

Dedicated to the memory of the Master, Corresponding Member of the Russian Academy of Sciences  
A.A. Petrov, on the 100th anniversary of his birth

## Addition of Perfluoroalkanoic Acids to (*R*)-(+)-Limonene

Yu. G. Trishin, M. V. Shafeeva, and L. A. Tamm

St. Petersburg State Technological University of Plant Polymers,  
ul. Ivana Chernykh 4, St. Petersburg, 198095 Russia  
e-mail: trish@YT4470.spb.edu

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**Abstract**—Perfluoroalkanoic acids with different lengths of the perfluoroalkyl radical selectively add under mild conditions to the exocyclic double C=C of limonene to give the corresponding Markovnikov adducts,  $\alpha$ -terpinyl perfluoroalkanoates. The reaction in the presence of sulfuric acid 0°C involves both double C=C bonds in the limonene molecule with formation of *p*-menthane-1,8-diyl bis(perfluoroalkanoates).

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Addition of perfluoroalkanoic acids to alkenes underlies an important method for the synthesis of esters  $R_F C(O)OR$  whose properties essentially differ from the properties of nonfluorinated analogs. Such esters where R is a terpene radical attract specific attention as promising biologically active substances. For instance, menthyl trifluoroacetate was shown [1] to be more efficient house fly fumigant than menthyl acetate and trichloroacetate.

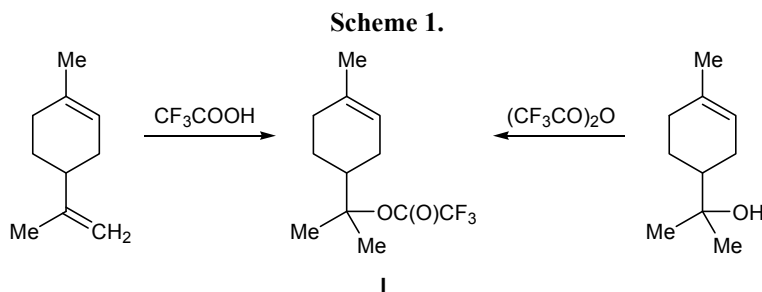
In this work we examined the reactions of (*R*)-(+)-limonene with perfluoroalkanoic acids containing perfluoroalkyl radicals of different lengths (trifluoroacetic, pentafluoropropionic, heptafluorobutanoic, and perfluorononanoic) under the conditions favoring addition to one or both double C=C bonds.

Only the addition of trifluoroacetic acid to the exocyclic double C=C bond of limonene with formation of  $\alpha$ -terpinyl trifluoroacetate (**I**) was reported previously [2–4]. This reaction was studied for the first time by Roberts [2] as an example while solving general problems of the kinetics and mechanism of addition of acids to olefins. The addition products were not isolated but were characterized by  $^1H$  NMR and mass spectra. De Mattos et al. [3] later reported that trifluoroacetic acid reacts with (*R*)-(+)- and (*S*)-(+)-limonene in cyclohexane at room temperature to form the corresponding Markovnikov adducts at the exocyclic double bond, (*R*)-(+)- and (*S*)-(+)- $\alpha$ -terpinyl trifluoroacetates with unchanged configuration of the chiral carbon atom. The products were not purified and were identified by  $^1H$  and  $^{13}C$  NMR, IR spectroscopy, and

mass spectrometry. The conditions for the addition of trifluoroacetic acid to the exocyclic C=C bond of (*R*)-(+)-limonene were optimized in [4]. (*R*)-(+)- $\alpha$ -Terpinyl trifluoroacetate (**I**) thus formed was subjected to hydrolysis (without isolation), and (*R*)-(+)- $\alpha$ -terpineol was obtained in high yield.

We studied in detail the reaction of trifluoroacetic acid with (*R*)-(+)-limonene and found conditions ensuring addition to both exocyclic and endocyclic C=C bonds in the terpene substrate. Trifluoroacetic acid reacted with (*R*)-(+)-limonene under the conditions described in [4] [trifluoroacetic acid–(*R*)-(+)-limonene ratio 1.2:1, toluene, 20–30°C] with high selectivity and afforded almost exclusively  $\alpha$ -terpinyl trifluoroacetate (**I**), the Markovnikov adduct to the exocyclic C=C bond. The  $^{19}F$  NMR spectrum of the reaction mixture recorded after neutralization of excess trifluoroacetic acid contained only one signal at  $\delta_F$  –76.50 ppm, which is typical of ester **I**. In the  $^1H$  NMR spectrum, the intensity of the signal at  $\delta$  4.69 ppm [ $C^{10}H_2=$  in (*R*)-(+)-limonene] was very low, but a signal at  $\delta$  1.54 ppm appeared due to methyl protons on  $C^{10}$  in **I**. The signal from  $C^9H_3$  was displaced upfield ( $\delta$  1.53 against 1.72 ppm) owing to altered shielding. On the other hand, the signal from the olefinic proton on  $C^2$  did not change its position ( $\delta$  5.39 ppm) and intensity (1H).

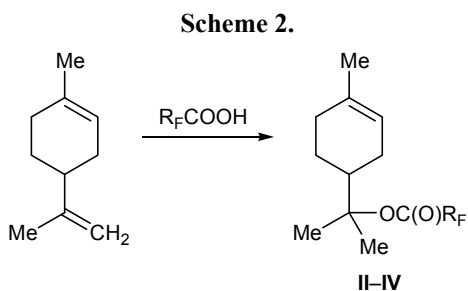
(*R*)-(+)- $\alpha$ -Terpinyl trifluoroacetate (**I**) was isolated for the first time as individual substance by vacuum distillation (yield 57%). In contrast to the assumed [3] thermal instability of compound **I**, it can be distilled



under reduced pressure without appreciable decomposition, leaving a small still residue. (*R*)-(+)- $\alpha$ -Terpinyl trifluoroacetate (**I**) is a colorless mobile liquid with a weak characteristic odor. Its structure was confirmed by the  $^1\text{H}$ ,  $^{19}\text{F}$ , and  $^{13}\text{C}$  NMR and IR spectra and elemental analysis. Its  $^{19}\text{F}$  NMR spectrum contains a signal at  $\delta_{\text{F}} -76.50$  ppm, which is typical of  $\text{CF}_3$  group in trifluoroacetic acid esters. The  $^1\text{H}$  and  $^{13}\text{C}$  NMR and IR spectral parameters of ester **I** coincided with those given in [3, 4].

$\alpha$ -Terpinyl trifluoroacetate (**I**) was also synthesized by us in 67% yield by acylation of  $\alpha$ -terpineol with trifluoroacetic anhydride in carbon tetrachloride at  $-10$  to  $0^\circ\text{C}$  (Scheme 1). This procedure was used previously [5] to obtain a large number of trifluoroacetates for identification of terpene alcohols by  $^{19}\text{F}$  NMR spectroscopy; however, it was not applied to the synthesis of **I** on a preparative scale. The physical constants and spectral parameters ( $^1\text{H}$  and  $^{19}\text{F}$  NMR, IR) of samples of **I** prepared by the two methods were fully identical.

(*R*)-(+)-Limonene reacted with other perfluoroalkanoic acids in a similar way, yielding exclusively the corresponding  $\alpha$ -terpinyl perfluoroalkanoates **II–IV** (Scheme 2). Only the reaction times were different. According to the  $^1\text{H}$  NMR data, the reaction time increased in parallel with the length of the perfluorinated hydrocarbon radical. Almost complete conversion of (*R*)-(+)-limonene in the reactions with trifluoroacetic and pentafluoropropionic acids was attained in  $\sim 2$  h,



**II**,  $\text{R}_\text{F} = \text{CF}_3\text{CF}_2$ ; **III**,  $\text{R}_\text{F} = \text{CF}_3\text{CF}_2\text{CF}_2$ ; **IV**,  $\text{R}_\text{F} = \text{CF}_3(\text{CF}_2)_7$ .

whereas analogous reactions with perfluorobutanoic and perfluorononanoic acids required 2.5 and 6 h, respectively.

Compounds **II–IV** were isolated as colorless liquids with a weak characteristic odor. Like trifluoroacetate **I**, esters **II–IV** are readily soluble in acetone, chloroform, and hexane and poorly soluble in water. Pure  $\alpha$ -terpinyl perfluoropropionate (**II**) and  $\alpha$ -terpinyl perfluorobutanoate (**III**) were isolated by vacuum distillation, and compound **IV** was isolated by thorough washing of the reaction mixture and removal of volatile components under reduced pressure. The structure of esters **II–IV** was confirmed by their elemental analyses and IR and  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{19}\text{F}$  NMR spectra. The IR spectra of **II–IV** contained strong absorption bands due to stretching vibrations of the carbonyl group ( $1769$ – $1772$   $\text{cm}^{-1}$ ) and C–F bonds in  $\text{CF}_3$  ( $1207$ – $1244$   $\text{cm}^{-1}$ ) and  $\text{CF}_2$  groups ( $1125$ – $1157$   $\text{cm}^{-1}$ ). Fluorine nuclei resonated in the  $^{19}\text{F}$  NMR spectra of **II–IV** at  $\delta_{\text{F}} -75.5$  to  $-82.6$  ( $\text{CF}_3$ ) and  $-116.8$  to  $-123.9$  ppm ( $\text{CF}_2$ ). The olefinic proton signal in their  $^1\text{H}$  NMR spectra was located at  $\delta$  5.37 ppm, and methyl protons gave rise to signals at  $\delta$  1.64, 1.55, and 1.53 ppm for  $\text{C}^7\text{H}_3$ ,  $\text{C}^9\text{H}_3$ , and  $\text{C}^{10}\text{H}_3$ , respectively. In the  $^{13}\text{C}$  NMR spectra of **II–IV** we observed signals from the carbonyl carbon atom ( $\delta_{\text{C}} 156.9$ – $157.8$  ppm) and double-bonded carbon atoms  $\text{C}^1$  and  $\text{C}^2$  at  $\delta_{\text{C}} 133.9$  and 119.6 ppm, respectively. Methyl carbon nuclei resonated in the region  $\delta_{\text{C}} 22.37$ – $23.07$  ppm, the  $\text{C}^8$  signal appeared at  $\delta_{\text{C}} 92.43$ – $92.57$  ppm, and the signal at  $\delta_{\text{C}} 42.87$ – $43.04$  ppm was assigned to the tertiary  $\text{C}^4$  atom. The chemical shifts of the methylene carbon nuclei ( $\text{C}^3$ ,  $\text{C}^5$ ,  $\text{C}^6$ ) ranged from  $\delta_{\text{C}} 23.55$  to 30.56 ppm. Distinct multiplet signals were observed from carbon atoms in the perfluoroalkyl groups:  $\delta_{\text{C}} 117.0$ – $117.8$  ( $\text{CF}_3$ ) and 102.80–114.52 ppm ( $\text{CF}_2$ ). The above assignment of  $^{13}\text{C}$  signals was refined using DEPT pulse sequence.

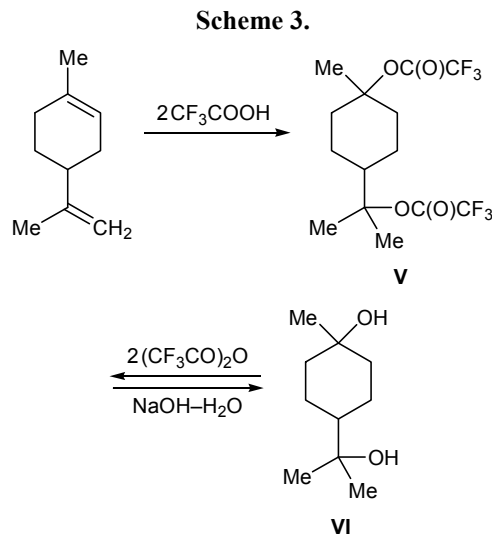
Our attempts to obtain addition products at both C=C bonds of (*R*)-(+)-limonene by increasing the amount of perfluoroalkanoic acid and raising the tem-

perature (in the reaction with trifluoroacetic acid) were unsuccessful. When a mixture of 2.5 mol of trifluoroacetic acid and 1 mol of limonene in toluene was kept for 12 h at 20–25°C, the major product was  $\alpha$ -terpinyl trifluoroacetate **I** whose signals were the most intense in the  $^{19}\text{F}$  and  $^1\text{H}$  NMR spectra of the reaction mixture. Heating of a mixture with the same composition for 2 h at 110°C resulted in participation of both C=C bonds of the terpene substrate, as followed from the disappearance of signals assignable to protons at the exocyclic ( $\delta$  4.69 ppm) or endocyclic double bond ( $\delta$  5.39 ppm). The reaction mixture contained several products: its  $^{19}\text{F}$  NMR spectrum displayed five signals with different intensities in the region  $\delta_{\text{F}}$  –76.05 to –76.80 ppm. Here, the major process is disproportionation of cyclohexene derivatives to aromatic. This is indicated by the presence in the  $^1\text{H}$  NMR spectrum of intense signals from aromatic protons ( $\delta$  7.12 ppm), as well as of those typical of methyl protons in *p*-cymene ( $\delta$  1.24, 1.26, 2.33 ppm) and *p*-menthane derivatives ( $\delta$  0.86–0.88 ppm). These findings are consistent with published data [6, 7], according to which elevated temperature favors isomerization and disproportionation processes in reactions of terpenes belonging to the *p*-menthane series. To avoid disproportionation, the reaction of limonene with trifluoroacetic acid is likely to be carried out at a considerably lower temperature. On the other hand, a stronger proton donor than trifluoroacetic acid should be used to promote the addition to the endocyclic C=C bond of limonene.

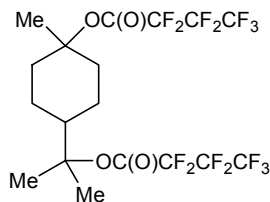
We succeeded in synthesizing bis-trifluoroacetate **V** with high selectivity by reacting 2.5 mol of trifluoroacetic acid with 1 mol of limonene in toluene at 0°C in the presence of a catalytic amount of sulfuric acid. According to the  $^{19}\text{F}$  and  $^1\text{H}$  NMR data, the reaction mixture obtained under these conditions contained compound **V** and almost no other product. Pure bis-trifluoroacetate **V** was isolated as a colorless liquid in 53% yield by vacuum distillation. Its structure was confirmed by the IR and  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{19}\text{F}$  NMR spectra and elemental analysis. In the IR spectrum of **V** we observed absorption bands at 1772 and 1223  $\text{cm}^{-1}$  due to stretching vibrations of the ester carbonyl group and C–F bonds ( $\text{CF}_3$ ), respectively. Compound **V** displayed in the  $^1\text{H}$  NMR spectrum a singlet at  $\delta$  1.58 ppm from the  $\text{C}^7\text{H}_3$  methyl group and a singlet at  $\delta$  1.53 ppm from  $\text{C}^9\text{H}_3$  and  $\text{C}^{10}\text{H}_3$ . The  $^{19}\text{F}$  NMR spectrum of **V** contained two signals at  $\delta_{\text{F}}$  –76.56 and –76.60 ppm with equal intensities due to the presence of two non-equivalent  $\text{CF}_3$  groups. The  $^{13}\text{C}$  NMR signals were distinguished using the DEPT technique. Signals from

the carbonyl carbon atoms appeared as two quartets at  $\delta_{\text{C}}$  156.0 and 155.9 ppm ( $^2J_{\text{CF}} = 41.2$  Hz), the  $\text{CF}_3$  groups were also represented by quartets at  $\delta_{\text{C}}$  114.4 and 114.5 ppm with a direct  $^{13}\text{C}$ – $^{19}\text{F}$  coupling constant  $^1J_{\text{CF}}$  of 287.1 Hz, and methyl carbon atoms resonated at  $\delta_{\text{C}}$  25.1 ( $\text{C}^7$ ) and 22.7 ppm ( $\text{C}^9$ ,  $\text{C}^{10}$ ).

We also synthesized compound **V** by reaction of terpin hydrate **VI** with trifluoroacetic anhydride in  $\text{CCl}_4$  at –10 to 0°C (yield 64%; Scheme 3). The spectral parameters, boiling points, and refractive indices of samples of **V** prepared by the two methods were identical. Bis-trifluoroacetate **V** underwent almost quantitative hydrolysis on treatment with sodium hydroxide in aqueous alcohol. The resulting terpin hydrate (**VI**, 73%) was identified by comparing its melting point and spectral data ( $^1\text{H}$  NMR, IR) with those of an authentic sample. Thus, the addition of two trifluoroacetic acid molecules to limonene, followed by hydrolysis of bis-trifluoroacetate **V**, may be regarded as a method of synthesis of terpin hydrate from limonene.



Likewise, the reaction of limonene with heptafluorobutanoic acid afforded 68% of bis-heptafluorobutanoate **VII**. Ester **VII** is a colorless liquid with a weak characteristic odor. Its structure was proved by IR and  $^1\text{H}$ ,  $^{19}\text{F}$ , and  $^{13}\text{C}$  NMR spectroscopy. The IR spectrum of **VII** contained strong absorption bands corresponding to C=O (1771  $\text{cm}^{-1}$ ) and C–F stretching vibrations ( $\text{CF}_3$ , 1224, 1236  $\text{cm}^{-1}$ ;  $\text{CF}_2$ , 1125  $\text{cm}^{-1}$ ). In the  $^1\text{H}$  NMR spectrum of **VII**, signals from methyl protons on  $\text{C}^7$  and  $\text{C}^9/\text{C}^{10}$  appeared as singlets at  $\delta$  1.60 and 1.56 ppm, respectively. Three couples of signals with equal intensities were present in the  $^{19}\text{F}$  NMR spectrum of **VII**: one couple at  $\delta_{\text{F}}$  –81.82/–81.90 ppm



VII

from two  $\text{CF}_3$  groups and two couples at  $\delta_{\text{F}} -119.89/-120.27$  and  $-127.61/-127.94$  ppm from four  $\text{CF}_2$  groups. Signals in the  $^{13}\text{C}$  NMR spectrum of VII were assigned using the DEPT pulse sequence: two carbonyl carbon atoms gave two quartets at  $\delta_{\text{C}} 156.7$  ( $^2J_{\text{CF}} = 28.9$ ) and  $156.8$  ppm ( $^2J_{\text{CF}} = 28.6$  Hz), two  $\text{CF}_3$  groups were represented by a quartet of triplets at  $\delta_{\text{C}} 117.42$  ppm ( $^1J_{\text{CF}} = 287.8$ ,  $^2J_{\text{CF}} = 33.7$  Hz), and four  $\text{CF}_2$  carbon nuclei resonated as multiplets in the region  $\delta_{\text{C}} 104.62-114.16$  ppm. The chemical shifts of  $\text{C}^7$  and  $\text{C}^9/\text{C}^{10}$  were  $\delta_{\text{C}} 25.2$  and  $21.5$  ppm, respectively.

We estimated the stability of trifluoroacetate I and bis-trifluoroacetate V. These compounds remained almost unchanged on storage for 6 months in a refrigerator ( $5-7^\circ\text{C}$ ); but their color changed first to light violet and then to yellow-brown. Considerable decomposition of I and V was observed after storage for 6-8 months at room temperature. These compounds turned dark brown, and their  $^{19}\text{F}$  NMR spectra displayed 5-7 signals in the region  $\delta_{\text{F}} -76.05$  to  $-76.75$  ppm; the major signal at  $\delta_{\text{F}} -76.50$  ppm is likely to belong to trifluoroacetic acid. The  $^1\text{H}$  NMR spectra revealed variation of the position of signals in the region  $\delta$  0.8- 2.3 ppm, typical of methyl protons, and appearance of aromatic proton signals at about  $\delta$  7.13 ppm. These findings indicated elimination of trifluoroacetic acid and disproportionation of compounds I and V with formation of *p*-cymene as one of the products.

## EXPERIMENTAL

The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were recorded on a Bruker Avance 400 spectrometer at 400.13 and 100.61 MHz, respectively, using  $\text{CDCl}_3$  as solvent. The  $^{19}\text{F}$  NMR spectra were measured on a Bruker AM-500 instrument at 470.6 MHz from solutions in  $\text{CDCl}_3$  using  $\text{CFCl}_3$  as reference. The IR spectra were obtained on a Shimadzu FTIR-8400S spectrometer from thin films. The elemental compositions were determined on a Carlo Erba 1106 analyzer.

(*R*)-(+)-Limonene (97%, Acros),  $\alpha$ -terpineol (98%, Acros), terpin hydrate (Russian Pharmacopeia, article

no. 659), trifluoroacetic anhydride (99%, Acros), trifluoroacetic acid (99%, Acros), pentafluoropropionic acid (99%, P&M), heptafluorobutanoic acid (99%, P&M), and heptadecafluorononanoic acid (99%, P&M) were commercial products. Toluene and carbon tetrachloride were purified and dried according to standard procedures [8].

**$\alpha$ -Terpinyl perfluoroalkanoates I-III (general procedure).** *R*-(+)-Limonene, 0.05 mol, was dissolved in 10 ml of toluene, 0.06 mol of perfluoroalkanoic acid was slowly added dropwise under stirring at  $20-30^\circ\text{C}$ , and the mixture was stirred for 2-6 h at  $30^\circ\text{C}$ . The mixture was then washed with water (20 ml), 5% aqueous  $\text{NaHCO}_3$  (20 ml), and 5% aqueous  $\text{NaCl}$  (20 ml), the organic phase was separated and dried over magnesium sulfate, and the solvent and excess perfluoroalkanoic acid were removed under reduced pressure. The residue was subjected to fractional distillation under reduced pressure.

**2-(4-Methylcyclohex-3-en-1-yl)propan-2-yl trifluoroacetate (I,  $\alpha$ -terpinyl trifluoroacetate).** Yield 57%, bp  $58-59^\circ\text{C}$  (1 mm),  $n_{\text{D}}^{20} = 1.4215$ . IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1772 (C=O), 1223 (C-F).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 1.27-1.40 m (1H, 4-H), 1.53 s (3H, 10-H), 1.54 s (3H, 9-H), 1.64 s (3H, 7-H), 1.67-2.12 m (6H, 3-H, 5-H, 6-H), 5.35 s (1H, 2-H).  $^{13}\text{C}$  NMR spectrum,  $\delta_{\text{C}}$ , ppm: 22.67 ( $\text{C}^{10}$ ), 22.93 ( $\text{C}^7$ ), 23.18 ( $\text{C}^9$ ), 23.72 ( $\text{C}^5$ ), 26.15 ( $\text{C}^3$ ), 30.61 ( $\text{C}^6$ ), 42.60 ( $\text{C}^4$ ), 92.02 ( $\text{C}^8$ ), 119.61 ( $\text{C}^2$ ), 134.00 ( $\text{C}^1$ ), 114.79 q.t ( $\text{CF}_3$ ,  $^1J_{\text{CF}} = 285.5$ ,  $^2J_{\text{CF}} = 40.9$  Hz), 156.43 q (C=O,  $^2J_{\text{CF}} = 28.9$  Hz).  $^{19}\text{F}$  NMR spectrum:  $\delta_{\text{F}} -76.50$  ppm. Found, %: C 57.67; H 6.74.  $\text{C}_{12}\text{H}_{17}\text{F}_3\text{O}_2$ . Calculated, %: C 57.59; H 6.85.

**2-(4-Methylcyclohex-3-en-1-yl)propan-2-yl pentafluoropropanoate (II,  $\alpha$ -terpinyl perfluoropropionate).** Yield 64%, bp  $80-81^\circ\text{C}$  (2 mm),  $n_{\text{D}}^{22} = 1.4180$ . IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1772 (C=O), 1222 ( $\text{CF}_3$ ), 1157 ( $\text{CF}_2$ ).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 1.23-1.37 m (1H, 4-H), 1.53 s (3H, 10-H), 1.54 s (3H, 9-H), 1.64 s (3H, 7-H), 1.69-2.06 m (6H, 3-H, 5-H, 6-H) 5.36 s (1H, 2-H).  $^{13}\text{C}$  NMR spectrum,  $\delta_{\text{C}}$ , ppm: 22.58 ( $\text{C}^{10}$ ), 22.85 ( $\text{C}^7$ ), 23.06 ( $\text{C}^9$ ), 23.58 ( $\text{C}^5$ ), 26.07 ( $\text{C}^3$ ), 30.56 ( $\text{C}^6$ ), 42.87 ( $\text{C}^4$ ), 92.43 ( $\text{C}^8$ ), 119.64 ( $\text{C}^2$ ), 133.97 ( $\text{C}^1$ ), 102.80-109.86 m ( $\text{CF}_2$ ), 117.81 q.t ( $\text{CF}_3$ ,  $^1J_{\text{CF}} = 286.5$ ,  $^2J_{\text{CF}} = 33.7$  Hz), 156.87 t (C=O,  $^2J_{\text{CF}} = 28.9$  Hz).  $^{19}\text{F}$  NMR spectrum,  $\delta_{\text{F}}$ , ppm:  $-82.65$  ( $\text{CF}_3$ ),  $-121.42$  ( $\text{CF}_2$ ). Found, %: C 51.82; H 5.63.  $\text{C}_{13}\text{H}_{17}\text{F}_5\text{O}_2$ . Calculated, %: C 52.00; H 5.71.

**2-(4-Methylcyclohex-3-en-1-yl)propan-2-yl heptafluorobutanoate (III,  $\alpha$ -terpinyl perfluorobutyrate).** Yield 68%, bp  $89-90^\circ\text{C}$  (2 mm),  $n_{\text{D}}^{20} =$

1.4001. IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1769 (C=O); 1225, 1235 ( $\text{CF}_3$ ); 1125 ( $\text{CF}_2$ ).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 1.33–1.42 m (1H, 4-H), 1.55 s (6H, 9-H, 10-H), 1.65 s (3H, 7-H), 1.81–2.04 m (6H, 3-H, 5-H, 6-H), 5.37 s (1H, 2-H).  $^{13}\text{C}$  NMR spectrum,  $\delta_{\text{C}}$ , ppm: 22.41 ( $\text{C}^{10}$ ), 22.73 ( $\text{C}^7$ ), 22.98 ( $\text{C}^9$ ), 23.56 ( $\text{C}^5$ ), 26.07 ( $\text{C}^3$ ), 30.56 ( $\text{C}^6$ ), 43.04 ( $\text{C}^4$ ), 92.48 ( $\text{C}^8$ ), 119.65 ( $\text{C}^2$ ), 133.96 ( $\text{C}^1$ ), 104.32–111.74 m ( $\text{CF}_2$ ), 117.45 q.t ( $\text{CF}_3$ ,  $^1J_{\text{CF}} = 288.1$ ,  $^2J_{\text{CF}} = 33.7$  Hz), 157.76 t (C=O,  $^2J_{\text{CF}} = 28.9$  Hz).  $^{19}\text{F}$  NMR spectrum,  $\delta_{\text{F}}$ , ppm: –77.65 ( $\text{CF}_3$ ), –116.77 ( $\text{CF}_2$ ), –123.82 ( $\text{CF}_2$ ). Found, %: C 48.14; H 4.75.  $\text{C}_{14}\text{H}_{17}\text{F}_7\text{O}_2$ . Calculated, %: C 48.01; H 4.89.

**2-(4-Methylcyclohex-3-en-1-yl)propan-2-yl heptadecafluorononanoate (IV,  $\alpha$ -terpinyl perfluoropelargonate).** A mixture of 2.5 g (18.3 mmol) of (R)-(+)-limonene and 10.2 g (22.0 mmol) of perfluoropelargonic acid in 10 ml of toluene was stirred for 6 h at 30°C. The mixture was then washed with 0.1 N aqueous KOH until neutral reaction and extracted with diethyl ether (2×15 ml), the extract was dried over  $\text{MgSO}_4$ , and the solvent was distilled off under reduced pressure. Yield 8.4 g (76%), yellow mobile liquid,  $n_{\text{D}}^{20} = 1.3716$ . IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1771 (C=O); 1224, 1244 ( $\text{CF}_3$ ); 1153 ( $\text{CF}_2$ ).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 1.29–1.42 m (1H, 4-H), 1.53 s (3H, 10-H), 1.55 s (3H, 9-H), 1.65 s (3H, 7-H), 1.80–2.04 m (6H, 3-H, 5-H, 6-H), 5.37 s (1H, 2-H).  $^{13}\text{C}$  NMR spectrum,  $\delta_{\text{C}}$ , ppm: 22.37 ( $\text{C}^{10}$ ), 22.69 ( $\text{C}^7$ ), 22.91 ( $\text{C}^9$ ), 23.55 ( $\text{C}^5$ ), 26.06 ( $\text{C}^3$ ), 30.52 ( $\text{C}^6$ ), 43.01 ( $\text{C}^4$ ), 92.57 ( $\text{C}^8$ ), 119.62 ( $\text{C}^2$ ), 133.98 ( $\text{C}^1$ ), 105.14–114.52 m ( $\text{CF}_2$ ), 117.07 q.t ( $\text{CF}_3$ ,  $^1J_{\text{CF}} = 288.1$ ,  $^2J_{\text{CF}} = 32.9$  Hz), 156.90 t (C=O,  $^2J_{\text{CF}} = 28.9$  Hz).  $^{19}\text{F}$  NMR spectrum,  $\delta_{\text{F}}$ , ppm: –82.03 ( $\text{CF}_3$ ); –119.33, –122.71, –123.06, –123.57, –123.90 ( $\text{CF}_2$ ). Found, %: C 37.69; H 2.41.  $\text{C}_{19}\text{H}_{17}\text{F}_{17}\text{O}_2$ . Calculated, %: C 38.01; H 2.85.

***p*-Menthane-1,8-diyl bis(perfluoroalkanoates) V and VII (general procedure).** A solution of 0.07 mol of (R)-(+)-limonene in 20 ml of toluene was cooled to 0°C, 0.18 mol of trifluoroacetic or heptafluorobutanoic acid was added dropwise under stirring, and a few drops of concentrated (95%) sulfuric acid were then added. The mixture was stirred for 45 min (in the synthesis of V) or 2.5 h (in the synthesis of VII), maintaining the temperature about 0°C. The mixture was then allowed to warm up to room temperature and treated in succession with 10 ml of water, 10 ml of 5% aqueous  $\text{NaHCO}_3$ , and 10 ml of 5% aqueous NaCl. The organic phase was dried over  $\text{MgSO}_4$ , the solvent was distilled off under reduced pressure, and the residue was purified by vacuum distillation.

**2-[4-Methyl-4-(trifluoroacetyloxy)cyclohexyl]propan-2-yl trifluoroacetate (V, terpin bis-trifluoro-**

**acetate).** Yield 53%, bp 79–80°C (1 mm),  $n_{\text{D}}^{20} = 1.3972$ . IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1772 (C=O); 1223, 1235 (C–F).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 1.34–1.44 m (4H, 3-H, 5-H), 1.53 s (6H, 9-H, 10-H), 1.58 s (3H, 7-H), 1.60–1.68 m (2H, 2- $\text{H}_{\text{ax}}$ , 6- $\text{H}_{\text{ax}}$ ), 1.93 m (1H, 4-H), 2.42–2.47 m (2H, 2- $\text{H}_{\text{eq}}$ , 6- $\text{H}_{\text{eq}}$ ).  $^{13}\text{C}$  NMR spectrum,  $\delta_{\text{C}}$ , ppm: 21.52 ( $\text{C}^3$ ,  $\text{C}^5$ ), 22.68 ( $\text{C}^9$ ,  $\text{C}^{10}$ ), 25.14 ( $\text{C}^7$ ), 35.35 ( $\text{C}^2$ ,  $\text{C}^6$ ), 45.82 ( $\text{C}^4$ ), 86.78 ( $\text{C}^8$ ), 91.10 ( $\text{C}^1$ ), 114.4 q ( $\text{CF}_3$ ,  $^1J_{\text{CF}} = 287.1$  Hz), 156.0 q and 155.9 q (C=O,  $^2J_{\text{CF}} = 41.2$  Hz).  $^{19}\text{F}$  NMR spectrum,  $\delta_{\text{F}}$ , ppm: –76.60, –76.56. Found, %: C 46.32; H 5.12.  $\text{C}_{14}\text{H}_{18}\text{F}_6\text{O}_4$ . Calculated, %: C 46.16; H 4.98.

**2-[4-(Heptafluorobutanoyloxy)-4-methylcyclohexyl]propan-2-yl heptafluorobutanoate (VII, terpin bis-perfluorobutyrate).** Yield 68%, bp 104–105°C (1 mm). IR spectrum,  $\nu$ ,  $\text{cm}^{-1}$ : 1771 (C=O); 1224, 1236 ( $\text{CF}_3$ ); 1125, 1144 ( $\text{CF}_2$ ).  $^1\text{H}$  NMR spectrum,  $\delta$ , ppm: 1.41–1.70 m (4H, 3-H, 5-H), 1.56 s (6H, 9-H, 10-H), 1.60 s (3H, 7-H), 1.91 m (1H, 4-H), 2.26–2.51 m (4H, 2-H, 6-H).  $^{13}\text{C}$  NMR spectrum,  $\delta_{\text{C}}$ , ppm: 21.48 ( $\text{C}^9$ ,  $\text{C}^{10}$ ), 22.68 ( $\text{C}^3$ ,  $\text{C}^5$ ), 25.24 ( $\text{C}^7$ ), 35.63 ( $\text{C}^2$ ,  $\text{C}^6$ ), 45.32 ( $\text{C}^4$ ), 87.74 ( $\text{C}^8$ ), 91.87 ( $\text{C}^1$ ), 104.62–128.93 m ( $\text{CF}_2$ ), 117.43 d.t ( $\text{CF}_3$ ,  $^1J_{\text{CF}} = 287.5$ ,  $^2J_{\text{CF}} = 33.7$  Hz), 156.79 t and 156.68 t (C=O,  $^2J_{\text{CF}} = 28.9$  Hz).  $^{19}\text{F}$  NMR spectrum,  $\delta_{\text{F}}$ , ppm: –81.82, –81.90 ( $\text{CF}_3$ ); –119.89, –120.26 ( $\text{CF}_2$ ); –127.61, –127.94 ( $\text{CF}_2$ ). Found, %: C 38.92; H 3.51.  $\text{C}_{18}\text{H}_{18}\text{F}_{14}\text{O}_4$ . Calculated, %: C 38.31; H 3.22.

**$\alpha$ -Terpinyl trifluoroacetate (I) from  $\alpha$ -terpineol and terpin bis-trifluoroacetate (V) from terpin hydrate.** A solution of 0.25–0.5 mol of trifluoroacetic anhydride in 8–15 ml of carbon tetrachloride was added dropwise under stirring and cooling to a solution of 0.05 mol of terpin hydrate in 7 ml of carbon tetrachloride, maintaining the temperature not higher than 10°C. The mixture was then allowed to warm up to room temperature and stirred for 0.5–1 h. The solvent, excess trifluoroacetic anhydride, and trifluoroacetic acid formed during the reaction were distilled off under reduced pressure at a bath temperature not exceeding 40°C, and the residue was subjected to vacuum distillation.

**$\alpha$ -Terpinyl trifluoroacetate (I).** Yield 67%, bp 59–61°C (1 mm),  $n_{\text{D}}^{20} = 1.4215$ . The IR and  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectra of the product were fully identical to those of a sample synthesized from limonene.

**Terpin bis-trifluoroacetate (V).** Yield 51%, bp 80–81°C (1 mm),  $n_{\text{D}}^{22} = 1.3955$ . The IR and  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectra of the product were fully identical to those of a sample synthesized from limonene.

**4-(2-Hydroxypropan-2-yl)-1-methylcyclohexanol (VI, terpin hydrate).** Compound **V**, 2.00 g (5.5 mmol), was dissolved in 4 ml of methanol, 3.0 g of 20% aqueous sodium hydroxide was slowly added at 20–30°C, and the mixture was stirred for 3 h at 40–45°C. The mixture was cooled to 20°C, 10 ml of water and 7 drops of concentrated aqueous HCl were added, and the precipitate was filtered off, washed with water (15 ml), and dried. Yield 0.76 g (73%), mp 116–117°C [9]. The <sup>1</sup>H NMR spectrum of the product was identical to that of an authentic sample.

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