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Perfluoroacylation of Alkenes

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Key Words: electrophilic perfluoroacylation; trifluoroacetic anhydride; boron trifluoride dimethyl sulfide complex; perfluorinated group; sulfonium salt

Abstract: *Reaction of direct electrophilic perfluoroacylation of diffferent structure alkenes with trifluoroacetic anhydride activated by* $BF_3 \cdot SMe_2$ *complex leads to trifluoromethylalkenylketones with different structure of alkenyl group. Possible composition of the reactive species is considered on the basis of IR and NMR data. Dependence of the reaction course on the substrate structure is discussed.*

Organic fluorine chemistry is one of dramatically developing fields of organic chemistry. This is due to some unique properties of fluorine containing compounds, particularly their biological activity[1,2].

There are many examples of perfluoroacylation of different S, O, N nucleophiles with active hydrogen atoms[1,2] and of organometallic compounds[3-5]. However, perfluoroacylation of carbon-carbon double bonds is known only for electron rich alkenes, *i.e.* enamines[6,7], vinyl thioethers[8,9], vinyl ethers[10] but such reactions with non-activated alkenes were not described previuosly. Perfluoracylating reagents are restricted in trifluoroacetic anhydride and other derivatives of trifluoroacetic acid. However, electrophilicity of these reagents is insufficient for acylation of alkenes. Attempts of their activation by Lewis acids (as in the case of aromatic hydrocarbons' trifluoroacylation[11-13]) lead to cationic polymerization of unsaturated substrates. Perfluorinated acylium salts which could be used for the perfluoracylation of unsaturated hydrocarbons are unstable and decompose readily with decarbonylation[14,15].

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

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

In this paper we report investigation of the nature of trifluoroacylating reagent and results of trifluoroacylation of different structure alkenes containing mono-, 1,1-di-, 1,2-di-, tri- and tetra-substituted double bonds as well as alkenes with exo- and endo-cyclic double bonds.

Study of the system $(CF_3CO)_2O—BF_3 \cdot SMe_2$

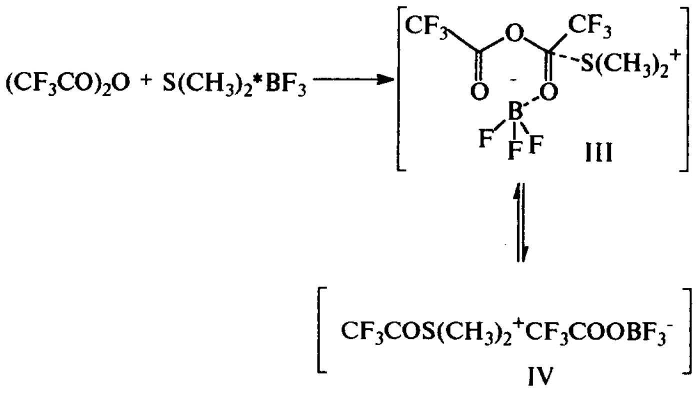
Addition of trifluoroacetic anhydride to a solution of dimethyl sulfide boron trifluoride complex in dichloromethane at −60 °C leads to formation of a suspension, which is active in trifluoroacylation of alkenes in the temperature interval −60÷0 °C. At higher temperatures trifluoroacylating activity is being lost rapidly due to irreversible chemical reactions. Specially performed reaction of trifloroacetic anhydride with $BF_3 \cdot SMe_2$ complex at −60 °C with following raise of the temperature to 25 °C and storage at this temperature for 3 h lead to formation of S-methyl trifluorothioacetate **I** (all constants and spectra are the same as literature data[19,20]) and trimethylsulfonium-(trifluoroacetoxy)trifluorborate **II** with nearly quantitative yields:

$$(CF_3CO)_2O + 2BF_3 \cdot S(CH_3)_2 \xrightarrow{25°C,\ 3h} \underset{\mathbf{I}}{CF_3COSCH_3} + BF_3 + \underset{\mathbf{II}}{S(CH_3)_3^+\ CF_3COOBF_3^-}$$

Earlier it was shown that reaction of acylium salts with dimethyl sulfide gives rise to formation of coresponding dimethylacylsulfonium salts, which are capable to acylate unsaturated hydrocarbons. Structure of these compounds was determined by IR and NMR spectroscopy.[21]

$$CH_3CO^+BF_4^- + S(CH_3)_2 \longrightarrow CH_3COS(CH_3)_2^+\ BF_4^-$$

We believe that in the case of system $(CF_3CO)_2O—BF_3 \cdot SMe_2$ formation of similar sulfonium salts could take place. Therefore it would be natural to assume, that at low temperature molecule of the complex $BF_3 \cdot SMe_2$ coordinates at C=O bonds of trifuoroacetic anhydride, as it is shown in Scheme 1.



Scheme 1.

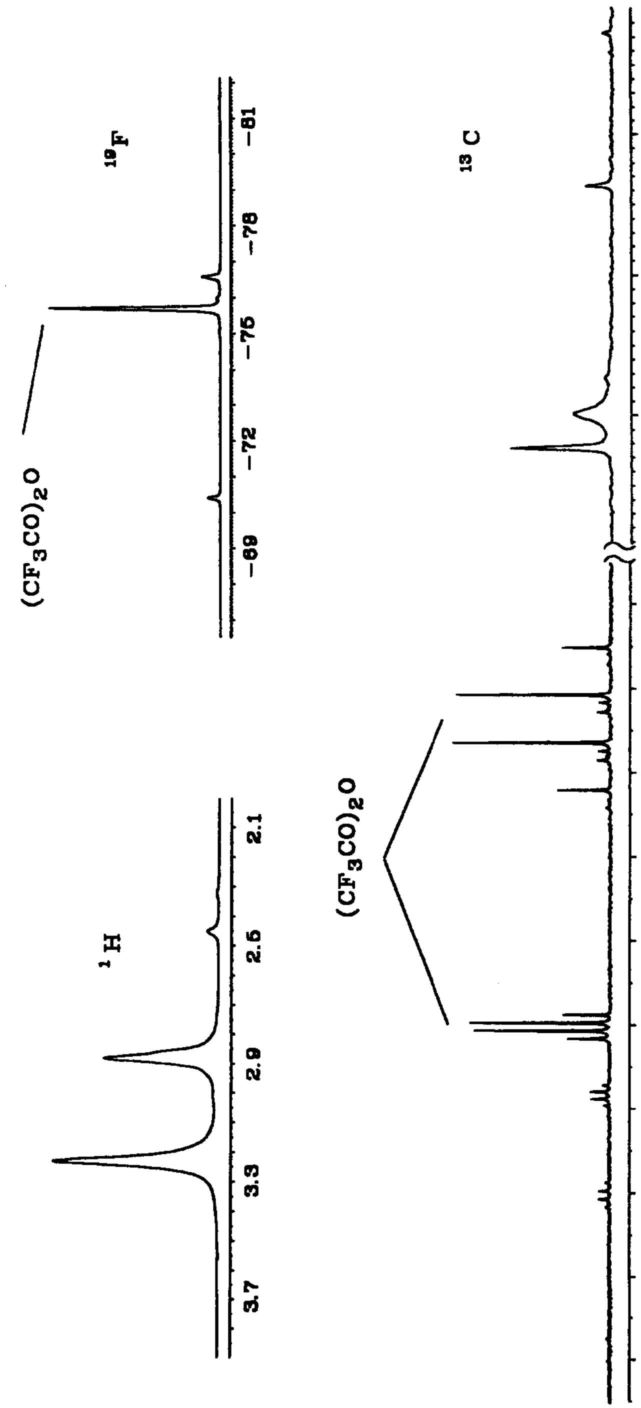


Figure 1. NMR spectra of system $(CF_3CO)_2O-BF_3-SMe_2$ at −70 °C.

It is known that sulfonium salts with two methyl groups in presence of dimethyl sulfide[22] have a propensity to transform via remethylation to trimethylsulfonium salts, therefore formation of products **I** and **II** can proceeds analogously.

In the IR spectrum of the suspension active in trifluoroacylation reaction taken at -60 °C, together with two bands characteristic for free trifluoroacetic anhydride at 1880 and 1810 cm^{-1}, two new bands at 1790 and 1720 cm^{-1} were observed. These bands differ from those of final products at 1710 (**I**) and 1770 (**II**) cm^{-1}. Shift down 50-120 cm^{-1} is characteristic for carbonyl group coordinated with Lewis acid on oxygen atom.[23]

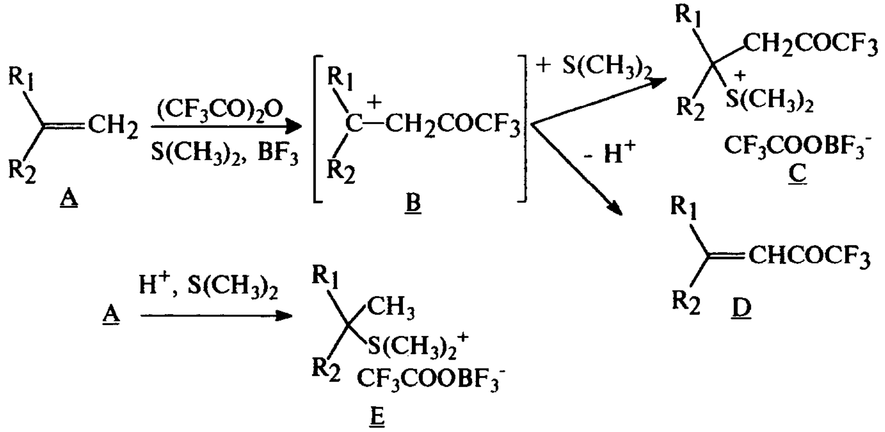
We have also recorded ^1H, ^{13}C, and ^{19}F of a mixture of $BF_3 \cdot SMe_2$ complex with the excess of trifluoroacetic anhydride in a mixture CD_2Cl_2 — CH_3NO_2 (nitromethane was added to increase homogeneity of the solution), these spectra are presented in Figure 1. In all three spectra two sets of signals are observed which do not belong to any of the starting compounds or final reaction products **I** and **II**. Signals of carbonyl carbon atoms in ^{13}C NMR spectra are significantly low-field shifted ($\Delta\delta$ = 8 and 20 ppm) compared to the same signal of trifluoroacetic anhydride[24], that corresponds to a proposal about additional polarisation of C=O bond after complexation with $BF_3 \cdot SMe_2$. Signals of methyl groups at 3.3-2.9 ppm in ^1H NMR and 26-24 ppm in ^{13}C NMR are characteristic for sulfonium methyls. Significant downfield shift indicates a considerable positive charge at sulfur atom. Further NMR investigation has shown, that coordination compounds of the type **III** or **IV** forming in the system $(CF_3CO)_2O$—$BF_3 \cdot SMe_2$ are very labile, that manifests in intense spectral dynamics in the temperature interval $-70 \div 0$ °C. Therefore NMR data do not indicate any definite structure of a reactive species of the trifluoroacylation reaction. Nevertheless, both IR and NMR studies allow to conclude, that activation of trifluoroacetic anhydride is achived by coordination of a $BF_3 \cdot SMe_2$ complex on its C=O bond.

Scope of trifluoroacylation

To study scope and limitations of trifluoroacylation we have investigated behaviour of different type alkenes in this reaction, *i.e.* alkenes containing mono-, 1,1-di-, 1,2-di-, tri- and tetra-substituted double bonds as well as alkenes with exo- and endo-cyclic double bonds. Results are summarised in Table 1.

Trifluoroacylation of styrene 1 and vinylcyclopropane 2 proceeds stereospecifically, yielding E-isomers of corresponding α,β-unsaturated ketones 15 and 16. In the case of styrene a product of conjugated addition of CF_3CO moiety and SMe_2 was detected by NMR spectrum (the yield is 11%, but the sulfonium salt was unstable and quickly decomposed in one day)[16]. Conjugated addition of an electrophile (CF_3CO moiety) and nucleophile (SMe_2) in the considered reaction is not characteristic, since the process of spontaneous proton elimination from the forming cation B is more common (Scheme 2). Proton forming by elimination from cation B react with alkene to produce sulfonium salt E, which is a product of conjugated addition of proton and dimethyl sulfide.

Trifluoroacylation of alkenes containing monosubstituted double bond takes place only in the case of cation stabilising substituents, for example phenyl or cyclopropyl moiety. Alkenes with terminal double bond such as 1-hexene and 1-octene or alkenes with cyclic double bond as cyclohexene or cyclopentene do not react with the reagent. The perfluoroacylation of these alkenes does not take place under usual conditions, raise of the temperature leads to destruction of the reagent.

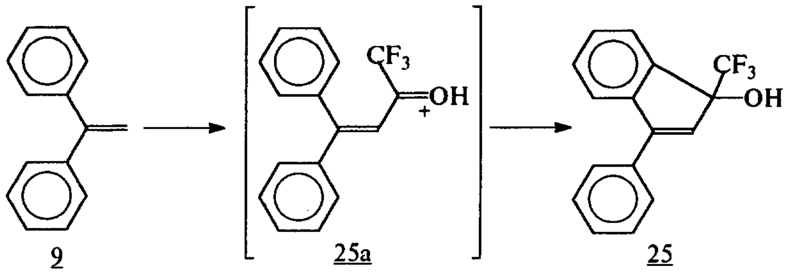


Scheme 2.

Trifluoroacylation of 1,1-disubstituted alkenes easily proceeds under low temperatures. These alkenes are very reactive due to formation of stable tertiary cations. Reaction products in this case are corresponding unsaturated ketones. Acylation of methylenecyclobutane 3 with trifluoroacetic and pentafluoropropionic anhydride in the presence of dimethyl sulfide boron trifluoride complex proceeds in a similar way resulting in corresponding α,β-unsaturated ketone with perfluorinated group 17, 18. Nevertheless, formation of β,γ-unsaturated ketones can also takes place as in the case of metylencycloheptane 4. If some orientation factors are present, for example, conjugation in α-methylstyrene 8 or propensity to have exo-cyclic double bond in methylenecyclobutane 3 the only products are corresponding α,β-unsaturated ketones.

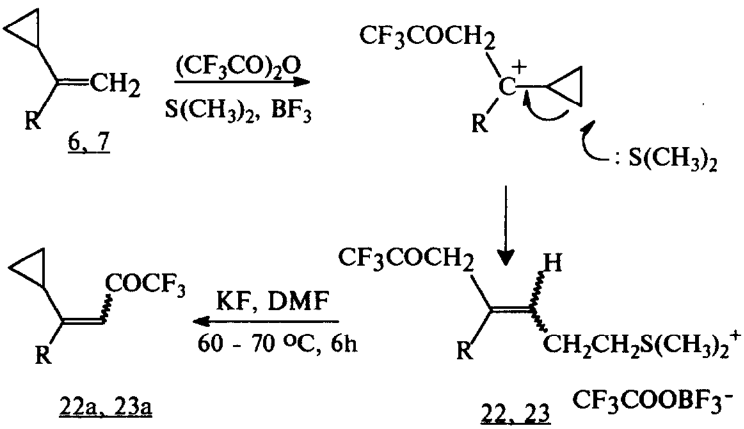
Trifluoroacylation of 1,1-diphenylethylene 9 proceeds unusually, reaction does not terminate on formation of a corresponding ketone. The latter undergoes an acid (boron trifluoride or proton) catalysed intramolecular cyclization to corresponding indenol 25. Carbonyl group in 25a is near to aromatic ring and the rate of electrophylic substitution is therefore very high. (Scheme 3.)

Trifluoroacylation of cyclopropane-containing alkenes such as isopropenylcyclopropane 6 and 1,1- dicyclopropylethylene 7 proved to proceed differently[18]. The reaction leads to formation with high yields of corresponding sulfonium salts 22 and 23, which are the products of trapping of the homoallyl cation formed by cyclopropane ring opening (Scheme 4.).



Scheme 3.

Trifluoroacylation of both alkenes 6 and 7 turned out to proceed stereoselectively. In the case of trifluoroacylation of alkenes 6 and 7 formation of corresponding α,β - unsaturated ketones does not take place due to the cation centre being removed from the CF_3CO moiety after ring cleavage. Sulfonium salts 22 and 23 are produced in quantitative yields. Skeletal rearrangements in the trifluoroacylation reaction of alkenes 6, 7 indicate the considerable electrophilicity of the reagent which is used for trifluoroacylation. The presence of electron withdrawing $COCF_3$ and leaving SMe_2 group in the molecules of the sulfonium salts 22 and 23 leads to the possibility of base-promoted intramolecular nucleophilic substitution. The elimination process was successful with potassium fluoride in DMF resulting in corresponding cyclopropane-containing ketones with trifluoroacyl group (Scheme 4).



R = CH_3 - 6, 22, 22a
R = cyclopropyl - 7, 23, 23a

E/Z isomers ratio

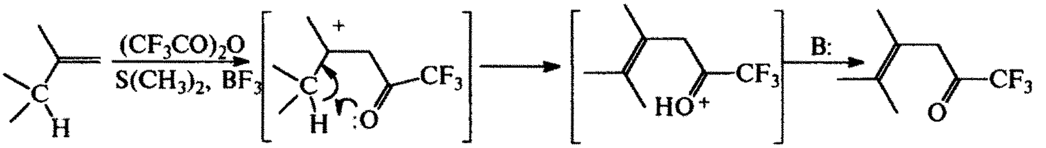
22	23	22a
10/1	1/3	2/1

Scheme 4.

Trifluoroacylation of indene 10 proceeds regiospecifically. Only product of acylation in the 2 position 26 is formed. Low yield of the target product in this case is caused by polymerisation of unsaturated hydrocarbon.

Trifluoroacylation of trimethylethylene 11, 1-methylcyclopentene 12 and 1-methylcyclohexene 13 proceeds at -20 -0 °C. In spite of the formation of stable tertiary cation, trisubstituted alkenes are less reactive in the reaction compared with 1,1-disubstituted alkenes. We assume that this phenomenon is connected with space hindrance of double bond.

It should be noted that trifluoroacylation of some alkenes leads to corresponding β,γ - unsaturated ketones rather than to thermodynamically controlled α,β - unsaturated ketones, *e.g.* in reaction with alkenes 4, 11, 13. These products form in spite of greater acidity of protons in α - position near strong electron withdrawing group CF_3CO in cation B compared to acidity of protons in γ - position (Scheme 2). It was suggested earlier that acylation of alkenes by acylim salts leading to corresponding β,γ - unsaturated ketone proceeds as ene-reaction via six-membered transition state[25,26]. We propose analogical mechanism for trifluoroacylation, *i.e.* elimination of proton proceeds via six-membered transition state (Scheme 5.).



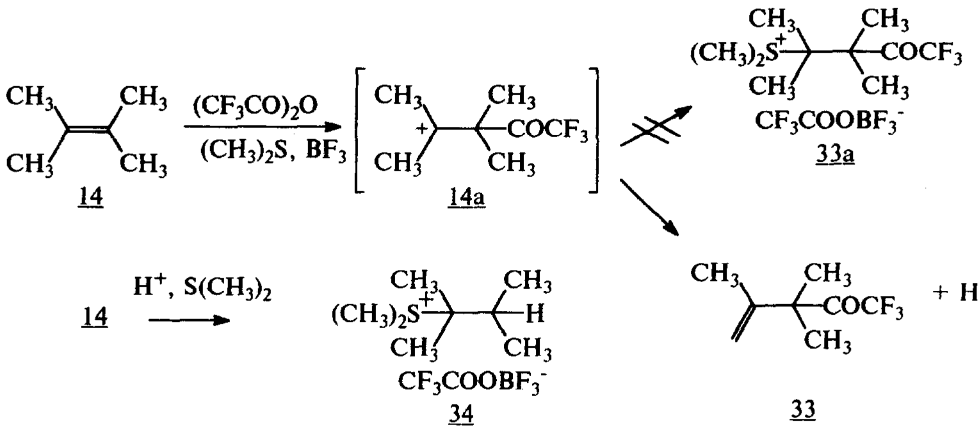
Scheme 5.

a,b-Unsaturated ketones can be obtained in pure form by izomerisation with p-toluenesulfonic acid. Thus, reaction with alkene 11 gives rise to formation of mixture of α,β- and β,γ- unsaturated ketones in a ratio 1/1.5, following reflux during 10h in dichloromethane with catalytic amount of toluenesulfonic acid gave pure α,β – unsaturated ketone.

It is interesting to note, that acylation of 1-methylcyclopentene 12 results in α,β – isomer of corresponding ketone 29 with only small admixture of β,γ - unsaturated ketone, but trifluoroacylation of 1-methylcyclohexene 30 gives mixture of corresponding α,β - and β,γ - unsaturated ketones 30, 31, 32, *i.e.* in spite of a similar structures of alkenes 12 and 13 a considerable difference in the course of the reaction takes place. We associate this phenomenon with the different geometry of intermediate cations forming in trifluoroacylation from alkenes 12 and 13. The molecular model analysis shows that in the case of 1-methylcyclohexane conformation of intermediate cation permits to realize six-membered transition state for proton elimination from γ - position either elimination from methyl group (if CF_3CO group is equatorial) resulting in ketone 32, or elimination from 3-methylene group (if CF_3CO group is axial) resulting in ketone 31. In the case of 1-methylcyclopentene due to more rigid conformation of cation the distance between carbonyl oxygen and γ - hydrogen atoms is greater and possibility of elimination via sixmembered transition state is lower.

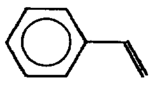
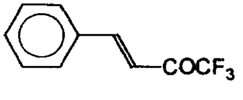
Thus, this reaction direction takes place in the case of alkenes having appropriate geometry for elimination of the proton from γ - position. However, as a rule , mixture of α,β - and β,γ - unsaturated ketones is formed because this direction competes with elimination of more acidic rom α - position to CF_3CO.

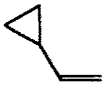
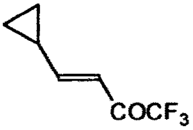
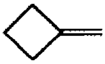
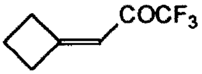
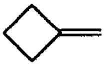
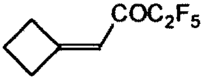
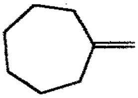
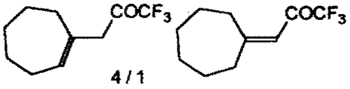
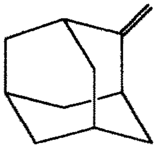
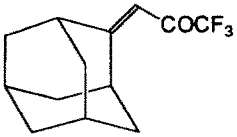
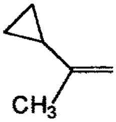
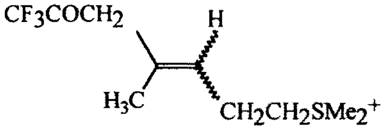
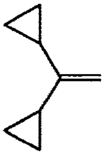
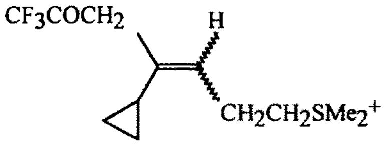
We hoped that trifluoroacylation of tetrasubstituted alkenes could proceeds as conjugated addition of CF_3CO group and dimethyl sulfide. Tetramethylethylene does not have proton in α-position to the CF_3CO group in cation 14a. Therefore, we supposed that elimination of proton would not take place and cation 14a would be stabilized by addition of nucleophile $S(CH_3)_2$. In such case product should be sulfonium salt 33a. We investigated in detail sulfonium salts forming in the reaction. However, formation of the conjugated addition product did not take place. We have found that in this case a mixture of trimethylsulfonium trifluoroacetyltrifluoroborate forming in process of reagent remethylation and product of conjugated addition of proton and dimetylsulfide 34 is formed together with corresponding β,γ – unsaturated ketone (Scheme 6.). We attribute this reaction direction to a considerable space hindrance for reaction of dimethyl sulfide with cation 14a.

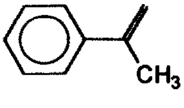
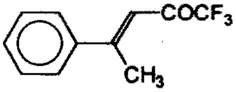
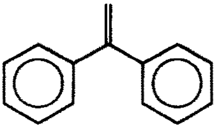
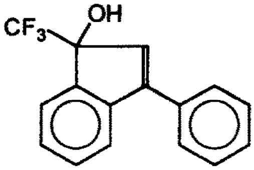
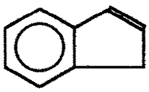
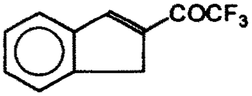
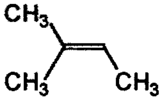
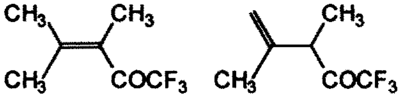
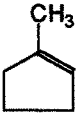
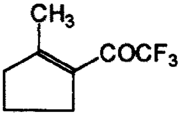
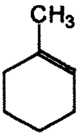
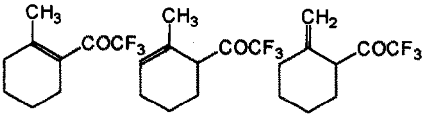
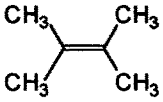
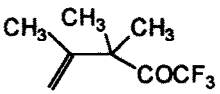


Scheme 6.

Table 1. The structure of trifluoroacylation products

Substrate	t,°C	Product	Yield, %
 1	-30 - 40	 15	45

 2	- 40	 16	32
 3	-50	 17	28
 3	-50	 18	32
 4	-40	 19, 20	27
 5	-40	 21	49
 6	-60	 E/Z - 10/1 $CF_3COOBF_3^-$ 22	95
 7	-60	 E/Z 1/3 $CF_3COOBF_3^-$ 23	91

 8	-50	 24	28
 9	-50	 25	46
 10	-50	 26	19
 11	0	 1/1.5 27, 28	28
 12	-20	 29	30
 13	-20	 3 /4 /1 30, 31, 32	31
 14	-30	 33	26

Thus, trifluoroacylation of alkenes of various structure with trifluoroacetic anhydride (or other anhydrides of perfluorinated acids) in the presence of dimethyl sulfide - boron trifluoride complex leads to corresponding unsaturated ketones containing a perfluorinated group with the yields 19-49%. Corresponding sulfonium salts forming as products of conjugated addition of proton (eliminated from the primary produced cations) and dimethyl sulfide to a double bond are by-products in this reaction. Under the reaction conditions a half of unsaturated substrate reacts with acylating reagent and a half of alkene reacts with proton, *i.e.* highest theoretically possible yield of ketone is 50%. The latter statement was confirmed by the results of trifluoroacylation of methylenadamantane 5. This alkene can not give products of polimerization or oligomerization due to space hindrance of double bond. The yield of target α,β–unsaturated ketone in this case 49% is close to the maximum possible yield.

The reaction takes place only for alkenes giving cations with stabilized groups - phenyl or cyclopropyl or forming tertiary cations. Thus, the electrophilicity of the reagent used in this investigation exceed the electrophilicity of trifluoroacetic anhydride which react only with electron rich alkenes having heteroatoms at double bond. In spite of a considerable increase of synthetic possibilities of this method compared with other perfluoroacylating reagent the reactivity of this new reagent is not sufficient to react with all alkenes. Another demerit of this reaction is moderate yield of ketones due to specific chemistry of acylation which restrict yield in 50%.

Experimental Section

NMR spectra were recorded on a Varian VXR-400 and Bruker AC 200P spectrometers with Me_4Si as an internal standard. 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 olefins

Well-stirred solution of 0.02 mole of dimethyl sulfide in 50 ml of dichloromethane was saturated by gaseous BF_3 at -60 ^oC. Then 0.02 mole of trifluoroacetic anhydride or pentafluoropropionic anhydride was added, the reaction mixture was stirred for 5 min. at -60 ^oC and then 0.02 mole of corresponding alkene dissolved in 10 ml of dichloromethane was added dropwise. The reaction mixture was stirred for 15 min. at - 40 ^oC and the temperature was raised up to 0 ^oC. The reaction mixture was stirred for 0.5 h, and then was added to the mixture of ether and aqueous Na_2CO_3. The organic layer was separated, the aqueous one was extracted with ether (2*50 ml). The organic solvents were removed in vacuo, the residue was mixed with 50 ml of ether, passed through short silica-gel column followed by evaporation and distillation in vacuo.

Products I and II was obtained by following procedure: 0.02 mole of dimethyl sulfide was saturated by gaseous BF_3 at -60 ^oC. Then 0.01 mole of trifluoroacetic anhydride was added dropwise and reaction mixture was stirred 3h at room temperature. Reaction mixture was evaporated in vacuo (30 mm Hg), S-methyl trifluorothioacetate was collected in bulb cooled to

-100 °C. Crude S-methyl trifluorothioacetate was distilled under 760 mm Hg. Sulfonium salt II obtained after evaporation of I was dryed in vacuo (1mm Hg).

S-Methyl trifluorothioacetate I, yield 87% (1.2 g), b.p. 67-68°C, n^{18}_D 1.3528. IR (ν, cm^{-1}): 1710 (CO), 1050-1300 (CF_3), ^1H NMR (200 MHz, $CDCl_3$, δ ppm): 2.42 q (3H, CH_3, $^5J_{HF}$ 0.63Hz). ^{13}C NMR (50 MHz, $CDCl_3$, δ ppm): 184.46 q (CO, $^2J_{CF}$ 39.22 Hz), 115.85 (CF_3, $^1J_{CF}$ 289.55 Hz), 11.75 (CH_3). ^{19}F NMR (187.2 MHz, CD_3COCD_3, δ_F ppm (CCl_3F)): -76.11 (CF_3). Mass spectrum (m/z, (I,%)): 144 (15)-M^+, 97 (3), 75 (100), 69 (60), 47 (33), 45 (25).

Trimethylsulfonium-(trifluoroacetoxy)trifluorborate II, yield 96% (2.6 g), oil, IR (ν, cm^{-1}): 1770 (CO), 1450 (COO^-), 1000-1300 (CF_3), ^1H NMR (200 MHz, CD_3COCD_3, δ ppm): 2.89 s (9H, $3(CH_3)_3S^+$). ^{13}C NMR (50 MHz, CD_3COCD_3, δ ppm): 157.71 q (COO^-, $^2J_{CF}$ 39.50 Hz), 115.94 q (CF_3, $^1J_{CF}$ 287.32 Hz), 2705 ($(CH_3)_3S^+$), ^{19}F NMR (187.2 MHz, CD_3COCD_3, δ_F ppm (CCl_3F)): -76.11 (CF_3), -146.98 (BF_3). Elemental analysis: found (%): C, 23.21; H, 4.02; Calc. for $C_5H_9F_6BSO_2$: C, 23.28; H, 3.52.

(E)-1,1,1-Trifluoro-4-phenyl-3-buten-2-one 15, yield 45%, the compound was earlier described[16].

(E)-1,1,1-Trifluoro-4-cyclopropyl-3-buten-2-one 16, yield 32%, the compound was earlier described[17].

1,1,1-Trifluoro-3-cyclbutilidenpropan-2-one 17, yield 26%, the compound was earlier described[16].

1,1,1,2,2-Pentafluoro-3-cyclbutilidenbutan-2-one 18, yield 32% (1.3g), b.p. 47-48°C (18 mm Hg), n^{20}_D 1.4028. IR (ν, cm^{-1}): 1720 (CO), 1640 (C=C), 1210, 1230 (C_2F_5). ^1H NMR (200 MHz, $CDCl_3$, δ ppm): 6.20 broadened s (1H, CH=), 3.40-1.90 m (6H, $3CH_2$). ^{13}C NMR (50 MHz, $CDCl_3$, δ ppm): 183.73 t (CO, $^2J_{CF}$ 25.7 Hz), 118.19 qt (CF_3, $^1J_{CF}$ 293.04 Hz, $^2J_{CF}$ 34.2 Hz), 115.00 (C-3), 107.62 tq (CF_2, $^1J_{CF}$ 267.5 Hz, $^2J_{CF}$ 37.6 Hz), 38.43 and 36.38 ($2CH_2$), 20.74 (CH_2). ^{19}F NMR (93.6 MHz, $CDCl_3$, δ_F ppm (CCl_3F)):-122.97 (CF_2), -81.02 (CF_3). Mass spectrum (m/z, (I,%)): 214 (6)-M^+, 199 (20), 145 (5), 95 (100), 67 (75). Elemental analysis: found (%): C, 45.06; H, 3.20, Calc. for $C_8H_7F_5O$: C, 44.86; H, 3.27.

Trifluoroacetonyl-cyclohept-1-ene 19 and 1,1,1-Trifluoro-3-cycloheptylidenpropan-2-one 20, mixture 4/1, yield 27% (1.11g), b.p. 60-62 °C (10 mm Hg), n^{20}_D 1.4480. IR (ν, cm^{-1}): 1710 (CO) for 19, 1770 (CO) for 20, 1600 (C=C), 1040-1300 (CF_3). ^1H NMR (400 MHz, $CDCl_3$, δ ppm): signals for 19 5.64 t (1H, CH, $^3J_{HH}$ 6.33 Hz), 3.32 s (2H, CH_2CO), 2.09 m (4H, $2CH_2$-allyl), 1.72-1.40 m (6H, $3CH_2$), signals for 20 6.28 broadened s (1H, CH=), 2.90 t (2H, CH_2, $^3J_{HH}$ 5.8 Hz), 2.46 t (2H, CH_2, $^3J_{HH}$ 5.8 Hz), 1.72-1.40 m (8H, $4CH_2$). ^{13}C NMR (100 MHz,

$CDCl_3$, δ ppm): signals for 19 189.84 q (CO, $^2J_{CF}$ 34.10 Hz), 134.23 (C-1), 133.58 (C-2), 115.67 q (CF_3, $^1J_{CF}$ 293.04 Hz), 47.50 (CH_2CO), 32.94 and 32.09 (CH_2-3 or CH_2-7), 28.46 and 26.68 (CH_2-4 or CH_2-6), 26.16 (CH_2-5) signals for 20 179.60 (Cq-4), 179.20 q (CO, $^2J_{CF}$ 33.61 Hz), 116.17 q (CF_3, $^1J_{CF}$ 292.29 Hz), 114.93 (CH-3), 40.08 (C-10), 34.05 (C-5), 29.74 (C-9), 29.21 (C-6), 27.74 (C-7), 25.94 (C-8). Elemental analysis: found (%): C, 53.59; H, 5.20; Calc. for $C_8H_9F_3O$: C, 53.94; H, 5.09.

1,1,1-Trifluoro-3-tricyclo[3.3.1.1^{1,7}]decylidenpropan-2-one **21**, yield 49% (2.4g), b.p. 102-104 °C (2 mm Hg), n^{18}_D 1.4858, IR (ν, cm^{-1}): 1720 (CO) , 1050-1250 (CF_3). ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 6.16 broadened s (1H, CH-3), 4.09 broadened s (1H, CH-allyl), 2.48 broadened s (1H, CH-allyl), 2.03-1.76 m (12H, adamantyl fragment), ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 184.70 (C-4), 180.05 q (CO, $^2J_{CF}$ 33.26 Hz), 116.13 q (CF_3, $^1J_{CF}$ 292.89 Hz), 108.59 (C-3), 42.57 (CH-allyl), 40.61 ($2CH_2$), 39.64 ($2CH_2$), 36.50 (CH_2), 34.39 (CH-allyl), 27.62 (2CH); Elemental analysis: found (%): C, 63.99; H, 6.34; Calc. for $C_{13}H_{15}F_3O$: C, 63.93; H, 6.19.

(E) - Dimethyl - (4 - methyl - 6 - oxo - 7,7,7 - trifluorohept - 3 - enyl) - sulfonium - (trifluoroacetoxy)trifluorborate **22**, yield 95%, the compound was earlier described[18].

1,1,1-Trifluoro-4-cyclopropylpent-3-en-2-one **22a**, (mixture of isomers E/Z - 3/1), yield 34%, the compound was earlier described[18].

(*E,Z*) - Dimethyl - (4 - cyclopropyl - 6 - oxo - 7,7,7 - trifluorohept - 3 - enyl) - sulfonium -(trifluoroacetoxy)trifluorborate 23, yield 91%, the compound was earlier described[18].

1,1,1-Trifluoro-4,4-dicyclopropylbut-3-en-2-one **23a**, yield 31%, the compound was earlier described[18].

E-1,1,1-Trifluoro-4-phenylpent-3-en-2-one **24**, yield 32% (1.3g), b.p. 93-95 °C (7 mm Hg), n^{20}_D 1.5215. IR (ν, cm^{-1}): 1720 (CO), 1605 (C=C), 1080-1320 (CF_3). ^1H NMR (100 MHz, $CDCl_3$, δ ppm): 7.6-7.2 m (5H, H-phenyl), 6.65 broadened s (1H, CH=), 2.62 broadened s (3H, CH_3), ^{13}C NMR (25 MHz, $CDCl_3$, δ ppm): 179.34 q (CO, $^2J_{CF}$ 34.2 Hz), 165.12 (Cq-4), 141.52 (Cq-arom.), 130.46 (CH-arom.), 128.56 (2CH-arom.), 126.47 (2CH-arom.), 116.43 q (CF_3, $^1J_{CF}$ 293.0 Hz), 114.77 (CH=), 19.05 (CH_3). ^{19}F NMR (93.6 MHz, $CDCl_3$, δ_F ppm (CCl_3F)):-76.59. Mass spectrum (m/z, (I,%)): 214 (57)-M^+, 145(100), 117(78), 115(95), 91(48). Elemental analysis: found (%): C, 53.59; H, 5.20, Elemental analysis: found (%): C, 61.30; H, 4.30; Calc. for $C_{11}H_9F_3O$: C, 61.68; H, 4.24.

3-Phenyl-1-trifluormethylindene-1-ol **25**, yield 46% (2.73g), b.p. 142-144 °C (1 mm Hg), n^{20}_D 1.4480. IR (ν, cm^{-1}): 3000-3600 (OH), 1000-1300 (CF_3). ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 7.50 - 7.05 m (9H, H -arom.), 6.11 s (1H, CH-2), 4.32 s (1H, OH). ^{13}C NMR (100

MHz, $CDCl_3$, δ ppm): 149.54, 142.33, 141.86, 133.46 (C-3 or C-8 or C-9 or Cq-arom.), 129.56 and 128.88 (CH-5 or CH-6), 128.51 and 127.39 (2CH-m. or 2CH-o.), 128.48 (CH), 127.22 and 124.05 and 121.45 (CH-2 or CH-4 or CH-7), 125.11 q (CF_3, $^1J_{CF}$ 283.99 Hz), 82.51 q (C-1, $^2J_{CF}$ 30.86 Hz). Mass spectrum (m/z, (I,%)): 276 (35)-M^+, 256 (10), 228 (10), 207 (100), 178 (25). Elemental analys is: found (%): C, 69.14; H, 4.00; Calc. for $C_{16}H_{11}F_3O$: C, 69.56; H, 4.01.

2-Trifluoroacetylindene 26, yield 19% (0.80g), b.p. 90-92 °C (1 mm Hg), n^{20}_D 1.5526. IR (ν, cm^{-1}): 1710 (CO), 1590 (C=C), 1050-1300 (CF_3). ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 7.86 qt (1H, CH=, $^5J_{HF}$ 1.86 Hz, $^4J_{HH}$ 0.76 Hz), 7.51 dm (1H, CH-4, $^4J_{HH}$ 1.05 Hz, $^3J_{HH}$ 7.31 Hz), 7.42 dm (1H, CH-7, $^4J_{HH}$ 1.28 , $^3J_{HH}$ 7.41 Hz), 7.34 ddd (1H, CH-5, $^4J_{HH}$ 1.28 Hz, $^3J_{HH}$ 7.41 Hz), 7.28 ddm (1H, CH-7, $^4J_{HH}$ 1.05 Hz, $^3J_{HH}$ 7.31 Hz), 3.61 d (2H, CH_2, $^5J_{HF}$ 1.72 Hz, $^4J_{HH}$ 0.82 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 177.33 q (CO, $^2J_{CF}$ 35.4 Hz), 147.22 q (CH=, $^4J_{CF}$ 2.96 Hz), 145.21 (C-9), 142.21 (C-8), 137.81 (C-2), 129.95, 127.54, 125.18, 124.52 (C-4, C-5, C-6, C-7), 116.70 q (CF_3, $^1J_{CF}$ 290.77 Hz), 37.80 (CH_2). Elemental analysis: found (%): C, 62.70; H, 3.50; Calc. for $C_{11}H_7F_3O$: C, 62.27; H, 3.33.

1,1,1-Trifluoro-3,4-dimethylpent-3-en-2-one 27 and **1,1,1-Trifluoro-3,4-dimethylpent-4-en-2-one 28**, mixture 1/1.5, yield 28% (0.93g), b.p. 110-113 °C, n^{20}_D 1.3703. IR (ν, cm^{-1}): 1720 (CO) for 27, 1770 (CO) for 28, 1100-1320 (CF_3). ^1H NMR (400 MHz, $CDCl_3$, δ ppm): signals of 27 1.99 q (3H, CH_3, $^5J_{HF}$ 1.50 Hz), 1.94 m (3H, CH_3), 1.91 broadened s (3H, CH_3), signals of 28 5.02 m (1H, CH=), 4.88 m (1H, CH=), 3.64 q (1H, CH-3, $^3J_{HH}$ 6.97 Hz), 1.76 dd (3H, CH_3, $^4J_{HH}$ 1.46 Hz, $^4J_{HH}$ 0.88 Hz), 1.30 d (3H, CH_3, $^3J_{HH}$ 6.97 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): signals of 27 184.84 q (CO, $^2J_{CF}$ 33.40 Hz), 151.55 (C-4), 124.53 (C-3), 116.33 q (CF_3, $^1J_{CF}$ 293.31 Hz), 23.38 (CH_3), 22.85 (CH_3), 13.77 q (CH_3, $^4J_{CF}$ 3.04 Hz). signals for 28 192.00 q (CO, $^2J_{CF}$ 33.33 Hz), 141.18 (C-4), 116.02 q (CF_3, $^1J_{CF}$ 293.18 Hz), 115.56 (C-5), 48.51 (C-3), 20.46 (CH_3), 15.03 (CH_3). Elemental analysis: found (%): C, 50.36; H, 5.41; Calc. for $C_7H_9F_3O$: C, 50.61; H, 5.46.

Izomerization of 1g izomers mixture by reflux during 10h in dichloromethane with catalytic amount of toluenesulfonic acid followed by distillation gave 0.78g (78%) pure α,β – unsaturated ketone 27 , b.p. 110-113 °C, n^{20}_D 1.3743. IR (ν, cm^{-1}): 1720 (CO), 1100-1320 (CF_3). ^1H NMR and ^{13}C NMR are as above. Elemental analysis: found (%): C, 50.44; H, 5.42; Calc. for $C_7H_9F_3O$: C, 50.61; H, 5.46

1-Trifluoroacetyl-2-methylcyclopent-1-ene 29, yield 30% (1.06g), b.p. 60-63 °C (40 mm Hg), n^{20}_D 1.4203. IR (ν, cm^{-1}): 1720 (CO), 1605 (C=C), 1080-1320 (CF_3). ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 2.75 m (2H, CH_2-5), 2.54 t (2H, CH_2-3, $^3J_{HH}$ 7.6 Hz), 2.16 broadened s (3H, CH_3), 1.88 dt (2H,CH_2-4, $^3J_{HH}$ 7.6 Hz). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 179.10 q (CO, $^2J_{CF}$ 34.68 Hz), 167.87 (C-2), 128.50 (C-1), 116.24 q (CF_3, $^1J_{CF}$ 291.68 Hz), 41.14 (CH_2-5), 32.16 q (CH_2-3, $^5J_{CF}$ 2.92 Hz), 22.06 (CH_2-4), 17.47 (CH_3). Elemental analysis: found (%): C, 53.59; H, 5.20; Calc. for $C_8H_9F_3O$: C, 53.94; H, 5.09.

1-Trifluoroacetyl-2-methylcyclohex-1-ene 30, **1-Trifluoroacetyl-2-methylcyclohex-2-ene** 31, **1-Trifluoroacetyl-2-methylencyclohexane** 32, mixture 3/ 4/ 1, yield 31% (1.2g), b.p. 60-62 °C (15 mm Hg), $n^{20}{}_D$ 1.4255. IR (ν, cm^{-1}): 1720 (CO) for 30, 1760 (CO) for 31 and 32, 1620 (C=C) for 30, 1120-1300 (CF_3). ^1H NMR (400 MHz, $CDCl_3$, δ ppm): signals of 30 2.25 broadened s (3H, CH_3), 2.0-1.45 m (8H, $4CH_2$), signals of 31 5.65 m (1H, CH=), 3.45 t (1H, CH-1, $^3J_{HH}$ 5.39 Hz), 2.14 broadened s (3H, CH_3), 2.0-1.45 m (6H, $3CH_2$), signals of 32 4.82 s (1H, CH=), 4.60 s (1H, CH=), 3.57 t (1H, CH-1, $^3J_{HH}$ 5.02 Hz), 2.0-1.45 m (8H, $4CH_2$). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): signals of 30 184.95 q (CO, $^2J_{CF}$ 33.54 Hz), 152.74 (C-1), 126.63 (C-2), 115.78 q (CF_3, $^1J_{CF}$ 293.54 Hz), 25.62 (C-3), 24.50 q (C-6, $^4J_{CF}$ 2.88 Hz), 22.04 (CH_3), 22.23 and 18.55 (C-4 and C-5) signals of 31 193.16 q (CO, $^2J_{CF}$ 33.23 Hz), 128.02 (C-2), 127.2 (C-3), 116.25 q (CF_3, $^1J_{CF}$ 293.26 Hz), 46.82 (C-1), 33.90 (C-4), 24.45 (C-6), 21.79 (CH_3), 21.66 (C-5), signals of 32 192.01 q (CO, $^2J_{CF}$ 33.31 Hz), 143.95 (C-2), 115.59 q (CF_3, $^1J_{CF}$ 293.74 Hz), 111.60 (CH_2=), 50.46 (C-1), 33.96 (C-3), 28.81 (C-6), 27.52 and 22.93 (C-4 and C-5). Mass spectrum of 30 (m/z, (I,%)): 192 (15)-M^+, 123 (100), 95 (90), 67 (62); Mass spectrum of 31 (m/z, (I,%)): 192 (10)-M^+, 123 (5), 95 (100), 67 (25); Mass spectrum of 32 (m/z, (I,%)): 192 (35)-M^+, 123 (40), 95 (100), 80 (100), 67 (80). Elemental analysis: found (%): C, 56.08; H, 5.85; Calc. for $C_9H_{11}F_3O$: C, 56.25; H, 5.77.

1,1,1-Trifluoro-3,3,4-trimethylpent-4-en-2-one 33, yield 26% (0.73g), b.p. 110-113 °C, $n^{20}{}_D$ 1.3983. IR (ν, cm^{-1}): 1770 (CO), 1100-1300 (CF_3). ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 4.96 s (1H, CH=), 4.79 s (1H, CH=), 1.67 s (3H, CH_3-4), 1.31 s (6H, $2CH_3$-3). ^{13}C NMR (100 MHz, $CDCl_3$, δ ppm): 194.30 q (CO, $^2J_{CF}$ 31.21 Hz), 144.47 (C-4), 116.22 q (CF_3, $^1J_{CF}$ 295.01 Hz), 113.15 (C-5), 51.25 (C-3), 22.93 (CH_3-4), 14.36 ($2CH_3$-3). Elemental analysis: found (%): C, 53.00; H, 6.24; Calc. for $C_8H_{11}F_3O$: C, 53.33; H, 6.15.

Dimethyl-(1,1,2-trimethylpropyl)-sulfonium-(trifluoroacetoxy)trifluorborate 34 and **trimethyl-sulfonium-(trifluoroacetoxy)trifluorborate II** mixture 1/1.45 with, yield 46% (3.3 g), IR (ν, cm^{-1}): 1770 (CO), 1000-1200 (CF_3). ^1H NMR (400 MHz, CD_2Cl_2, δ ppm): signals of II 2.89 s (9H, $3(CH_3)_3S^+$), signals of 34 2.72 s (6H, $(CH_3)_2S^+$), 2.05 hept (1H, CH-2, $^3J_{HH}$ 6.8 Hz), 1.42 s (6H, $2CH_3$-1), 1.08 d (6H, $2CH_3$-2, $^3J_{HH}$ 6.8 Hz). ^{13}C NMR (100 MHz, CD_2Cl_2, δ ppm): 157.71 q (COO^-, $^2J_{CF}$ 39.50 Hz), 115.94 q (CF_3, $^1J_{CF}$ 287.32 Hz), 63.83 (C-1), 34.58 (C-2), 2705 ($(CH_3)_3S^+$), 19.87 ($(CH_3)_2S^+$), 18.62 ($2CH_3$-2), 17.49 ($2CH_3$-1). Elemental analysis: found (%): C, 28.92; H, 4.82; Calc. for the mixture N/N 1/1.45: C, 29.71; H, 4.63.

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