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Perfluoroacylation of Alkynes

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Abstract: *Direct electrophilic perfluoroacylation of acetylenes with trifluoroacetic anhydride activated by $BF_3 \cdot SMe_2$ complex leads to the corresponding sulfonium salts, which are the products of conjugate addition of the CF_3CO- group and dimethyl sulfide. Demethylation of the sulfonium salts leads to corresponding vinyl sulfide bearing CF_3CO - moiety. Oxidation of sulfides gives rise to α,β - unsaturated sulfones with trifluoroacyl group.*

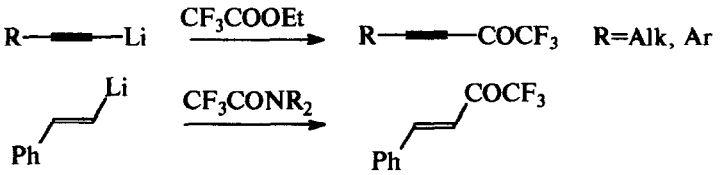
Introduction of fluorine into organic compounds is a current problem in organic synthesis due to the specific properties of fluorine-containing compounds, particularly their biological activity[1,2].

Acylation of alkynes leads in the case of conjugated addition to substituted α,β - unsaturated ketones which are very valuable synthons. However, this reaction was investigated only for the case of acyl chlorides in the presence of Lewis acids, which provided β-chlorovinyl ketones[3]. Very interesting results were obtained in the case of acylation of alkynes by acylium salts[4]. This reaction leads to the formation of very reactive vinyl cations stabilized in different ways. These transformations are skeletal rearrangements, hydride shifts and reaction with some nucleophiles such as nitromethane and aromatic hydrocarbons[5,6]. In the latter cases it is possible to obtain conjugate addition products.

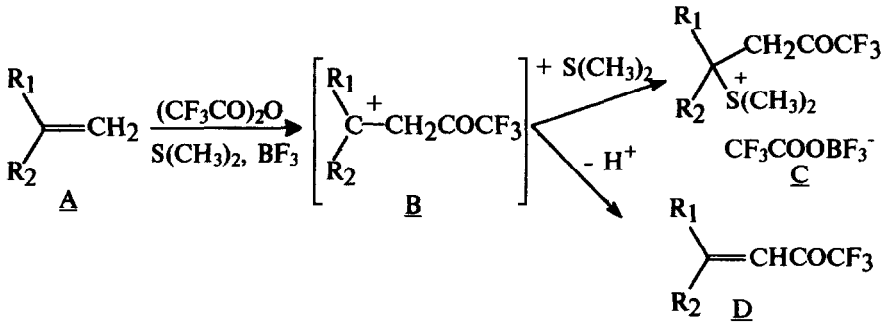
Perfluoroacylation of unsaturated hydrocarbons so far is not quite investigated. This reaction is known only for electron rich alkenes with heteroatoms at multiple bond[7-11], but such reactions with non-activated alkenes and acetylenes were not described previously. Perfluorinated acylium salts which could be used for this purpose are unstable and decompose readily with decarbonylation[12,13].

$$R_fCOCl + AgSbF_6 \longrightarrow [R_fCO^+SbF_6^-] \longrightarrow R_fF + SbF_5 + CO$$

Unsaturated ketones with perfluorinated groups have been previously obtained by reaction of trifluoroacetic acid derivatives with organometallic compounds[14,15].



Recently we have proposed a novel method of direct electrophilic perfluoroacylation of alkenes, which is based on the use of trifluoroacetic anhydride (or other anhydrides of perfluorinated acids) in the presence of dimethyl sulfide - boron trifluoride complex[16-18]. This method allows the preparation of unsaturated ketones containing perfluoroacyl groups. (Scheme 1.)



Scheme 1.

In this paper we report results of trifluoroacylation of different structure acetylenes by this new method.

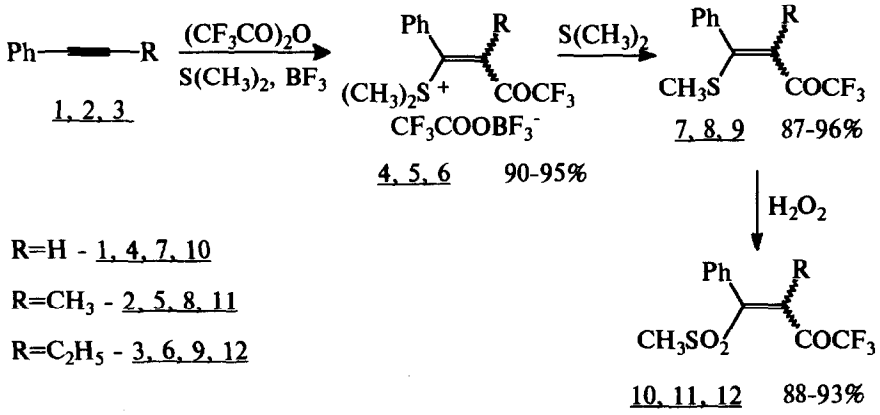
Results and discussion

We investigated trifluoroacylation of different acetylenes having both terminal and internal triple bonds by trifluoroacetic anhydride in the presence of dimethyl sulfide - boron trifluoride complex. The reaction takes place only in the case of phenyl-substituted acetylenes. Less active acetylenes such as 1-hexyne or 1-decyne do not react with this reagent.

The reaction with phenylacetylene, 1-phenyl-1-propyne, and 1-phenyl-1-butyne leads to the formation of the corresponding sulfonium salts 4, 5 and 6, which are the products of conjugate addition of the CF_3CO group and dimethyl sulfide to the acetylene molecule (Scheme 2). The reaction leads to formation of a mixture of E and Z isomers in the cases of phenylacetylene 1 and 1-phenyl-1-butyne 3, and in the case of 1-phenyl-1-propyne 2 only the Z isomer is formed. It should be noted that in all cases Z isomers predominate. Molecular model analysis shows that in the case of *cis* orientation of dimethylsulfonium and CF_3CO groups van

der Waals' interactions are minimal. Therefore, we explaine preferable formation of Z-isomers by steric factors. The configuration of the products was established by NOE experiments.

We have investigated the reaction of sulfonium salt 4 with bases to transform then into the corresponding acetylenic ketone. However, reactions with aqueous solution of Na_2CO_3 or triethylamine did not result in target product. Reaction with triethylamine gave sulfide 7 in low yield. We believe that this product is formed by nucleophilic substitution at the methyl group of the sulfonium moiety. These data indicate a possibility to transform sulfonium salts 4-6 to corresponding vinylsulfide 7-9 which have CF_3CO group in β-position. This reaction proceeds readily with the excess of dimethyl sulfide under mild conditions. Vinyl sulfides 7-9 are produced in high yields. It is possible to perform reaction without sulfonium salt isolation, in which case the yields of target sulfides are in the range of 80-88%.



Scheme 2.

Oxidation of sulfides 7-9 by hydrogen peroxide in acetic acid gives rise to the corresponding unsaturated sulfones with CF_3CO moiety in β-position 10-12. These products have two electron withdrawing groups at one double bond and therefore sulfones 10-12 are potentially valuable synthons for many purposes, for example as Michael acceptors or dienophiles. We intend to investigate their reactions in the future.

Thus, trifluoroacylation of phenyl-substituted acetylenes proceeds by the addition of electrophile CF_3CO moiety and nucleophile dimethyl sulfide resulting in corresponding vinylsulfonium salts in high yields. Demethylation of sulfonium salts with dimethyl sulfide gives rise to vinyl sulfide. It is possible to carry out a one-pot reaction for sulfide formation. Oxidation of vinyl sulfides by hydrogen peroxide yields unsaturated sulfones with a trifluoroacetyl group in β-position.

Experimental Section

NMR spectra were recorded on Varian VXR-400 spectrometer with Me_4Si as an internal standard. The NOE measurements were performed in the difference spectroscopy mode

(NOEDIF program). The IR spectra were obtained with UR-20 spectrometer as films. Chromato-mass experiments were performed on Finnigan MAT 112S spectrometer, capillary column 50000-0.25 mm, OV-101, ionization energy 80 eV.

General procedure for perfluoroacylation of acetylenes

A well-stirred solution of 0.02 mole of dimethyl sulfide in 50 ml of dichloromethane was saturated with gaseous BF_3 at -60 °C. Then 0.02 mole of trifluoroacetic anhydride was added, and the reaction mixture was stirred for 5 min. at -60 °C and then 0.02 mole of the appropriate acetylene dissolved in 10 ml of dichloromethane was added dropwise. The reaction mixture was stirred for 15 min. at - 40 °C and pentane/ether mixture (1/1) was then added. The corresponding sulfonium salt was precipitated, and the solution was decanted. A crude product (oil) was purified three times by the dissolving in dichloromethane followed by reprecipitation with pentane. The organic solvents were removed in vacuo and sulfonium salt was obtained as a viscous syrup.

(E,Z) - Dimethyl - (1 - phenyl - 3 - oxo - 4,4,4 - trifluorobut - 1 - enyl) - sulfonium - (trifluoroacetoxy)trifluoroborate 4, E/Z 2/3, (8.4 g, oil), yield 95%, IR (ν, cm^{-1}): 1770 (CO), 1680 (C=C), 1000-1300 (CF_3). ^1H NMR (400 MHz, $CDCl_3$, δ ppm): signals of E isomer 7.70-7.55 m (6H, 5H-Phenyl and CH=), 3.21 s (3H, SCH_3), 3.18 s (3H, SCH_3); signals of Z isomer 7.70-7.55 m (5H, H-Phenyl), 6.46 s (1H, CH=), 3.13 s (3H, SCH_3), 3.04 (3H, SCH_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): signals of Z isomer 180.02 q (CO, $^2J_{CF}$ 37.92 Hz), 157.20 q (COO^-, $^2J_{CF}$ 37.29 Hz), 149.05 (C-1), 130.32 (Cq-arom.), 130.17 (C-para), 130.10 and 130.00 (2C-meta or 2C-ortho), 128.84 (C-2), 116.23 q (anion CF_3, $^1J_{CF}$ 290.33 Hz), 116.07 q (CF_3, $^1J_{CF}$ 289.50 Hz), 26.71 (2C, $S(CH_3)_2$); signals of E isomer 178.05 q (CO, $^2J_{CF}$ 37.47 Hz), 157.20 q (COO^-, $^2J_{CF}$ 37.29 Hz), 148.36 (C-1), 132.60 (Cq-arom.), 132.45 (C-para), 131.52 and 130.96 (2C-meta or 2C-ortho), 128.89 (C-2), 116.23 q (anion CF_3, $^1J_{CF}$ 290.33 Hz), 116.00 q (CF_3, $^1J_{CF}$ 291.02 Hz), 25.04 (2C, $S(CH_3)_2$). NOE data: for E-isomer $\eta_{CH=}$ ($S(CH_3)_2$) - 8.4%, data: for Z-isomer $\eta_{S(CH_3)_2}$ (CH=) - 0%. Elemental analysis: found (%): C, 37.88; H, 3.19; Calc. for $C_{14}H_{12}F_9O_3BS$: C, 38.04; H, 2.74.

Z - Dimethyl - (1 - phenyl - 2 - methyl - 3 - oxo - 4,4,4 - trifluorobut - 1 - enyl) - sulfonium - (trifluoroacetoxy)trifluoroborate 5, (8.2 g, oil), yield 90%, IR (ν, cm^{-1}): 1770 (CO), 1680 (C=C), 1000-1300 (CF_3). ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 7.67-7.35 m (5H, H-Phenyl), 2.98 s (6H, $S(CH_3)_2$), 2.55 s (3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 184.87 q (CO, $^2J_{CF}$ 38.06 Hz), 157.19 q (COO^-, $^2J_{CF}$ 38.15 Hz), 150.18 (C-1), 132.84 (Cq-arom.), 132.31 and 130.02 (2C-meta or 2C-ortho and C-para), 127.11 (C-2), 115.37 q (anion CF_3, $^1J_{CF}$ 290.48 Hz), 115.47 q (CF_3, $^1J_{CF}$ 291.88 Hz), 26.04 and 26.00 (2C, $S(CH_3)_2$), 17.57 (CH_3). Elemental analysis: found (%): C, 39.10; H, 3.18; Calc. for $C_{15}H_{14}F_9O_3BS$: C, 39.50; H, 3.09.

(E,Z) - Dimethyl - (1 - phenyl - 2 - ethyl - 3 - oxo - 4,4,4 - trifluorobut - 1 - enyl) - sulfonium - (trifluoroacetoxy)trifluoroborate 6, (8.7 g, oil), E/Z 1/2, yield 94%, IR (ν, cm^{-1}): 1770 (CO), 1680 (C=C), 1000-1300 (CF_3). ^1H NMR (400 MHz, $CDCl_3$, δ ppm): signals of E isomer 7.6-7.35 m (5H, H-Phenyl), 2.70 s (6H, $S(CH_3)_2$), 2.21 q (2H, CH_2, $^3J_{HH}$ 7.42 Hz), 0.90 t (3H, CH_3, $^3J_{HH}$ 7.42 Hz); signals of Z isomer 7.6-7.35 m (5H, H-Phenyl), 3.02 q (2H, CH_2, $^3J_{HH}$ 7.55 Hz), 2.97 s (6H, $S(CH_3)_2$), 1.16 t (3H, CH_3, $^3J_{HH}$ 7.55 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): signals of Z isomer 186.02 q (CO, $^2J_{CF}$ 38.58 Hz), 159.89 q (COO^-, $^2J_{CF}$ 38.60 Hz), 155.95 (C-1), 131.33 (C-para), 132.39 and 130.05 (2C-meta or 2C-ortho), 129.65 and 129.27 (Cq-arom. or C-2), 116.36 q (CF_3, $^1J_{CF}$ 287.92 Hz), 116.30 q (anion CF_3, $^1J_{CF}$ 290.43 Hz), 27.20 (CH_2), 26.37 (2C, $S(CH_3)_2$), 11.94 (CH_3); signals of E isomer 184.32 q (CO, $^2J_{CF}$ 38.5 Hz), 159.89 q (COO^-, $^2J_{CF}$ 38.60 Hz), 159.59 (C-1), 131.96 (C-para), 131.13 and 130.15 (2C-meta or 2C-ortho), 130.6 and 130.4 (Cq-arom. or C-2), 115.10 q (CF_3, $^1J_{CF}$ 281.87 Hz), 116.30 q (anion CF_3, $^1J_{CF}$ 290.43 Hz), 26.75 (CH_2), 25.85 (2C, $S(CH_3)_2$), 13.97 (CH_3). NOE data: for Z-isomer $\eta_{CH\text{-}ortho}$ (CH_2) - 1.7%, data: for E-isomer $\eta_{CH\text{-}ortho}$ (CH_2) - 0.1%. Elemental analysis: found (%): C, 40.48; H, 3.29; Calc. for $C_{16}H_{16}F_9O_3BS$: C, 40.87; H, 3.43.

General procedure for sulfonium salt demethylation

0.02 mole of corresponding sulfonium salt obtained as above described were dissolved in 50 ml of dichloromethane. 0.05 mole of dimethyl sulfide was added to this solution or to acylation reaction mixture without sulfonium salt separation. In three days the reaction mixture was evaporated in vacuo. The residue was mixed with 20 ml of ether and passed through short silica-gel column followed by evaporation and distillation of the product in vacuo or crystallization from hexane.

(E,Z) - methyl - (1 - phenyl - 3 - oxo - 4,4,4 - trifluorobut - 1 - enyl) - sulfide 7, E/Z 1/3, yield 96%, (4.7 g), b.p. 90-93 °C (1 mm Hg), n^{20}_D 1.5610. IR (ν, cm^{-1}): 1700 (CO), 1000-1250 (CF_3). ^1H NMR (400 MHz, $CDCl_3$, δ ppm): signals of E isomer 7.37-7.16 m (5H, H-Phenyl), 6.14 s (1H, CH=), 2.38 s (3H, SCH_3); signals of Z isomer 7.37-7.16 m (5H, H-Phenyl), 6.50 s (1H,CH=), 1.94 s (3H, SCH_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): signals of E isomer 174.08 q (CO, $^2J_{CF}$ 33.59 Hz), 173.07 (C-1), 136.30 (Cq-arom.), 129.72 (C-para), 128.08 and 127.54 (2C-meta or 2C-ortho), 116.30 q (CF_3, $^1J_{CF}$ 292.98 Hz), 107.14 (C-2), 16.39 (SCH_3); signals of Z isomer 176.79 q (CO, $^2J_{CF}$ 34.01 Hz), 175.06 (C-1), 137.18 (Cq-arom.), 129.53 (C-para), 128.65 and 127.26 (2C-meta or 2C-ortho), 116.26 q (CF_3, $^1J_{CF}$ 291.46 Hz), 113.25 (C-2), 16.67 (SCH_3). NOE data: for E-isomer $\eta_{CH=}$ (CH_3) - 0.63%, data: for Z-isomer $\eta_{CH=}$ (CH_3) - 17.5%, η_{CH_3} (CH=) - 2.6%. Mass spectrum (m/z, (I,%)): 246 (59)-M^+, 231 (29), 177 (100), 149 (22), 134 (97), 102 (31), 77 (22), 75 (94), 69 (24). Elemental analysis: found (%): C, 53.85; H, 3.59; Calc. for $C_{11}H_9F_3OS$: C, 53.65; H, 3.68.

(Z) - methyl - (1 - phenyl - 2 - methyl- 3 - oxo - 4,4,4 - trifluorobut - 1 - enyl) - sulfide 8, (4.9 g), yield 94%, m.p. 77-79 °C (hexane). IR (ν, cm^{-1}): 1670 (CO), 1000-1200 (CF_3). ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 7.45-7.06 m (5H, H-Phenyl), 1.79 q (3H, CH_3, $^5J_{HF}$ 1.65 Hz), 1.72 s (3H, SCH_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 179.32 q (CO, $^2J_{CF}$ 33.49 Hz), 166.36 (C-1), 136.73 (Cq-arom.), 128.82 (C-para), 129.15 and 127.18 (2C-meta or 2C-ortho), 121.73 (C-2), 116.68 q (CF_3, $^1J_{CF}$ 291.32 Hz), 17.05 (SCH_3) 16.04 (CH_3). NOE data: η_{CH3S} (CH-ortho) - 0.5%, η_{CH3} (CH-ortho) - 0.76%. Mass spectrum (m/z, (I,%)): 260 (47)-M^+, 245 (49), 192 (100), 163 (49), 148 (46), 115 (78), 77 (36), 75 (66), 69 (18). Elemental analysis: found (%): C, 54.81; H, 4.20; Calc. for $C_{12}H_{11}F_3OS$: C, 55.38; H, 4.26.

(E,Z) - methyl - (1 - phenyl -2 - ethyl - 3 - oxo - 4,4,4 - trifluorobut - 1 - enyl) - sulfide 9, E/Z 2/3, (4.8 g), yield 87%, b.p. 105-107 °C (1 mm Hg), $n^{20}D$ 1.5340. IR (ν, cm^{-1}): 1720 (CO), 1680 (C=C), 1000-1250 (CF_3). ^1H NMR (400 MHz, $CDCl_3$, δ ppm): signals of E isomer 7.41-7.07 m (5H, H-Phenyl), 2.23 q (2H, CH_2, $^3J_{HH}$ 7.47 Hz), 1.69 s (3H, SCH_3), 0.82 t (3H, CH_3, $^3J_{HH}$ 7.47 Hz); signals of Z isomer 7.41-7.07 m (5H, H-Phenyl), 2.80 q (2H, CH_2, $^3J_{HH}$ 7.52 Hz), 1.77 s (3H, SCH_3), 1.05 t (3H, CH_3, $^3J_{HH}$ 7.52 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): signals of E isomer 181.95 q (CO, $^2J_{CF}$ 34.08 Hz), 159.96 (C-1), 135.67 (C-2), 131.64 (Cq-arom.), 127.88 (C-para), 128.78 and 128.02 (2C-meta or 2C-ortho), 116.44 q (CF_3, $^1J_{CF}$ 291.56 Hz), 23.58 (CH_2), 16.32 (SCH_3), 14.23 (CH_3); signals of Z isomer 185.16 q (CO, $^2J_{CF}$ 34.10 Hz), 153.96 (C-1), 136.28 (C-2), 133.83 (Cq-arom.), 127.70 (C-para), 129.03 and 128.62 (2C-meta or 2C-ortho), 115.50 q (CF_3, $^1J_{CF}$ 291.93 Hz), 25.38 (CH_2), 15.04 (SCH_3), 12.36 (CH_3). Mass spectrum (m/z, (I,%)): 274 (50)-M^+, 259 (44), 207 (100), 177 (22), 129 (99), 115 (25), 77 (14), 75 (22), 69 (8). Elemental analysis: found (%): C, 56.63 ; H, 4.70 ; Calc. for $C_{13}H_{13}F_3OS$: C, 56.92; H, 4.78.

General procedure for sulfide oxidation

10 ml of 30% hydrogen peroxide was added to solution of 0.01 mole of corresponding sulfide in 20 ml of acetic acid. The reaction mixture was refluxed for 2h and then was a water/ether mixture added. Organic layer was washed twice with water, once with saturated solution of $NaHCO_3$ in water and once with pure water. The organic fraction was separated and dried with calcium chloride The organic solvents were removed in vacuo, and the residue was crystallized from heptane.

(E) - methyl - (1 - phenyl - 3 - oxo - 4,4,4 - trifluorobut - 1 - enyl) - sulfone 10, (2.45 g), yield 88%, m.p. 106-107 °C (heptane). IR (ν, cm^{-1}): 1760 (CO), 1320 and 1160 (SO_2), 1000-1230 (CF_3). ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 7.48 s (1H, CH=), 7.43-7.35 m (5H, H-Phenyl), 2.72 s (3H, SCH_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 178.99 q (CO, $^2J_{CF}$ 37.90 Hz), 158.84 (C-1), 131.10 (C-para), 129.14 and 129.00 (2C-meta or 2C-ortho), 128.42 (Cq-arom.), 122.96 (C-2), 115.18 q (CF_3, $^1J_{CF}$ 291.11 Hz), 39.62 (SO_2CH_3). NOE data: $\eta_{CH=}$ (CH_3) - 1.7%. Mass spectrum (m/z, (I,%)): 278 (4)-M^+, 217 (29), 200 (46), 151 (100), 129

(13), 103 (39), 76 (16), 69 (30). Elemental analysis: found (%): C, 47.39; H, 3.30; Calc. for $C_{11}H_9F_3O_3S$: C, 47.48; H, 3.26.

(Z) - methyl - (1 - phenyl - 2 -methyl - 3 - oxo - 4,4,4 - trifluorobut - 1 - enyl) - sulfone 11, (2.7 g), yield 93%, m.p. 73-74 °C (heptane). IR (ν, cm^{-1}): 1750 (CO), 1310 and 1140 (SO_2), 1000-1230 (CF_3). ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 7.47-7.35 m (5H, H-Phenyl), 2.74 s (3H, SCH_3), 1.90 (3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 186.77 q (CO, $^2J_{CF}$ 37.78 Hz), 142.84 and 142.74 (C-1 or Cq-arom.), 130.47 (C-para), 130.01 and 129.38 (2C-meta or 2C-ortho), 129.36 (C-2), 115.38 q (CF_3, $^1J_{CF}$ 291.33 Hz), 40.73 (SO_2CH_3), 18.96 (CH_3). Mass spectrum (m/z, (I,%)): 292 (1)-M^+, 229 (5), 224 (13), 219 (5), 214 (48), 164 (83), 116 (100). Elemental analysis: found (%): C, 49.45; H, 3.68; Calc. for $C_{12}H_{11}F_3O_3S$: C, 49.31; H, 3.79.

(E,Z) - methyl - (1 - phenyl -2 - ethyl - 3 - oxo - 4,4,4 - trifluorobut - 1 - enyl) - sulfone 12, E/Z 4/3, (2.7 g), yield 88%, m.p. 50-52 °C. IR (ν, cm^{-1}): 1740 and 1760 (CO), 1310 and 1140 (SO_2), 1000-1250 (CF_3). ^1H NMR (400 MHz, $CDCl_3$, δ ppm): signals of E isomer 7.5-7.22 m (5H, H-Phenyl), 3.01 q (2H, CH_2, $^3J_{HH}$ 7.51 Hz), 2.70 s (3H, SO_2CH_3), 1.15 t (3H, CH_3, $^3J_{HH}$ 7.51 Hz); signals of Z isomer 7.5-7.22 m (5H, H-Phenyl), 2.72 s (3H, SO_2CH_3), 2.19 q (2H, CH_2, $^3J_{HH}$ 7.55 Hz), 0.94 t (3H, CH_3, $^3J_{HH}$ 7.55 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): signals of E isomer 187.16 q (CO, $^2J_{CF}$ 37.85 Hz), 148.52 (C-1), 143.23 (Cq-arom.), 130.79 (C-2), 130.48 (C-para), 130.91 and 129.89 (2C-meta or 2C-ortho), 114.28 q (CF_3, $^1J_{CF}$ 292.78 Hz), 42.21 (SO_2CH_3), 23.15 (CH_2), 12.28 (CH_3); signals of Z isomer 186.01 q (CO, $^2J_{CF}$ 37.73 Hz), 147.59 (C-1), 142.92 (Cq-arom.), 129.31 (C-2), 130.26 (C-para), 129.17 and 128.86 (2C-meta or 2C-ortho), 115.21 q (CF_3, $^1J_{CF}$ 291.39 Hz), 40.51 (SO_2CH_3), 25.78 (CH_2), 11.39 (CH_3). NOE data: for Z-isomer $\eta_{CH\text{-}ortho}$ (CH_2) - 2.9%, data: for E-isomer $\eta_{CH\text{-}ortho}$ (CH_2) - 1.6%. Mass spectrum (m/z, (I,%)): 306 (1)-M^+, 237 (79), 227 (79), 179 (15), 158 (34), 142 (29), 115 (62), 102 (11), 76 (18), 69 (11). Elemental analysis: found (%): C, 50.58; H, 4.32; Calc. for $C_{13}H_{13}F_3O_2S$: C, 50.98; H, 4.28.

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