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The Perfluoroacylation of Cyclopropyl-containing Alkenes

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Key Words: electrophilic perfluoroacylation; trifluoroacetic anhydride; α,β- unsaturated ketones with perfluorinated radical; homoallyl ring opening of cyclopropane cycle; sulfonium salt

Abstract: *The reaction of direct electrophilic perfluoroacylation of cyclopropylcontaining alkenes by the novel reagent is given. The stereochemistry and the dependence of the reaction course on the substrate are discussed.*

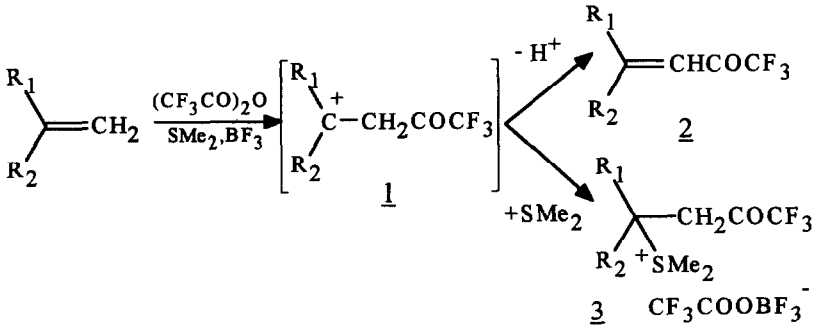
Introduction of fluorine into organic molecules often changes their properties dramatically, particularly the physiological activity of resulting compounds[1,2].

Perfluoroacylation of unsaturated hydrocarbons could be one useful method to introduce fluorine. Unfortunately, methods of direct electrophilic perfluoroacylation of alkenes are not available. The scope of perfluoroacylating reagents is generally restricted to trifluoroacetic anhydride and other derivatives of trifluoroacetic acid. These reagents interact at first with different S, O, N nucleophiles with active hydrogen atoms[1,2] and organometallic compounds[3-5], but alkenes (except β-activated alkenes - enamines[6,7], vinyl thioethers[8,9], vinyl ethers[10]) do not react with trifluoroacetic anhydride. This is due to the limited electrophilicity of the reagents used. Attempts at their activation by Lewis acids (as in the cases of aromatic hydrocarbons' trifluoroacylation[11-13]) lead to cationic polymerization of unsaturated substrates.

Recently we have proposed a novel method of direct electrophilic perfluoroacylation of alkenes, which is based on utilisation of trifluoroacetic anhydride (or other anhydrides of perfluorinated acids) in the presence of the dimethylsulfide - borontrifluoride complex[14,15]. This method permits α,β - unsaturated ketones containing perfluoroacyl groups to be obtained. The formation of the products of conjugated addition of an electrophile (CF_3CO moiety) and nucleophile (SMe_2) in the considered reaction is less characteristic, since the process of spontaneous proton elimination from the produced cation 1 is more common (Scheme 1).

Alkenes containing small cycles are known to have a propensity to skeletal rearrangements in electrophilic reaction conditions. Sometimes it gives valuable information about the electrophile used and its

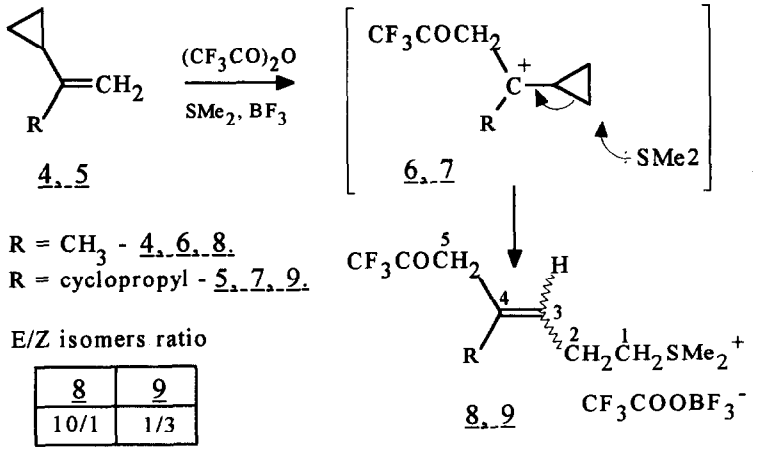
reactivity. In this paper we report the results of isopropenylcyclopropane and 1,1-dicyclopropylethylene trifluoroacylation by the method developed in our laboratory.



Scheme 1.

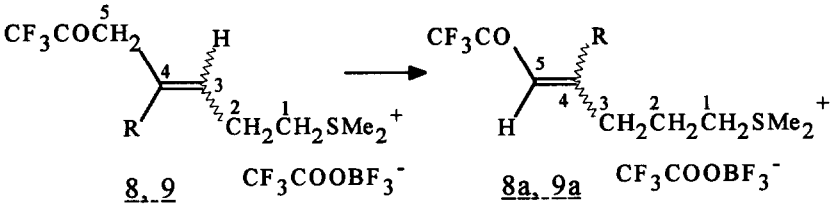
Results and discussion

The trifluoroacylation of isopropenylcyclopropane and 1,1- dicyclopropylethylene appeared to proceed differently from the cases presented in Scheme 1. The reaction leads to the formation of corresponding sulfonium salts 8 and 9, which are the products of trapping of the homoallyl cation formed in the process of cyclopropane ring opening with high yields (Scheme 2).



Scheme 2.

Since compounds 8 and 9 are β,γ - unsaturated ketones, they are prone to spontaneous transformation to corresponding α,β - unsaturated ketones 8a and 9a. The rearrangement of the compounds 8 and 9 proceeds during *ca.* two months at room temperature with no catalyst with quantitative yield. The transformation of the sulfonium salt 9 into 9a proceeds stereoselectively and only the E isomer is formed (Scheme 3).



8, 9 8a, 9a

R=CH3 - 8, 8a R=Cyclopropyl - 9, 9a

Scheme 3.

We have studied the stereochemistry of the products thus formed. Trifluoroacylation of both alkenes 4 and 5 turned out to proceed stereoselectively, with one isomer forming in the case of 4. Due to the considerable NOE values, which were observed between H-3 proton and CH_2-5 group protons in E isomers, the configuration of the substituents at the double bond in sulfonium salts 8 and 9 was unambiguously determined by NOE measurements (Table 1).

Table 1. The NOE Data (η, %) for Compounds 8 and 9.

Observed protons	Compound 8.		Compound 9 (minor isomer).		Compound 9 (major isomer).	
	Saturated protons.					
	CH-3	CH_2-5	CH-3	CH_2-5	CH-3	CH_2-5
CH_2-1	1.1	b	1.3	b	0.4	b
CH_2-2	1.2	b	1.6	1.4	2.4	b
CH-3	-	11.3	-	b	-	8.0
Me [a]	b	1.7				
CH-cycl. [a]			4.8	3.2	b	b
CH_2-5	3.4	-	b	-	3.5	-

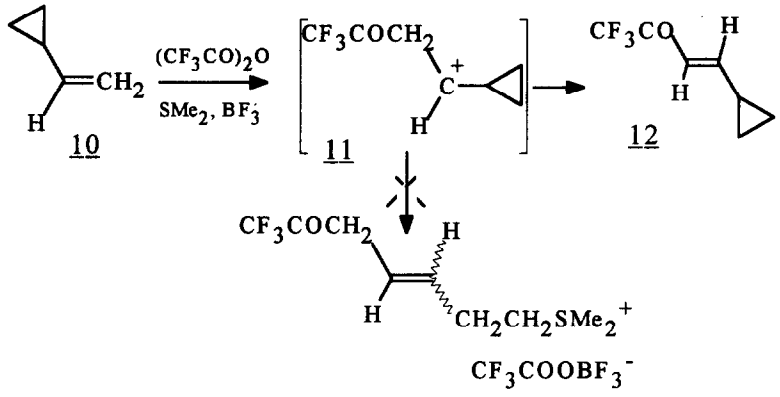
a - Me for compound 8 and CH-cycl. for compound 9.

b - these values are less than sensitivity threshold.

We believe that the observed stereochemistry of the cyclopropane cleavage is due to the preferable conformation of the cyclopropylcarbinyl cation 6, which has cyclopropyl ring directed towards to less bulky methyl group for van der Waals' interactions to be minimal. A considerable activation energy for rotation about cyclopropyl-carbocation bond which is *ca.* 14 Kcal/mol[16] makes the conformation much more rigid. Ring cleavage results in *E*-isomer in the case of sulfonium salt 8. In the case of cation 7 transformation less stereoselectivity takes place, giving rise to only 3/1 ratio of sulfonium salt 9 isomers.

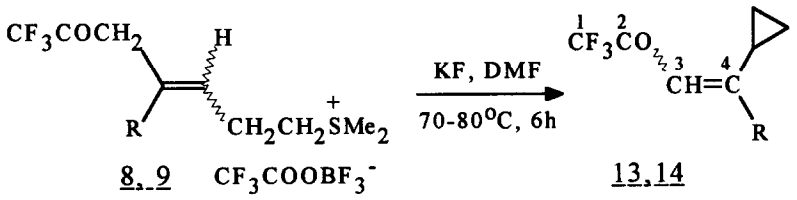
The products and the path of trifluoroacylation reaction in the case described here and in the case of alkenes not undergoing rearrangement differ considerably. In later examples the main products are α,β-unsaturated ketones, and their formation is associated with proton elimination from cation 1. This process proceeds readily owing to high acidity of protons in α–position near the strong electron withdrawing group CF_3CO.

In the case of trifluoroacylation of alkenes 4 and 5 this direction does not take place due to the cation centre being removed from the CF_3CO moiety after ring cleavage . The products of homoallyl ring opening of the cyclopropylcarbinyl cation are thermodynamically more stable and they are produced when the formation of products composition is controlled thermodynamically. Alternatively, in analogous conditions vinylcyclopropane 10 (structurally close to alkenes 4, 5) gives α,β-unsaturated ketone 12 rather than ring opening product[15] (Scheme 4).



Scheme 4.

We associate this phenomenon with the increase in cation stability when replacing vinylcyclopropane with alkenes 4 and 5. This results in a longer life time of the cation and correspondingly more profound transformation of cations. In the case of vinylcyclopropane proton elimination proceeds faster than its transformation into the corresponding homoallyl cation. i.e., the fastest process out of several reaction paths takes place (kinetic control). Skeletal rearrangements in the trifluoroacylation reaction of alkenes 4, 5 indicate the considerable electrophilicity of the reagent which is used for trifluoroacylation.



8, 9 $CF_3COOBF_3^-$ 13, 14

R = CH_3 - 8, 13 (isomers ratio Z/E-1/2)
R = cyclopropyl - 9, 14

Scheme 5.

The presence of electron withdrawing $COCF_3$ and leaving SMe_2 group in the molecules of the sulfonium salts 8 and 9 leads to the possibility of intramolecular nucleophilic substitution promoted by base. We have studied a number of eliminating agents. However, the reaction with traditional bases e.g. NEt_3 in CH_2Cl_2 and sodium ethoxide in ethanol gave no desirable products in appropriate yields. Fluoride anions (e.g., KF) are used as a base in many modern techniques[17]. This approach often leads to an increase in the target product yield and to minimization of the competitive processes. The elimination process was successful with potassium fluoride in DMF (Scheme 5).

^1H NMR data for the compounds 13 and 14 seem to be very interesting . It should be noted that in the cases of *cis* orientation of cyclopropane and trifluoroacetyl group signals of cyclopropane methine hydrogen in minor isomer of 13 and 14 has 3.37 and 3.50 ppm shifts.In the cases of *trans* orientation of these groups the corresponding signals are observed at 1.75 and 1.05 ppm (major isomer of 13 and the other cyclopropyl methin hydrogen for 14). Molecular model analysis for *cis* orientation of considered groups gives the distance between methine cyclopropane hydrogen and oxygen of the carbonyl group (in the preferable conformer of rotation about C_3-Cyclopr. bond) of *ca.* 0.15-0.17 nm. This gives rise to the strong space interaction[18] of the proton with the strong electron withdrawing group CF_3CO. This results in deshielding of interacting proton and the downfield shift to a value of 3.37-3.5 ppm.

Thus, trifluoroacylation of isopropenylcyclopropane and 1,1-dicyclopropylethylene according to the procedure described leads to the corresponding sulfonium salts, products of homoallyl cation stabilization formed by cleavage of cyclopropane ring. The succeeding action of potassium fluoride as a base on sulfonium salts furnished intramolecular nucleophilic substitution of the dimethylsulfide group which resulted in α,β-unsaturated ketones containing a perfluorinated group.

Experimental Section

NMR spectra were recorded on a Varian VXR-400 and Bruker AC 200P spectrometers with Me_4Si as an internal standard. The NOE measurements for compounds 8 and 9 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 olefins.

Well-stirred solution of 0.02 mole of dimethylsulfide in 50 ml of dichloromethane was saturated by gaseous BF_3 at -60 °C. Then 0.02 mole of trifluoroacetic anhydride was added, the reaction mixture was stirred for 5 min. at -60°C 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°C and then was added to the solution of ether in pentane 1/1. Corresponding sulfonium salt was precipitated, the solution was decanted. A crude product (oil) was purified tree times by the dissolving in dichloromethane followed by reprecipitation with pentane. The organic solvents were removed in vacuo resulted in sulfonium salt as a viscosous syrup. The storage of the forming products during *ca.* two months at room temperature with no catalyst leads to the corresponding α,β - unsaturated isomers 8a and 9a. with quantitative yield.

(E) - Dimethyl - (4 - methyl - 6 - oxo - 7,7,7 - trifluorohept - 3 - enyl) - sulfonium - (trifluoroacetoxy)trifluorborate 8, (8.0 g, oil), yield 95%, IR (ν, cm^{-1}): 1765 (CO), 1000-1220 (CF_3). ^1H NMR (400 MHz, CD_2Cl_2, δ ppm): 5.40 m (1H, H-3, $^3J_{HH}$ 7.26 Hz, $^4J_{HH}$ 1.35 Hz), 3.51 broadened s (2H, CH_2-5), 3.38 t (2H, CH_2-1, $^3J_{HH}$ 7.25 Hz), 2.92 s (6H, $S(CH_3)_2$), 2.63 dt (2H, CH_2-2, $^3J_{HH}$ 7.26 Hz, $^3J_{HH}$ 7.25 Hz), 1.73 d (3H, CH_3, $^4J_{HH}$ 1.35 Hz).^{13}C NMR (100 MHz, CD_2Cl_2, δ ppm): 190.10 q (CO, $^2J_{CF}$ 34.76 Hz), 158.3 q (COO^-, $^2J_{CF}$ 39.59 Hz), 131.55 (C-4), 125.63 (C-3), 116.3 q (anion CF_3 $^1J_{CF}$ 292 Hz), 115.93 q (CF_3, $^1J_{CF}$ 292.44 Hz), 46.51 and 43.55 (C-5) or (C-1), 25.00 (2C, $S(CH_3)_2$), 23.28 (C-2), 16.41 (CH_3). Elemental analysis: found (%): C, 33.92; H, 3.89; Calc. for $C_{12}H_{16}F_9SO_3B$: C, 34.15; H, 3.82.

(E,Z) - Dimethyl - (4 - methyl - 6 - oxo - 7,7,7 - trifluorohept - 4 - enyl) - sulfonium - (trifluoroacetoxy)trifluorborate 8a, mixture of isomers ratio E/Z = 4/3, yield 100%, IR (ν, cm^{-1}): 1720 (CO), 1620 (C=C), 1000-1220 (CF_3). Signals of E-isomer: ^1H NMR (200 MHz, CD_2Cl_2, δ ppm): 6.29 broadened s (1H, H-5), 2.98-3.15 m (4H, CH_2-1 and CH_2-3), 2.65 s (6H, $S(CH_3)_2$), 2.25-2.40 m (2H, CH_2-2, $^3J_{HH}$ 7.50 Hz, $^3J_{HH}$ 7.84 Hz), 1.94 d (3H, CH_3, $^4J_{HH}$ 1.06 Hz). ^{13}C NMR (50 MHz, CD_2Cl_2, δ ppm): 180.34 q (CO, $^2J_{CF}$ 34.3 Hz), 170.38 (C-4), 159.2 q (COO^-, $^2J_{CF}$ 39.58 Hz), 122.0 q (CF_3 $^1J_{CF}$ 291 Hz), 115.61 (C-5), 42.00 and 39.33 (C-3) or (C-1), 24.16 (2C, $S(CH_3)_2$), 21.47 (C-2), 19.90 (CH_3). Signals of Z-isomer: ^1H NMR (200 MHz, CD_2Cl_2, δ ppm): 6.35 broadened s (1H, H-5), 2.98-3.15 m (2H, CH_2-1), 2.65 s (6H, $S(CH_3)_2$), 2.10 m (2H, CH_2-3), 2.10 d (3H, CH_3, $^4J_{HH}$ 1.36 Hz), 1.90-1.73 m (CH_2-2).^{13}C NMR (50 MHz, CD_2Cl_2, δ ppm): 180.10 q (CO, $^2J_{CF}$ 34.3 Hz), 171.53 (C-4), 159.2 q (COO^-, $^2J_{CF}$ 39.58 Hz), 122.0 q (CF_3 $^1J_{CF}$ 291 Hz), 116.39 (C-5), 42.84 (C-1), 33.00 (C-3), 25.56 (CH_3), 24.56 (2C, $S(CH_3)_2$), 21.83 (C-2). Elemental analysis: found (%): C, 33.85; H, 3.91; Calc. for $C_{12}H_{16}F_9SO_3B$: C, 34.15; H, 3.82.

***(E,Z)* - Dimethyl - 4 - cyclopropyl - 6 - oxo - 7,7,7 - trifluorohept - 3 - en) - sulfonium - (trifluoroacetoxy)trifluorborate 9**, mixture of isomers ratio E/Z = 1/3 (8.2 g, oil), yield 91%, IR (ν, cm^{-1}): 1770 (CO),

1000-1260 (CF_3). Signals of E-isomer: ^1H NMR (400 MHz, CD_2Cl_2, δ ppm): 5.48 m (1H, H-3, $^3J_{HH}$ 7.16 Hz, $^4J_{HH}$ 1.14 Hz), 3.58 broadened s (2H, CH_2-5), 2.90 s (6H, $S(CH_3)_2$), 2.52 dt (2H, CH_2-2, $^3J_{HH}$ 7.36 Hz, $^3J_{HH}$ 7.16 Hz), 1.34 m (1H, CH-cycloprop.), 0.64 m, 0.40 m (4H, $2CH_2$-cycloprop.); ^{13}C NMR (100 MHz, CD_2Cl_2, δ ppm): 189.84 q (CO, $^2J_{CF}$ 35.03 Hz), 157.54 q (COO^- , $^2J_{CF}$ 40.2 Hz), 136.10 (C-4), 123.19 (C-3), 116.06 (CF_3, $^1J_{CF}$ 292.39 Hz), 115.9 (anion CF_3, $^1J_{CF}$ 290 Hz), 43.70 and 38.72 (C-5 or C-1), 25.27 (2C, $S(CH_3)_2$), 23.62 (C-2), 17.95 (CH-cycloprop.), 5.48 (2C, CH_2-cycloprop.); Signals of Z-isomer: ^1H NMR (400 MHz, CD_2Cl_2, δ ppm): 5.43 m (1H, H-3, $^3J_{HH}$ 7.26 Hz, $^4J_{HH}$ 1.15 Hz), 3.42 t (2H, CH_2-1, $^3J_{HH}$ 7.20 Hz), 3.30 broadened s (2H, CH_2-5), 2.94 s (6H, $S(CH_3)_2$), 2.83 dt (2H, CH_2-2, $^3J_{HH}$ 7.26Hz, $^3J_{HH}$ 7.20Hz), 1.59 m (1H, CH-cycloprop.), 0.78 m and 0.38 m (4H, $2CH_2$-cycloprop.). ^{13}C NMR (100 MHz, CD_2Cl_2, δ ppm): 190.07 q (CO, $^2J_{CF}$ 34.79 Hz), 157.54 q (COO^- , $^2J_{CF}$ 40.2 Hz), 135.62 (C-4), 127.47 (C-3), 116.06 q (CF_3, $^1J_{CF}$ 292.39 Hz), 115.9 (anion CF_3, $^1J_{CF}$ 290 Hz), 43.55 and 42.14 (C-5) or (C-1), 25.20 (2C, $S(CH_3)_2$), 23.28 (C-2), 12.03 (CH-cycloprop.), 5.48 ($2CH_2$-cycloprop.). Elemental analysis: found (%): C, 37.27; H, 4.57; Calc. for $C_{14}H_{18}F_9SO_3B$: C, 37.44; H, 4.49

(*E*) - Dimethyl - 4 - cyclopropyl - 6 - oxo - 7,7,7 - trifluorohept - 4 - en) - sulfonium - (trifluoroacetoxy)trifluorborate 9a, yield 100%, IR (ν, cm^{-1}): 1715 (CO), 1620 (C=C), 1000-1260 (CF_3). ^1H NMR (400 MHz, CD_2Cl_2, δ ppm): 6.31 broadened s (1H, H-5), 3.45 t (2H, CH_2-1, $^3J_{HH}$ 7.20 Hz), 2.62-2.58 m (2H, CH_2-3), 2.96 s (6H, $S(CH_3)_2$), 1.96 tt (2H, CH_2-2, $^3J_{HH}$ 7.20 Hz), 1.70 m (1H, CH-cycloprop.), 1.15 m, 0.90 m (4H, $2CH_2$-cycloprop.). NOE data: $\eta_{CH\text{-}CYCL.}$ (H-5) - 8.0%. Elemental analysis: found (%): C, 37.20; H, 4.55; Calc. for $C_{14}H_{18}F_9SO_3B$: C, 37.44; H, 4.49

General procedure for elimination

The freshly calcinated on air potassium fluoride in amount of 0.1 mole was added to solution of 0.02 mole sulfonium salt in 50 ml of dry dimethylformamide. The reaction mixture was stirred for 6 hours at 70-80 °C and then cooled to the room temperature . To the reaction mixture 100 ml of pentane was added and then resulting was washed by saturated solution of potassium chloride. Organic fraction was separated dried with calcium chloride and than distiled with Vigreux column.

(E)-1,1,1-Trifluor-4-cyclopropylbut-3-en-2-one 12, yield 32%, the compound was earlier described[15].

1,1,1-Trifluor-4-cyclopropylpent-3-en-2-one (mixture of isomers E/Z - 3/1) **13**, yield 34% (1.2g), b.p. 66-67 °C (25 mm Hg), n^{19}_D 1.4518. IR (ν, cm^{-1}): 1710 (CO), 1600(C=C), 1050-1250 (CF_3). signals of E-isomer: ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 6.38 broadened s (1H, CH-3), 2.05 d (3H, CH_3, J_{HH} 0.92 Hz), 1.70-1.80 m (1H, CH-cycloprop.), 0.87-1.10 m (4H, $2CH_2$-cycloprop.), ^{13}C NMR (50 MHz, $CDCl_3$, δ ppm): 178.23 q (CO, $^2J_{CF}$ 33.2 Hz), 174.91 (C-4), 116.31 q (CF_3, $^1J_{CF}$ 290.2 Hz), 112.72 (C-3), 21.56 (CH_3), 19.18 (CH-cycloprop.), 8.96 ($2CH_2$-cycloprp.); signals of Z-isomer: ^1H NMR (400 MHz, $CDCl_3$, δ ppm): 6.34 broadened s (1H, CH-3), 3.37 m (1H, CH-cycloprop.), 1.72 d (3H, CH_3, $^4J_{HH}$ 1.17 Hz), 0.87-1.10 m (4H, $2CH_2$-cycloprop.). ^{13}C NMR (50 MHz, $CDCl_3$, δ ppm): 178.92 q (CO, $^2J_{CF}$ 33.2 Hz), 174.35 (C-4), 116.31 q (CF_3, $^1J_{CF}$ 290.2 Hz), 115.47 (C-3), 16.21 (CH_3), 15.84 (CH-cycloprop.), 9.20 ($2CH_2$-cycloprp.). NOE data: for Z-isomer $\eta_{H\text{-}3.}$ (CH_3) - 6.6%, for E-isomer $\eta_{H\text{-}3.}$(CH-cycl.) - 6.23%, η_{CH3} (CH-cycl.) - 3.74%.

^{19}F NMR (187.2 MHz, $CDCl_3$, δ ppm, (CCl_3F)): -76.94 (both isomer, CF_3). Mass spectrum (m/z, (I,%)): 164 (11)-M^+, 149(15), 95(100), 67(82). Elemental analysis: found (%): C, 53.59; H, 5.20; Calc. for $C_8H_9F_3O$: C, 53.91; H, 5.09.

1,1,1-Trifluor-4,4-dicyclopropylbut-3-en-2-one 14, yield 31% (1.26g), b.p. 106-108 °C (30 mm Hg), n^{18}_D 1.4806. IR (ν, cm^{-1}): 1710 (CO), 1590 (C=C), 1050-1300 (CF_3). ^1H NMR (200 MHz, $CDCl_3$, δ ppm): 5.88 broadened s (1H, CH=), 3.50 m (1H, CH-cycloprop.), 1.20-0.75 m (9H, cycloprop.). ^{13}C NMR (50 MHz, $CDCl_3$, δ ppm): 181.25 (C-4), 179.5 q (CO, $^2J_{CF}$ 33.4 Hz), 116.52 q (CF_3, $^1J_{CF}$ 292.33 Hz), 108.36 (C-3), 16.71 (CH-cycloprop.), 12.39 (CH-cycloprop.), 10.60 ($2CH_2$-cycloprp.), 10.02 ($2CH_2$-cycloprp.). ^{19}F NMR (187.2 MHz, $CDCl_3$, δ ppm, (CCl_3F)): -78.26 (CF_3). Mass spectrum (m/z, (I,%)): 204 (1)-M^+, 176 (40), 107 (100), 91 (51), 79 (98), 77(61). Elemental analysis: found (%): C, 58.90; H, 5.50; Calc. for $C_{10}H_{11}F_3O$: C, 58.80; H, 5.43.

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