfoxyde **8** as a practical reagent which is easy to handle. Under acylating conditions, *t*-butyl sulfoxyde **8** is a valuable electrophilic trifluoroethyl sulfenylating agent. In contrast, under thermal conditions, **8** becomes a trifluoroethyl sulfinylating agent.

ACKNOWLEDGEMENTS

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EXPERIMENTAL

Melting points were taken in sealed capillaries using a Dr. Tottoli apparatus and are uncorrected. IR (n_{max} in cm^{-1}) and mass spectra were measured on a Perkin Elmer 1710 and Finnigan Mat TSQ 70 apparatus, respectively. ^{1}H, ^{19}F an ^{13}C-NMR spectra were recorded in CDCl3 solutions on a Varian VXR or Gemini 200 spectrometers using TMS as the internal reference for ^{1}H and ^{13}C spectra and CFCl3 for ^{19}F spectra. Chemicals 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 isomer.

2,2,2-Trifluoroethyl *t*-butyl sulfoxide 8. A solution of 2.36g (0.06 mole) of NaH (60%) in 20 ml of dry DMF was cooled to 0°C. To this vigorously stirred mixture was added dropwise *t*-butane thiol (5.32g; 0.06 mole). The resulting solution was stirred for 30 min. at ambiant temperature and cooled again at 0°C. 2,2,2-Trifluoroethyl *p*-toluenesulfonate (10g; 0.04 mole) dissolved in DMF was then added dropwise and heated at 80°C for 4 hours. The reaction mixture was poured into ice water and stirred for 15 min.. The resulting solution was extracted repeatedly with ether (5x20ml) and washed with brine (2x20ml). The extracts were dried over anhydrous magnesium sulfate and evaporated. Kugelrohr distillation gave 4.88g of 2,2,2-trifluoroethyl *t*-butyl sulfide (72%)[7] as a colourless oil. **Bp** : 20°C/0.4 Torr; **IR** (neat) : 1460-1410, 1370, 1310-1080, 700, 700-490; **MS** : 172, 157, 110, 83, 69, 57; **^{1}H-NMR** : δ = 1.35 (s, 9H), 3.12 (q, $^3J_{HF}$=10.2, 2H); **^{19}F-NMR** : δ = -66.24 (t, $^3J_{HF}$=10.2, 3F); **^{13}C-NMR** : δ = 31.12 (q, J=127.0), 31.80 (tq, J=139.4, $^2J_{CF}$=30.0), 43.61 (s), 125.67 (qt, $^1J_{CF}$=275.2, J=6.1); **Analysis** : calculated for $C_6H_{11}SF_3$: C (41.85), H (6.44), S (18.62) - found C (42.58), H (6.51), S (18.64) %.

A mixture of 10g (0.06 mole) of 2,2,2-trifluoroethyl *t*-butyl sulfide and 100 ml of dry dichloromethane was cooled in a dry ice/acetone bath to -40°C. To this vigorously stirred solution was added 13.63g (0.06 mole) of *m*-CPBA (75%) in several portions. The resulting mixture was stirred for 5 hours at room temperature and then filtered through celite. The solution was mixed with water and extracted repeatedly with dichloromethane. The extracts were washed with aqueous sodium bicarbonate and dried over anhydrous magnesium sulfate. After evaporation, the residual solid was recrystallized from ether to provide pure sulfoxide **8** (9.84g) in 90% yield. **Bp** : 65°C; **IR** (KBr) : 1465-1370, 1295-1080, 1040, 520; **MS** : 189, 105, 69, 56; **^{1}H-NMR** : δ = 1.31 (s, 9H), 3.05 (dq, J=14.3, $^3J_{HF}$=10.3, 1H), 3.36 (dq, J=14.3, $^3J_{HF}$=10.2); **^{19}F-NMR** : δ = -61.53 (t, $^3J_{HF}$=10.2, 3F); δ' = -61.46 (t, $^3J_{HF}$=10.3, 3F); **^{13}C-NMR**: δ = 22.90 (q, J=128.1), 52.08 (tq, J=142.1, $^2J_{CF}$=28.6), 55.27 (s), 124.94 (qt, $^1J_{CF}$=277.4, J=6.1); **Analysis** : calculated for $C_6H_{11}OSF_3$: C (38.29), H (5.89), S (17.04) - found C (38.64), H (5.65), S (16.15) %.

Addition of various unsaturated compounds to 8 under acylating conditions : General Procedure

A solution of 0.50g (0.003 mole) of sulfoxide **8** in 5 ml of dichloromethane was stirred under argon atmosphere. 2 Equivalents of unsaturated compound were added. The mixture was cooled in a dry ice/acetone bath to -40°C. To this vigorously stirred solution were added 2 equivalents (0.61g; 0.4 ml; 0.005 mole) of TFA followed by 1.5 equivalents (0.84g; 0.6 ml; 0.004 mole) of TFAA by means of a syringe through a septum. The resulting mixture was stirred for 2 hours at room temperature; then mixed with water and extracted repeatedly with dichloromethane. The extracts were washed with aqueous sodium bicarbonate and dried over anhydrous magnesium sulfate. After evaporation, the residue was purified by Kugelrohr distillation.

1-Trifluoroethylthio-2-trifluoroacetoxy pentene 10a. 0.42 g (0.006 mole) of 1-pentene were used to obtain 0.66g of **10a** as a mixture of M/AM adducts (7/3 ratio M/AM; 83%). **Bp** : 55°C/0.015 Torr; **IR** (neat) : 2970, 1785, 1350-1130, 1170-1080, 750, 640; **MS** : 298, 185, 184, 155, 129, 109, 101, 97, 69, 55; **^{1}H-NMR** : δ = 0.96 (t, J=7.4, 3H), 1.26-1.78 (m, 4H), 2.90 (ddd, J=14.4-7.7-4.6, 2H), 3.13 (q, $^{3}J_{HF}$=9.8, 2H), 5.19 (tt, J=7.6-5.0, 1H); δ' = 0.99 (t, J=7.1, 3H), 1.26-1.78 (m, 4H), 3.13 (quint, J=6.3, 1H), 4.44 (d, J=6.3, 2H); **^{19}F-NMR** : δ (M, 70%) = -67.01 (t, $^{3}J_{HF}$=9.8, 3F), -75.59 (s, 3F); δ' (AM, 30%) = -67.19 (t, $^{3}J_{HF}$=9.8, 3F), -75.47 (s, 3F); **^{13}C-NMR** : δ = 13.44 (q, J=125.6), 18.24 (t, J=126.2), 33.49 (t, J=140.8), 34.32 (tqt, J=140.5-4.6, $^{2}J_{CF}$=32.9), 36.00 (t, J=140.6), 77.15 (dtt, J=151.1-8.0-3.1), 114.58 (q, $^{1}J_{CF}$=285.7), 125.69 (qt, $^{1}J_{CF}$=276.1, J=5.5), 157.19 (sq, $^{2}J_{CF}$=42.5); δ' = 13.61 (q, J=125.7), 19.65 (t, J=127.2), 70.05 (t, J=151.7), 33.71 (tqd, J=140.7-3.9, $^{2}J_{CF}$=32.9), 34.97 (t, J=140.3), 44.68 (d, J=141.9), 114.49 (q, $^{1}J_{CF}$=285.4), 125.53 (qt, $^{1}J_{CF}$=275.8, J=5.5), 157.06 (sq, $^{2}J_{CF}$=42.5).

1-Trifluoroethylthio-2-trifluoroacetoxy-2-methyl propene 10b. 5 ml of isobutene were used to obtain 0.64g (85%) of **10b** as single pure product. **Bp** : 45°C/0.05 Torr; **IR** (neat) : 3000, 1790, 1350-1150, 1150-1010, 750, 600; **MS** : 284, 170, 139, 113, 83, 69, 57; **^{1}H-NMR** : δ = 1.66 (s, 6H), 3.13 (s, 2H), 3.15 (q, $^{3}J_{HF}$=9.6, 2H); **^{19}F-NMR** : δ = -59.72 (t, $^{3}J_{HF}$=9.6, 3F), -75.25 (s, 3F); **^{13}C-NMR** : δ = 24.71 (q, J=128.6), 35.30 (tqt, J=140.7-4.2, $^{2}J_{CF}$=32.9), 43.16 (t, J=140.9), 87.77 (s), 107.01 (q, $^{1}J_{CF}$=286.7), 125.62 (qt, $^{1}J_{CF}$=276.0, J=5.5), 173.84 (sq, $^{2}J_{CF}$=41.8).

2-Trifluoroethylthio-3-trifluoroacetoxy butene 10c. 3 ml of *cis*-butene were used to obtain 0.53g (70%) of **10c** as single pure product. **Bp** : 50°C/0.06 Torr; **IR** (neat) : 3000, 1795, 1300-1100, 1150-1010, 750, 650; **MS** : 284, 215, 171, 141, 116, 69, 55; **^{1}H-NMR** : δ = 1.35 (d, J=7.1, 3H), 1.43 (d, J=6.4, 3H), 3.11 (q, $^{3}J_{HF}$=10.1, 2H), 3.19 (q, J=9.7, 1H), 5.18 (d, J=6.4, 1H); **^{19}F-NMR** : δ = -67.36 (t, $^{3}J_{HF}$=10.1, 3F), -75.77 (s, 3F); **^{13}C-NMR** : δ = 15.03 (q, J=128.4), 15.95 (q, J=128.8), 33.87 (tqd, J=140.5-4.1, $^{2}J_{CF}$=33.0), 44.75 (d, J=143.7), 78.21 (d, J=151.7), 114.56 (q, $^{1}J_{CF}$=280.4), 128.44 (qt, $^{1}J_{CF}$=270.4, J=5.6), 156.89 (sqd, $^{2}J_{CF}$=42.4, J=3.0); **Analysis** : calculated for $C_8H_{10}O_2SF_6$: C (33.81), H (3.55), S (11.28) - found C (33.87), H (3.71), S (11.18) %.

1-Trifluoroethylthio-2-trifluoroacetoxy cyclohexene 10d. 3 ml of cyclohexene were used to obtain 0.67g (82%) of **10d** as single pure product. **Bp** : 60-65°C/0.03 Torr; **IR** (neat) : 2950-2870, 1785, 1345-1170, 1160-1080, 640, 570; MS : 310, 196, 155, 129, 113, 97, 81, 69; **^{1}H-NMR** : δ = 1.32-1.71 (m, 4H), 1.78-1.85 (m, 2H), 2.12-2.25 (m, 2H), 2.90 (td, J=10.0-4.2, 1H), 3.18 (ddq, J=15.6-15.3, $^{3}J_{HF}$=10.0, 2H), 4.88 (td, J=9.4-4.2, 1H); **^{19}F-NMR** : δ = -67.30 (t, $^{3}J_{HF}$=10.0, 3F), -75.75 (s, 3F); **^{13}C-NMR** : δ = 23.25 (t, J=129.5), 24.85 (t, J=129.6), 30.65 (t, J=129.9), 31.80 (t, J=128.1), 34.25 (tq, J=140.8, $^{2}J_{CF}$=32.9), 48.39 (d, J=141.6), 81.11 (d, J=150.8), 114.55 (q, $^{1}J_{CF}$=285.9), 125.54 (qt, $^{1}J_{CF}$=275.8, J=5.5), 156.68 (sqd, $^{2}J_{CF}$=42.5, J=3.2); **Analysis** : calculated for $C_{10}H_{12}O_2SF_6$: C (38.71), H (3.90), S (10.34) - found C (38.27), H (4.03), S (10.15) %.

2(4)-Trifluoroethylthio methoxybenzene 13. 3 ml of methoxybenzene were used to obtain 0.19g of **13** as a mixture of *para/ortho* substituted adducts (75/25 *para/ortho* ratio; 32%). **Bp** : 115°C/0.02 Torr; **IR** (neat) : 3030-2950, 1785, 1310-1180, 1120-1030, 820-780, 755, 800-735, 665; **MS** : 222, 207, 179, 149, 139, 124, 109, 95, 77, 69; **^{1}H-NMR** : δ (*para* isomer) = 3.30 (q, $^3J_{HF}$=9.8, 2H), 3.77 (s, 3H), 6.84 (d, J=8.4, 2H), 7.46 (d, J=8.4, 2H); δ' (*ortho* isomer) = 3.44 (q, $^3J_{HF}$=9.8, 2H), 3.89 (s, 3H), 7.21-7.34 (m, 4H); **^{19}F-NMR** : δ (75%) = -66.89 (t, $^3J_{HF}$=9.8, 3F); δ' (25%) = -66.55 (t, $^3J_{HF}$=9.8, 3F); **^{13}C-NMR** : δ = 39.98 (tq, J=141.1, $^2J_{CF}$=32.0), 55.19 (q, J=144.1), 114.75 (dd, J=160.4-5.0), 124.02 (s), 126.08 (q, $^1J_{CF}$=278.6), 135.78 (dd, J=162.0-6.7), 160.17 (s); δ' = 38.49 (tq, J=141.2, $^2J_{CF}$=32.3), 55.67 (q, J=144.7), 114.75 (dd, J=160.4-5.0), 124.02 (s), 126.08 (q, $^1J_{CF}$=278.6), 135.78 (dd, J=162.0-6.7), 158.64 (s); **Analysis** : calculated for $C_9H_9OSF_3$: C (48.64), H (4.08) - found C (47.89), H (4.05) %.

2(4)-Trifluoroethylthio thiomethoxybenzene 14. 3 ml of thiomethoxybenzene were used to obtain 0.31g of **14** as a mixture of *para/ortho* adducts (70/30 *para/ortho* ratio; 49%). **Bp** : 120°C/0.02 Torr; **IR** (neat) : 3000-2955, 1785, 1300-1125, 1240-1080, 810-780, 750, 800-730, 640; **MS** : 238, 223, 155, 140, 124, 109, 77, 69; **^{1}H-NMR** : δ (*para* isomer) = 2.37 (s, 3H), 3.32 (q, $^3J_{HF}$=9.6, 2H), 7.12 (d, J=8.5, 2H), 7.35 (d, J=8.5, 2H); δ' (*ortho* isomer) = 2.40 (s, 3H), 3.39 (q, $^3J_{HF}$=9.8, 2H), 7.21-7.23 (m, 4H); **^{19}F-NMR** : δ (70%) = -66.86 (t, $^3J_{HF}$=9.6, 3F); δ' (30%) = 66.41 (t, $^3J_{HF}$=9.8, 3F); **^{13}C-NMR** : δ = 15.04 (q, J=139.9), 38.25 (tq, J=141.3, $^2J_{CF}$=32.3), 125.27 (qt, $^1J_{CF}$=276.4, J=5.5), 126.54 (dd, J=162.8-6.4), 132.64 (dd, J=163.8-6.3), 138.29 (s), 139.40 (s); δ' = 15.43 (q, J=139.6), 36.36 (tq, J=141.8, $^2J_{CF}$=32.1), 125.27 (qt, $^1J_{CF}$=276.4, J=5.5), 124.83 (d, J=164.0), 128.72 (dd, J=161.0-6.4), 138.29 (s), 139.40 (s); **Analysis** : calculated for $C_9H_9S_2F_3$: C (45.36), H (3.81), S (26.91) - found C (46.17), H (4.10), S (25.46) %.

Trifluoroethylphenyl disulfide 16. 2 ml of thiophenol were used to obtain 0.35g (59%) of **16** as single pure product. **Bp** : 100°C/0.05 Torr; **IR** (neat) : 3030-2950, 1480-1130, 1260-1020, 770-730, 740, 665, 500; **MS** : 224, 141, 109, 77, 69, 65; **^{1}H-NMR** : δ = 3.57 (q, $^3J_{HF}$=9.8, 2H), 7.24-7.56 (m, 5H); **^{19}F-NMR** : δ = -66.48 (t, $^3J_{HF}$=9.8, 3F); **^{13}C-NMR** : δ = 41.96 (tq, J=142.2, $^2J_{CF}$=31.7), 122.29 (qt, $^1J_{CF}$=275.9, J=5.5), 127.18 (dt, J=161.6-7.2), 127.84 (dt, J=162.3-6.9), 128.72 (dd, J=161.2-6.9), 129.18 (s); **Analysis** : calculated for $C_8H_7S_2F_3$: C (42.84), H (3.15), S (28.60) - found C (43.38), H (3.36), S (28.59) %.

1-Trifluoroethylthio-2-trifluoroacetoxy-1-hexene 17. 3 ml of 1-hexyne were used to obtain 0.77g (94%) of **17** as single pure product. **Bp** : 65°C/0.01 Torr; **IR** (neat) : 3000-2970, 1795, 1590, 1300-1130, 1150-1085, 750, 640; **MS** : 310, 266, 195, 129, 113, 84, 69; **^{1}H-NMR** : δ = 0.92 (t, J=7.1, 3H), 1.30-1.51 (m, 2H), 2.50 (t, J=7.2, 2H), 2.41 (t, J=7.2, 2H), 3.20 (q, $^3J_{HF}$=9.8, 2H), 6.05 (s, 1H); **^{19}F-NMR** : δ = -66.86 (t, $^3J_{HF}$=9.8, 3F), -76.33 (s, 3F); **^{13}C-NMR** : δ = 13.50 (q, J=124.7), 21.83 (t, J=125.5), 28.02 (t, J=128.3), 29.41 (t, J=128.5), 36.27 (tq, J=141.5, $^2J_{CF}$=33.2), 113.28

(d, J=176.2), 114.42 (q, $^1J_{CF}$=285.7), 127.90 (qt, $^1J_{CF}$=276.5, J=5.4), 150.97 (s), 154.90 (sq, $^2J_{CF}$=43.3).

1-Trifluoroethylthio-2-hexanone 19. A solution of 0.78g (0.0025 mole) of sulfide **17** in 5 ml of methanol was stirred in the presence of 1 equivalent (0.08g) of sodium hydroxide pellets for 3 hours in an open flask. The reaction mixture was poured into water and the resulting solution was extracted repeatedly with ether and washed with water. The extracts were dried over anhydrous magnesium sulfate and evaporated. The residue was purified by Kugelrohr distillation to provide 0.38g of **19** (71%). **Bp** : 110°C/0.05 Torr; **IR** (neat) : 2970-2875, 1710, 1380-1130, 1170-1085, 845, 640; **MS** : 215, 185, 129, 86, 84, 69; **^{1}H-NMR** : δ = 0.93 (t, J=7.2, 3H), 1.29-1.40 (m, 2H), 1.56-1.64 (m, 2H), 2.59 (t, J=7.4, 2H), 3.15 (q, $^3J_{HF}$=9.7, 2H), 3.42 (s, 2H); **^{19}F-NMR** : δ = -66.82 (t, $^3J_{HF}$=9.7, 3F); **^{13}C-NMR** : δ = 13.41 (qt, J=123.5-3.7), 21.94 (tq, J=125.0-3.8), 25.58 (tt, J=122.7-4.9), 33.12 (tqt, J=141.0-4.8, $^2J_{CF}$=33.0), 40.41 (tt, J=125.1-3.8), 40.71 (tt, J=139.6-4.7), 125.63 (qt, $^1J_{CF}$=276.2, J=5.5), 204.63 (s); **Analysis** : calculated for $C_8H_{13}OSF_3$: C (44.84), H (6.11), S (14.96) - found C (44.41), H (5.91), S (14.35) %.

Addition of DMAD to 8 under thermolytic conditions.

1-Trifluoroethylsulfoxy-1,2-dimethyl ethylene dicarboxylate 22. To a stirred solution of 0.16g (0.00085 mole) of sulfoxide **8** in 2 ml of dry toluene was added dropwise 1 ml of DMAD at room temperature. The resulting mixture was heated to refluxing solvent for 8 hours. After evaporation, the residue was purified by Kugelrohr distillation to provide 0.20g of sulfoxide **22** as white crystals in 87% yield. **Mp** : 67°C; **IR** (KBr) : 2900, 1740, 1650, 1350-1150, 1210, 1050, 790; **MS** : 274, 242, 226, 214, 206, 194, 160, 143, 111, 79, 69, 59; **^{1}H-NMR** : δ = 3.32 (dq, J=14.4, $^3J_{HF}$=9.8, 2H), 3.81 (s, 3H), 3.83 (s, 3H), 7.04 (s, 1H); **^{19}F-NMR** : δ = -61.30 (t, $^3J_{HF}$=9.8, 3F); **^{13}C-NMR** : δ = 52.93 (q, J=148.3), 54.57 (q, J=149.1), 57.65 (tq, J=142.7, $^2J_{CF}$=29.5), 123.27 (qt, $^1J_{CF}$=278.5, J=6.1), 132.18 (d, J=169.4), 145.23 (s), 161.45 (s), 164.09 (s); **Analysis** : calculated for $C_8H_9O_5SF_3$: C (35.04), H (3.31), S (11.69) - found C (34.88), H (3.30), S (12.37) %.

REFERENCES AND NOTES

† deceased 17th of July 1996

1. For a recent review, see : Kennedy, M.; Mc Kervey, M.A. in *Comprehensive Organic Synthesis*, ed. Trost, B.M.; Pergamon : Oxford, **1991**; vol.7, pp 193-216.

   a) Morin, R.B.; Spry, D.O.; Mueller, R.A.; *Tetrahedron Lett.* **1969**, 849; b) Bushby, R.J.; *J. Chem. Soc.,Perkin Trans. I* **1976**, 2590; c) Vedejs, E.; Buchanan, R.A.; Conrad, P.C.; Meier, G.P.; Mullins, M.J.; Schaffhausen, J.G.; Schwartz, C.E.; *J. Am. Chem. Soc.* **1989**, *111*, 8421.
2. a) Brichard, M.H.; *Thèse de doctorat*, Promoteur H.G. Viehe (U.C.L.) **1991**; b) Brichard, M.H.; Musick, M.; Janousek, Z.; Viehe, H.G.; *Synth. Commun.* **1990**, *20*, 2379; c) Brichard, M.H.;

Janousek, Z.; Merényi, R.; Viehe, H.G. *Tetrahedron Lett.* **1992**, *33*, 2511; d) Brichard, M.H.; Janousek, Z.; Viehe, H.G. *J. Prakt. Chem. Chem. Ztg* **1993**, *335*, 143; e) Harvey, J.; Brichard, M.H.; Viehe, H.G. *J. Chem. Soc. Perkin Trans.* I **1993**, 2275

3. Burteau, A.C.; *Thèse de doctorat,* Promoteur H.G. Viehe (U.C.L.) **1996**.
4. Morin, R.B.; Jackson, B.G.; Mueller, R.A.; Lavagnino, E.R.; Scanlon, W.B.; Andrews, S.L.; *J. Am. Chem. Soc.* **1969**, *91*, 1401.
5. *t*-Butyl sulfoxides non trifluoromethylated was added to *cis*-butene to give *threo* adduct and to *trans*-butene to give *erythro* adduct. For more details see reference 2.
6. The regioselectivity of the reaction is more complex and supports the formation of an intermediate episulfonium ion **12**. Previous studies in our laboratory have shown that initial products were obtained under kinetic control; the trifluoroacetate anion attacking preferentially the less hindered carbon. However, when temperature was increased, isomerisation of kinetic adduct (AM) into thermodynamic one (M) was observed.
7. a) Beck, J.R.; Yahner, J.A.; *J. Org. Chem.* **1978**, *43*, 2048; b) Cogolli, P.; Testaferri, L.; Tingoli, M.; Tiecco, M.; *J. Org. Chem.* **1979**, *44*, 2636; c) Ibidem; *J. Org. Chem.* **1979**, *44*, 2642.
8. *The Chemistry of Sulphenic Acids*, ed. Stirling, C.J.M.; Pataï, S.; Wiley, J. & sons, **1990**, chap. X.
9. Calo, V.; Modena, G.; Scorrano, G.; *J. Chem. Soc. (C)* **1968**, 1339.
10. Some examples of pyrolysis of sulfoxides : a) Barton D.H.R.; Coates I.H.; Sammes P.G.; Copper C.M.; *J. Chem. Soc., Perkin Trans. I* **1974**, 1459; b) Jones D.N.; Lewton D.A.; *J. Chem. Soc., Chem. Commun.* **1974**, 457; c) Jones D.N.; Hill D.R.; Lewton D.A.; *Tetrahedron Lett.* **1975**, *27*, 2235.
11. Few other unsaturated compounds were tested (cyclohexene, thiophene) unsuccessfully. In fact, in reaction, with "nucleophilic" olefins, *t*-butyl sulfoxide **8** condenses to give sulfonate ($CF_3CH_2SO_2S(O)CH_2CF_3$) as major product. This lack of reactivity could be explained by the presence of the electrocaptor CF_3 group tending to decrease the nucleophilicity of S in the intermediate sulfenic acid.

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