

**RADICAL ADDITION OF 2-PROPANOL TO TRIFLUOROETHYLENE.  
PREPARATION OF TRIFLUOROETHYLENE OLIGOMERS  
FROM CHLOROTRIFLUOROETHYLENE OLIGOMERS**Jiri FIKAR<sup>1</sup>, †Petr TRSKA, Pavel PECH and Frantisek LISKA<sup>2</sup>*Department of Organic Chemistry, Prague Institute of Chemical Technology, 166 28 Prague 6,  
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Photochemically initiated addition of 2-propanol to trifluoroethylene afforded the 1 : 1 adducts 3,3,4-trifluoro-2-methyl-2-butanol **1** and 3,4,4-trifluoro-2-methyl-2-butanol **2**, as well as the 1 : 2 telomers 3,4,4,5,5,6-hexafluoro-2-methyl-2-hexanol **3** and 3,4,4,5,6,6-hexafluoro-2-methyl-2-hexanol **4**. The other possible 1 : 2 and 1 : 3 telomers, in which the CF<sub>2</sub>-CFH- groups regularly alternate ("head-tail") – 3,3,4,5,5,6-hexafluoro-2-methyl-2-hexanol **13** and 3,3,4,5,5,6,7,7,8-nonafluoro-2-methyl-2-octanol **14** – and which did not arise in the reaction, were obtained by photochemical reduction of addition products of 2-propanol to chlorotrifluoroethylene (alcohols **15**–**17**) with secondary and tertiary amines. Dehydrofluorination of alcohols **1** and **2** gave 3,3-difluoro-2, 2-dimethyloxetane **18** and 3-difluoromethyl-2,2-dimethyloxirane **19**.

**Key words:** Trifluoroethylene; 2-Propanol; Photoaddition to fluoroethylenes; Photoreduction of chlorofluoro compounds.

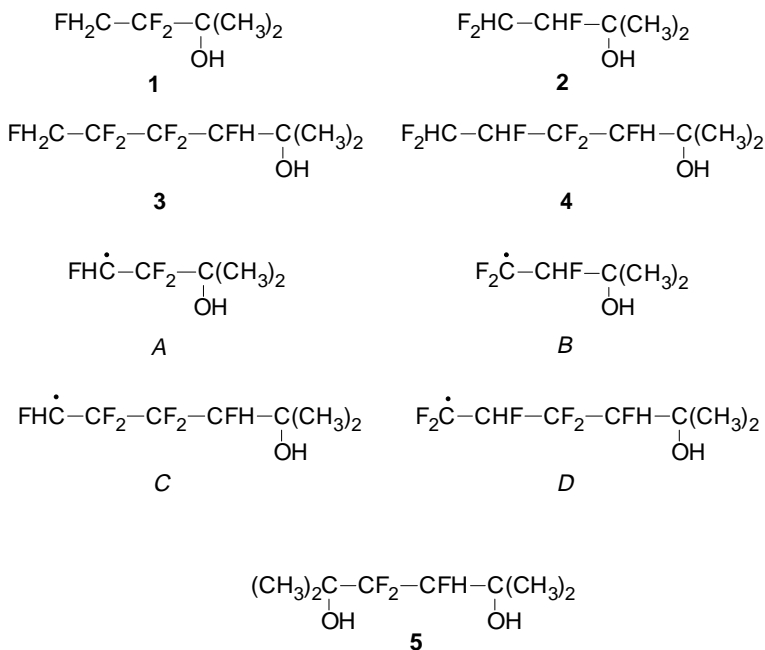
Radical addition reactions of various substrates to trifluoroethylene were studied from the viewpoint of both the synthesis of fluorinated compounds with various functional groups<sup>1</sup> and the regioselectivity of radical additions to fluorinated alkenes<sup>2</sup>.

The present communication deals with the photochemically initiated addition of 2-propanol to trifluoroethylene with the aim of possible synthetic exploitation of the arising products. As the principal products we obtained both the 1 : 1 adducts – 3,3,4-trifluoro-2-methyl-2-butanol **1** and 3,4,4-trifluoro-2-methyl-2-butanol **2**, as well as the 1 : 2 telomers – 3,4,4,5,5,6-hexafluoro-2-methyl-2-hexanol **3** and 3,4,4,5,6,6-hexafluoro-2-methyl-2-hexanol **4**.

We explain the formation of products **1**–**4** by the mechanism of radical and telomerization reactions. From the structure of the addition (**1** and **2**) and telomerization (**3** and **4**) products and their ratio we derive that the 2-hydroxy-2-propyl radical adds both to the CF<sub>2</sub> and the CFH group of trifluoroethylene under formation of the corresponding 1 : 1 adduct-radicals **A** and **B** which by chain transfer to 2-propanol afford adducts **1** and **2**. Only the radical **B** then adds to another trifluoroethylene molecule to give 1 : 2

telomer-radicals **C** and **D** and these by chain transfer to 2-propanol give rise to the 1 : 2 telomers **3** and **4**.

A similar conclusion about the telomerization of trifluoroethylene can also be derived from the structure of adducts and telomers, obtained by Ankudinov and co-workers<sup>3</sup> in the addition of 1,2-dichloro-4-iodoperfluorobutane to trifluoroethylene. When we carried out the addition of 2-propanol to trifluoroethylene with acetone as sensitizer, we isolated also 3,3,4-trifluoro-2,5-dimethyl-2,5-hexanediol **5** which is probably formed by recombination of the 1 : 1 adduct-radicals **A** or **B** with the 2-hydroxy-2-propyl radical.



An alternative way how to prepare addition and telomerization products with regular head-to-tail arrangement of the monomeric units (which do not arise in the described addition of 2-propanol to trifluoroethylene) can be the reduction of the C-Cl bonds in the corresponding products formed by addition of 2-propanol to chlorotrifluoroethylene. We observed this reduction already in the 1 : 2 and 1 : 3 telomers formed in the radiation-initiated addition of 2-propanol to chlorotrifluoroethylene<sup>4</sup>. Further study revealed<sup>5</sup> that this photochemically or radiation-initiated reduction with 2-propanol is chemoselective, affecting only the C-Cl bonds in the -CFCl- groups whereas in the terminal group -CHFCl the chlorine atom is not reduced. The radical mechanism of this photochemically initiated reduction of C-Cl bonds in polyhalogeno compounds

with 2-propanol was proved by measurement of quantum yields<sup>6,7</sup> and the reaction was used also on the preparative scale<sup>8,9</sup>.

In the photochemically initiated addition of trialkylamines to chlorotrifluoroethylene<sup>10,11</sup> we observed products in which the chlorine atoms in the -CHClF groups of the primarily arising 1 : 1 adducts were reduced with amines. Therefore, we made use of this reaction for converting the addition and telomerization products of the radi-

TABLE I  
Reaction conditions and results of photochemical reduction of chlorofluoro compounds with amines

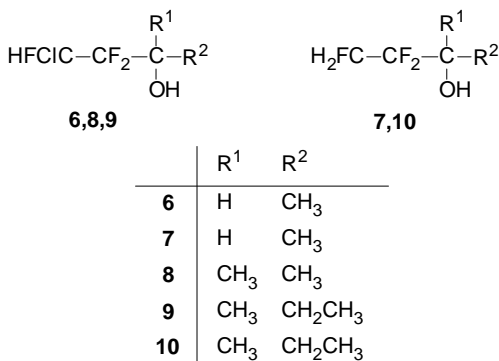
Starting compound mol · 10 <sup>-3</sup>	Amine, mol	Irradiation time h	Product/ Starting compound <sup>a</sup>	Yield, %
<b>6</b> 74	Et <sub>2</sub> NMe 0.82	68	<b>4</b> 83/17	63
<b>8</b> 23	Et <sub>3</sub> N 0.57	16	<b>1</b> 44/56	18
<b>8</b> 57	Et <sub>3</sub> N 0.68	39	<b>1</b> 90/10	26
<b>8</b> 57	Et <sub>3</sub> N 0.84	63	<b>1</b> 92/8	28
<b>8</b> 68	Et <sub>2</sub> NMe 0.82	46	<b>1</b> 78/22	47 <sup>c</sup>
<b>8</b> 62	iPrNMe <sub>2</sub> 0.81	26	<b>1</b> 53/47	44 <sup>c</sup>
<b>8</b> 57	Et <sub>2</sub> NH 0.96	49	<b>1</b> 35/65	33 <sup>c</sup>
<b>8</b> 57	PrNH <sub>2</sub> 1.20	52	<b>1</b> 20/80	19 <sup>c</sup>
<b>9</b> 42	Et <sub>3</sub> N 0.71	61	<b>10</b> 100/0	46
<b>11</b> 22	Et <sub>3</sub> N 0.50	1	<b>12</b> 36/64	25
<b>12</b> 22	Et <sub>3</sub> N 0.50	20	<b>13</b> 84/16	38
<b>12</b> 39	Et <sub>3</sub> N 0.71	67	<b>13</b> 99/1	36
<b>17<sup>b</sup></b> 8.9	Et <sub>3</sub> N 0.71	50	<b>14</b> 93/7	44 <sup>c</sup>

<sup>a</sup> GLC; uncorrected. <sup>b</sup> According to GLC, alcohol **17** contained compounds **13** (3%) and **16** (15%).

<sup>c</sup> Crude product.

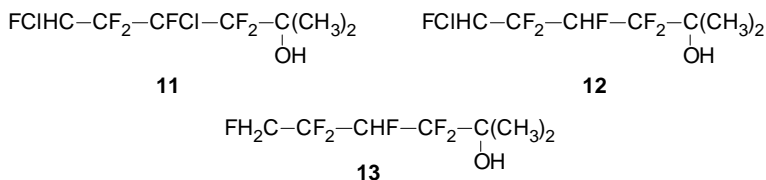
cal addition of alcohols to chlorotrifluoroethylene into the corresponding products of trifluoroethylene. The photochemical reduction was performed by irradiation of the corresponding substrates in solutions of an excess of the amine (propylamine, diethylamine, isopropylidimethylamine, diethylmethylamine and triethylamine). The reaction conditions and results are given in Table I.

Thus, on reduction with amines, 4-chloro-3,3,4-trifluoro-2-butanol<sup>12</sup> **6** afforded 3,3,4-trifluoro-2-butanol **7**, 4-chloro-3,3,4-trifluoro-2-methyl-2-butanol<sup>4</sup> **8** gave 3,3,4-trifluoro-2-methyl-2-butanol **1**, and 1-chloro-1,2,2-trifluoro-3-methyl-3-pentanol<sup>13</sup> **9** was converted into 1,2,2-trifluoro-3-methyl-3-pentanol **10**.



Photochemical reduction of 4,6-dichloro-3,3,4,5,5,6-hexafluoro-2-methyl-2-hexanol<sup>4</sup> **11** in triethylamine solution gave primarily 6-chloro-3,3,4,5,5,6-hexafluoro-2-methyl-2-hexanol **12** which was further reduced to 3,3,4,5,5,6-hexafluoro-2-methyl-2-hexanol **13**.

From the preparative viewpoint, however, it is better to reduce photochemically the 1 : 2 telomer **11** to alcohol **12** in 2-propanol and only then to reduce the alcohol **12** to hexanol **13** in an excess of triethylamine. This procedure prevents the formation of great amounts of triethylamine hydrochloride which accumulates on the outer quartz part of the reactor and has to be continuously removed to prevent darkening of the reaction mixture.



Similarly, in the preparation of 3,3,4,5,5,6,7,7,8-nonafluoro-2-methyl-2-octanol **14** it is more advantageous first to convert 4,6,8-trichloro-3,3,4,5,5,6,7,7,8-nonafluoro-2-methyl-2-octanol<sup>4</sup> **15** or 4,8-dichloro-3,3,4,5,5,6,7,7,8-nonafluoro-2-methyl-2-octanol<sup>4</sup>



## EXPERIMENTAL

The temperature data are uncorrected. The  $^1\text{H}$  and  $^{19}\text{F}$  NMR spectra were measured in deuteriochloroform on a Varian XL 100 or a Bruker AM 400 instrument (for protons 400 MHz, pro fluorine 376 MHz) with tetramethylsilane or fluorotrichloromethane as internal standard. Chemical shifts are given in ppm, coupling constants  $J$  in Hz. As shift reagent we used tris(heptafluorobutyropivaloyl)metanatoeuropium. Mass spectra were taken on a Gas Chromatograph–Mass Spectrometer LKB 9000.

## Photochemically Initiated Addition of 2-Propanol to Trifluoroethylene

Trifluoroethylene was introduced for 41 h at an average rate 0.707 l/h into 2-propanol (85 g, 1.42 mol) in a photochemical reactor with a water-cooled finger under irradiation with a 125 W mercury lamp, the temperature being maintained at 12–14 °C. The weight increase of the reaction mixture was 25 g (0.305 mol  $\text{CHF}=\text{CF}_2$ ). After the unreacted trifluoroethylene and 2-propanol had been removed by distillation, the residue (46.9 g) was fractionated under diminished pressure. The following fractions were collected: 1) A mixture of 1 : 1 adducts 3,3,4-trifluoro-2-methyl-2-butanol **1** and 3,4,4-trifluoro-2-methyl-2-butanol **2**, b.p. 37–42 °C/2.13 kPa (32.83 g, 75.7 mole %). Repeated fractionation of this fraction afforded an analytical sample, boiling at 36.0–38.5 °C/1.6 kPa and containing (NMR) the alcohols **1** and **2** in the ratio 3 : 1; 2) Fraction boiling at 42–76 °C/2.13 kPa (5.7 g, 8 mole %) from which preparative gas-liquid chromatography separated 3,4,4,5,5,6-hexafluoro-2-methyl-2-hexanol **3** and 3,4,4,5,6,6-hexafluoro-2-methyl-2-hexanol **4** in 1 : 1 ratio. In another experiment, under the same conditions and initiation with acetone, 3,3,4-trifluoro-2,5-dimethyl-2,5-hexanediol **5** (5.4 mole %) was isolated in addition to the products **1–4**.

*Alcohols 1 and 2.* For  $\text{C}_5\text{H}_9\text{F}_3\text{O}$  (142.1) calculated: 42.26% C, 6.38% H, 40.10% F; found: 42.51% C, 6.24% H, 39.91% F. *Alcohol 1.*  $^1\text{H}$  NMR spectrum: 1.34 s, 6 H ( $(\text{CH}_3)_2\text{C}$ ); 2.10 s, 1 H (OH); 4.68 dt, 2 H,  $^2J(\text{H},\text{F}) = 47$ ,  $^3J(\text{H},\text{F}) = 7$  (H-4).  $^{19}\text{F}$  NMR spectrum: -123.2 dt, 2 F,  $^3J(\text{H},\text{F}) = ^3J(\text{F},\text{F}) = 13$  (F-3); -239.6 tt, 1 F,  $^2J(\text{H},\text{F}) = 47$ ,  $^3J(\text{F},\text{F}) = 14$  (F-4). *Alcohol 2.*  $^1\text{H}$  NMR spectrum: 1.31 s, 6 H ( $(\text{CH}_3)_2\text{C}$ ); 2.6 s, 1 H (OH); 4.26 ddd, 1 H,  $^2J(\text{H},\text{F}) = 46$ ,  $^3J(\text{H},\text{F}) = 8.5$  (H-3); 5.95 dddd, 1 H,  $^2J(\text{H},\text{F}) = 53.6$ ,  $^3J(\text{H},\text{F}) = 6.9$  (H-4).  $^{19}\text{F}$  NMR spectrum: -126.39 and -130.03 ddt, 2 F,  $^2J(\text{H},\text{F}) = 54$ ,  $^3J(\text{H},\text{F}) = 9$  and 11,  $^2J(\text{F},\text{F}) = 304$ ,  $^3J(\text{F},\text{F}) = 10$  and 11 (F-4); -208.3 dd, 1 F,  $^2J(\text{H},\text{F}) = 46$ ,  $^3J(\text{F},\text{F}) = 11$  (F-3).

The relative ratio **1** : **2** was 75 : 25 as estimated from the signal integrals in the  $^{19}\text{F}$  and  $^1\text{H}$  NMR spectra and from GLC analyses.

*3,4,4,5,5,6-Hexafluoro-2-methyl-2-hexanol 3.* For  $\text{C}_7\text{H}_{10}\text{F}_6\text{O}$  (224.1) calculated: 37.51% C, 4.50% H; found: 37.72% C, 4.80% H.  $^1\text{H}$  NMR spectrum: 1.38  $2 \times$  s, 6 H ( $(\text{CH}_3)_2\text{C}$ ); 2.08 s, 1 H (OH), 4.60 ddd, 1 H,  $^2J(\text{H},\text{F}) = 46$ ,  $^3J(\text{H},\text{F}) = 13$  (H-3); 4.68 m, 2 H (H-6).  $^{19}\text{F}$  NMR spectrum: -124.9 m and -125.2 m, 4 F (F-4 and F-5); -204.2 dm, 1 F (F-3).

*3,4,4,5,6,6-Hexafluoro-2-methyl-2-hexanol 4.* For  $\text{C}_7\text{H}_{10}\text{F}_6\text{O}$  (224.1) calculated: 37.51% C, 4.50% H; found: 38.00% C, 4.75% H.  $^1\text{H}$  NMR spectrum: 1.38  $2 \times$  s, 6 H ( $(\text{CH}_3)_2\text{C}$ ); 2.05 s, 1 H (OH); 4.52 ddd, 1 H,  $^2J(\text{H},\text{F}) = 42$ ,  $^3J(\text{H},\text{F}) = 6$  (H-3); 4.80 dm, 1 H (H-5); 6.03 ddd, 1 H,  $^2J(\text{H},\text{F}) = 52$ ,  $^3J(\text{H},\text{F}) = 8$ ,  $^3J(\text{H},\text{H}) = 6$  (H-6).  $^{19}\text{F}$  NMR spectrum: -122.9 m, 2 F (F-4); -130.2 dm, 2 F,  $^3J(\text{F},\text{F}) = 80$  (F-6); -204.2 dm, 1 F,  $^2J(\text{H},\text{F}) = 42$  (F-3); -216.1 dm, 1 F,  $^2J(\text{H},\text{F}) = 45$  (F-5).

*3,3,4-Trifluoro-2,5-dimethyl-2,5-hexanediol 5.* For  $\text{C}_8\text{H}_{15}\text{F}_3\text{O}_2$  (200.2) calculated: 48.00% C, 7.55% H, 28.47% F; found: 47.97% C, 7.31% H, 32.2% F.  $^1\text{H}$  NMR spectrum: 1.22 s and 1.40 s, 12 H ( $2 \times (\text{CH}_3)_2\text{C}$ ), 3.29 s, 2 H ( $2 \times \text{OH}$ ), 4.52 ddd, 1 H,  $^2J(\text{H},\text{F}) = 45$ ,  $^3J(\text{H},\text{F}) = 12$  (H-4).  $^{19}\text{F}$  NMR spectrum: -117.3 dd, 2 F,  $^2J(\text{F},\text{F}) = 46$ ,  $^3J(\text{F},\text{F}) = 8$  (F-3); -198.9 dm, 1 F,  $^3J(\text{F},\text{F}) = 8$  (F-4). Mass spectrum,  $m/z$ : 185  $[\text{M} - \text{OH}]^+$ , 183  $[\text{M} - \text{F}]^+$ , 165, 147, 59/100  $[(\text{CH}_3)_2\text{COH}]^+$ , 43  $[\text{C}_3\text{H}_7]^+$ .

## Photochemically Initiated Reduction of C–Cl Bonds

A solution of the appropriate chlorofluoro compound in aliphatic amine (triethylamine, dimethylisopropylamine, diethylmethylamine, diethylamine or propylamine; see Table I) was irradiated with a Tesla RVK 125 water-cooled mercury lamp in a submersible photochemical reactor. During the irradiation the amine hydrochloride deposited on the quartz part of the reactor and the deposit was continuously removed by washing with water. The reaction mixture was stirred by introduction of nitrogen through a sintered glass in the bottom of the reactor.

When the irradiation was finished, the amine was distilled off, the residue was dissolved in ether, washed with dilute hydrochloric acid and aqueous sodium hydrogen carbonate, and dried over anhydrous magnesium sulfate. After filtration, the solvent was evaporated and the product distilled. The relative amount of the products and starting compounds was determined by GLC. The reaction conditions and results for the individual experiments are given in Table I. Alcohols **12** and **17** were identified by comparison of elution times with those of standards<sup>5</sup>.

*3,3,4-Trifluoro-2-butanol 7*, b.p. 108 °C. For  $C_4H_7F_3O$  (128.1) calculated: 37.51% C, 5.50% H, 44.50% F; found: 36.28% C, 5.25% H, 43.92% F.  $^1H$  NMR spectrum: 1.32 d, 1 H,  $^3J(H,H) = 6.6$  ( $CH_3-CH$ ); 3.3 s, 1 H (OH); 4.60 m, 1 H (CH); 6.43 dd, 2 H,  $^2J(H,F) = 47$ ,  $^3J(H,F) = 14$  ( $CH_2F$ ).  $^{19}F$  NMR spectrum: -119.9 d, and -127.6 d, 2 F,  $^2J(F,F) = 266$ ,  $^3J(F,F) = 13$  ( $CF_2$ ); -239.9 s, 1 F ( $CH_2F$ ).

*3,3,4-Trifluoro-2-methyl-2-butanol 1*, b.p. 120 °C. For  $C_5H_9F_3O$  (142.1) calculated: 42.26% C, 6.38% H, 40.10% F; found: 42.51% C, 6.24% H, 39.91% F.  $^1H$  NMR spectrum: 1.34  $2 \times$  s, 6 H ( $(CH_3)_2C$ ); 2.10 s, 1 H (OH); 4.68 dt, 2 H,  $^2J(H,F) = 47$ ,  $^3J(H,F) = 7$  ( $CH_2F-CF_2$ ).  $^{19}F$  NMR spectrum: -123.2 dt, 2 F,  $^3J(H,F) = J(F,F) = 13$  ( $CF_2$ ); -239.6 tt, 1 F,  $^2J(H,F) = 47$ ,  $^3J(F,F) = 14$  ( $CH_2F$ ).

*1,2,2-Trifluoro-3-methyl-3-pentanol 10*, b.p. 132–135 °C. For  $C_6H_{11}F_3O$  (156.1) calculated: 46.15% C, 7.10% H, 36.57% F; found: 46.57% C, 7.16% H, 36.87% F.  $^1H$  NMR spectrum: 0.99 t, 3 H,  $^3J(H,H) = 7.5$  ( $CH_3-CH_2$ ); 1.27 s and 1.28 s, 3 H ( $CH_3$ ), 1.66 dq, 2 H,  $^3J(H,H) = 7$  ( $CH_2-CH_3$ ); 4.68 dt, 2 H,  $^2J(H,F) = 47$ ,  $^3J(H,F) = 13$  ( $CH_2F$ ).  $^{19}F$  NMR spectrum: -122.4 ddt, 2 F,  $^2J(F,F) = 68$ ,  $^3J(F,F) = 14$ ,  $^3J(H,F) = 13$  ( $CF_2$ ); -240 tt, 1 F,  $^2J(H,F) = 47$ ,  $^3J(F,F) = 14$  ( $CH_2F$ ).

*3,3,4,5,5,6-Hexafluoro-2-methyl-2-hexanol 13*, b.p. 70–78 °C/4.26 kPa. For  $C_7H_{10}F_6O$  (224.1) calculated: 37.51% C, 4.50% H, 50.86% F; found: 38.78% C, 4.73% H, 49.88% F.  $^1H$  NMR spectrum: 1.41 s, 6 H ( $(CH_3)_2C$ ); 1.96 s, 1 H (OH); 4.69 dm, 1 H,  $^2J(H,F) = 45$  ( $CH_2F$ ); 5.26 d, 1 H,  $^2J(H,F) = 43$  (CHF).

*3,3,4,5,5,6,7,7,8-Nonafluoro-2-methyl-2-octanol 14*, b.p. 116–118 °C/3.73 kPa.  $^1H$  NMR spectrum: 1.39 s and 1.41 s, 6 H ( $(CH_3)_2C$ ); 1.96 s, 1 H (OH); 4.68 m, 2 H (H-8); 5.13 m, 1 H (H-6); 5.24 m, 1 H (H-4).

## Photochemical Reduction of Chlorotrifluoroethylene Oligomer Kel-F 10

The material used was Kel-F 10 from Carlo Erba. Elemental analysis: 18.50% C, 0.30% H, 31.55% Cl, 49.00% F.  $^{19}F$  NMR spectrum: -63.46 s, ( $CFCl_2-CF_2-$ ) together with multiplet -62 to -68 ppm ( $CF_2Cl-CFCl$ ); -105 to -110 m ( $CF_2-CFCl$ ); -125 to -130 m ( $CF_2-CFCl$ ).

A solution of Kel-F 10 (10.0 g, 0.085 mol) in 630 ml (504 g, 8.4 mol) of 2-propanol was irradiated with a high pressure 125 W mercury lamp in a photochemical reactor for 27 h at 15–20 °C. After evaporation of the 2-propanol, the product was dissolved in ether and washed with saturated aqueous solution of sodium hydrogen carbonate ( $2 \times 10$  ml) and water ( $2 \times 10$  ml) and dried over potassium carbonate. Removal of the solvent afforded 7.48 g of a dark oil which on steam distillation gave 4.2 g (42 wt.%) of a light yellow product. This was characterized by elemental analysis and NMR spectra.

Elemental analysis: 27.74% C, 1.45% H, 7.94% Cl, 63.81% F.  $^1\text{H}$  NMR spectrum: 5.15 dm, (CFH–CF<sub>2</sub>); 6.32 dt,  $^2J(\text{H,F}) = 47.7$ ,  $^3J(\text{H,F}) = 12$  (HCFCl–CF<sub>2</sub>).  $^{19}\text{F}$  NMR spectrum: –63.3 ddd (CF<sub>2</sub>Cl–CFH); –116 dm (CF<sub>2</sub>–CFH); –118.9 m and –123.5 m (CF<sub>2</sub>–CFH); –153.94 d,  $J(\text{H,F}) = 38$  (HCFCl–); –158.15 m and –159.06 m,  $^2J(\text{H,F}) = 47$  (HCFCl–CFH); –210 to –215 m (CF<sub>2</sub>–CFH–CF<sub>2</sub>).

### 3,3-Difluoro-2,2-dimethyloxetane **18** and 3-Difluoromethyl-2,2-dimethyloxirane **19**

A mixture of alcohols **1** and **2** (12 g, ratio 3 : 1) was heated at 80–100 °C with aqueous KOH (16 ml) for 17 h and the crude reaction mixture was steam-distilled to give 7.66 g of a mixture of oxetane **18** and oxirane **19** (75 : 25). Subsequent fractionation afforded oxetane **18**, b.p. 65.5–68.5 °C (76 mole %). For C<sub>5</sub>H<sub>8</sub>F<sub>2</sub>O (122.1) calculated: 49.17% C, 6.60% H, 31.08% F; found: 49.47% C, 7.05% H, 30.44% F.  $^1\text{H}$  NMR spectrum: 1.43 s, 6 H ((CH<sub>3</sub>)<sub>2</sub>–C); 4.60 t, 2 H,  $^3J(\text{H,F}) = 13$  (CH<sub>2</sub>).  $^{19}\text{F}$  NMR spectrum: –112.8 t,  $^3J(\text{H,F}) = 13$  (CF<sub>2</sub>). Mass spectrum,  $m/z$  (rel. int., %): 122 (0.01), 107 (3), 92 (10), 77 (21), 65 (5), 64 (9), 58 (34), 43 (100).

Preparative GLC afforded oxirane **19** (20 mole %). For C<sub>5</sub>H<sub>8</sub>F<sub>2</sub>O (122.1) calculated: 49.17% C, 6.60% H, 31.08% F; found: 49.37% C, 6.80% H, 32.97% F.  $^1\text{H}$  NMR spectrum: 1.36 s, 6 H ((CH<sub>3</sub>)<sub>2</sub>C); 2.98 q, 1 H,  $^3J(\text{H,H}) = 6$  (CHF<sub>2</sub>–CH); 5.50 dt, 1 H,  $^2J(\text{H,F}) = 54$ ,  $^3J(\text{H,H}) = 6$  (CHF<sub>2</sub>–CH).  $^{19}\text{F}$  NMR spectrum: –121.15 dd,  $^2J(\text{H,F}) = 54$ ,  $^3J(\text{H,F}) = 5$  (CHF<sub>2</sub>–CH). Mass spectrum,  $m/z$  (rel. int., %): 122 (0.25), 107 (0.75), 103 (1.2), 91 (1.7), 71 (9), 65 (6), 61 (9), 58 (56), 51 (20), 43 (100), 41 (80), 40 (50), 39 (60), 29 (20).

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