

## Photoinduced Fluorination of Hexafluoropropene Trimers: Synthesis of Branched Perfluoroalkanes

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Hexafluoropropene trimers, perfluoro-3-ethyl-2,4-dimethylpent-2-ene (**1**) and perfluoro-3-isopropyl-4-methylpent-2-ene (**2**) reacted with fluorine under u.v. irradiation to give the new and highly branched perfluoroalkanes perfluoro-2,3,3,4-tetramethylpentane (**7**) and perfluoro-2,3,4-trimethylpentane (**8**) through a mechanism involving the elimination–readdition of  $\text{CF}_3$  groups. Compound (**7**), which is very bulky, can be easily cleaved at  $< 200^\circ\text{C}$  to give two perfluoro radicals capable of initiating the polymerization of vinylic monomers.

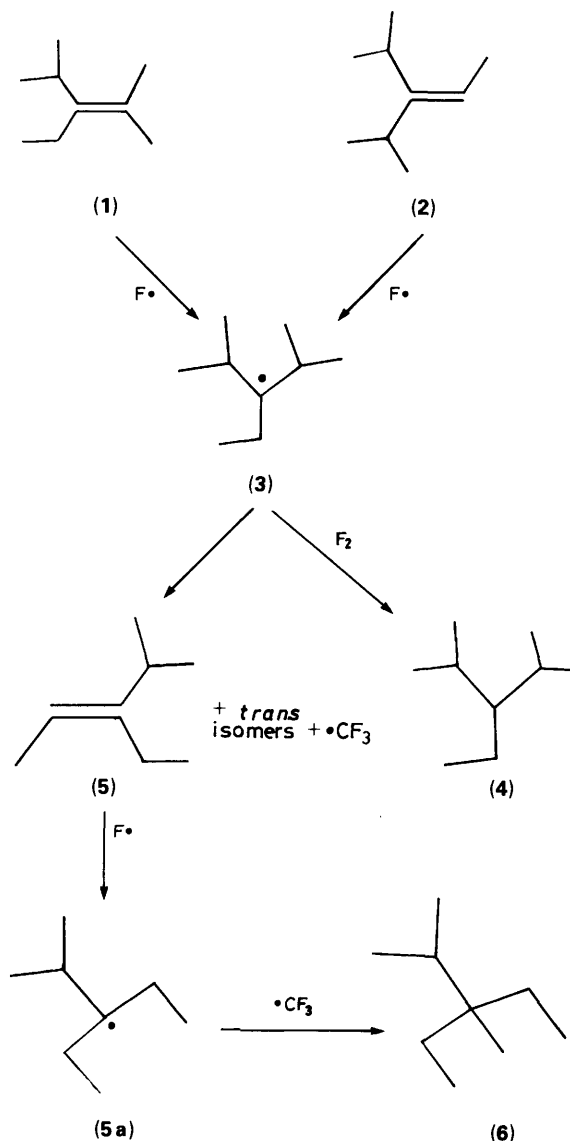
Anionic oligomerization of hexafluoropropene is a well known reaction<sup>1</sup> which gives branched internal olefins, useful starting materials in many industrial applications.<sup>2</sup> Fluorination of these olefins with fluorine<sup>3</sup> produces the corresponding perfluoroalkanes in moderate to good yield together with products of decomposition.

Recently Scherer<sup>4</sup> isolated the first air-stable perfluororadical, 3-ethyl-2,4-dimethylpentan-3-yl (**3**) during fluorination with  $\text{F}_2$  of (**1**) and (**2**), confirming once more the well established radical mechanism of fluorine attack on perfluoro-olefins (Scheme 1). He explained the surprising formation of (**6**) at  $104^\circ\text{C}$  by assuming a mechanism involving elimination–readdition of  $\text{CF}_3$  groups.

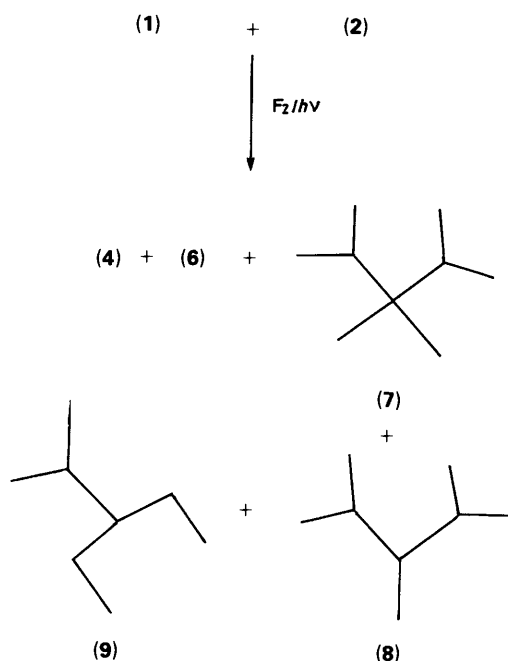
The key intermediate of the reaction is the stable radical (**3**), identified by g.l.c.–m.s. and e.s.r. analysis.

While we were studying the reaction of (**1**) and (**2**) with fluorine at  $\leq 0^\circ\text{C}$ , we observed in the presence of u.v. light a drastic change in the type of products produced: two new perfluoroalkanes, (**7**) and (**8**), were the main products of reaction together with small amounts of other known compounds (Scheme 2).

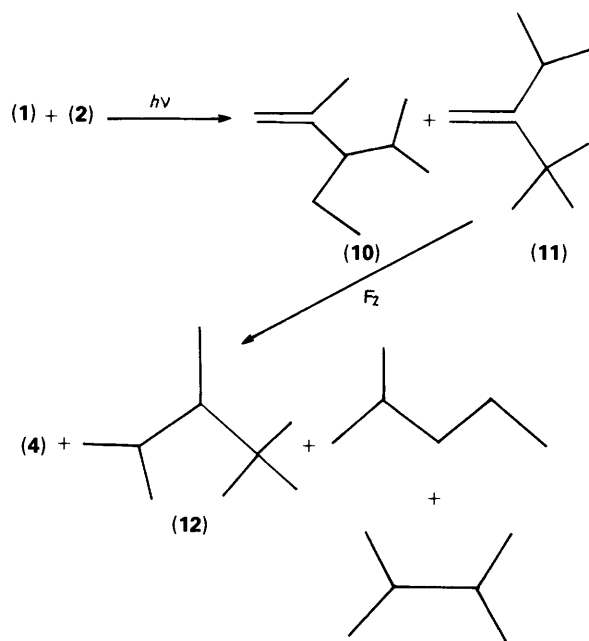
To confirm these surprising results we repeated the reaction several times varying the temperature, the concentration of starting olefins, and the fluorine feeding rate. In each case (**7**) and (**8**) were the main products. Very volatile compounds ( $\text{CF}_4$ ,  $\text{C}_2\text{F}_6$ ) were always present as minor by products (2–10% mol; recognized by g.l.c. comparison with authentic samples). All reaction products were isolated by fractional distillation and identified by g.l.c.–m.s. and n.m.r.<sup>19</sup> F analyses (see Experimental section). The results are summarized in Table 1. The unexpected course of the photoinduced reaction can be explained if we assume that the starting olefins or other intermediates interact with u.v. radiation. Therefore we measured the u.v. absorbance of some substituted fluoro-olefins in the range 200–450 nm (Table 2). It was confirmed that perfluoro-olefins with bulky substituents on the double bond, particularly when four substituents were present, had low but significant absorption at  $\lambda \approx 300$  nm. As a result we assumed that products came from fluorination of light-induced isomers of starting olefins. But photochemical isomerization of (**1**) and (**2**) gives two terminal olefins, perfluoro-3-ethyl-2,4-dimethylpent-1-ene (**10**) and perfluoro-2-isopropyl-3,3-dimethylbut-1-ene (**11**), which are not the unsaturated counterparts of photoinduced fluorination main products. In fact fluorination of (**10**) and (**11**) gives, respectively, (**4**) and perfluoro-2,2,3,4-tetramethylpentane (**12**), together with other decomposition products (Scheme 3).



Scheme 1. Photoinduced fluorination of hexafluoropropene trimers: synthesis of branched perfluoroalkanes



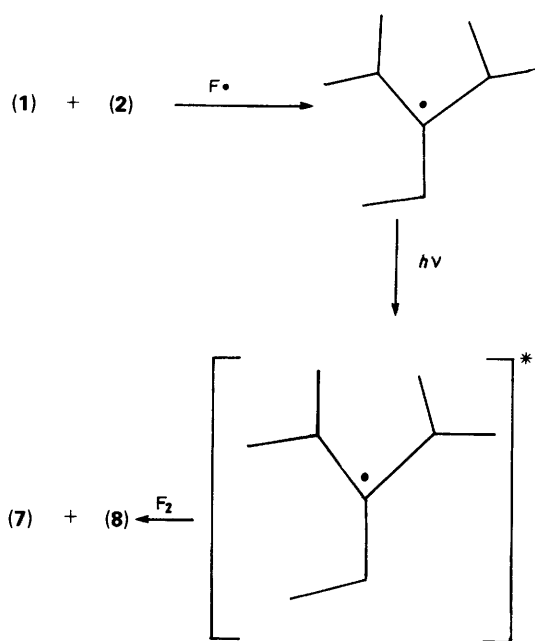
**Scheme 2.** Photoinduced fluorination of hexafluoropropene trimers: synthesis of branched perfluoroalkanes



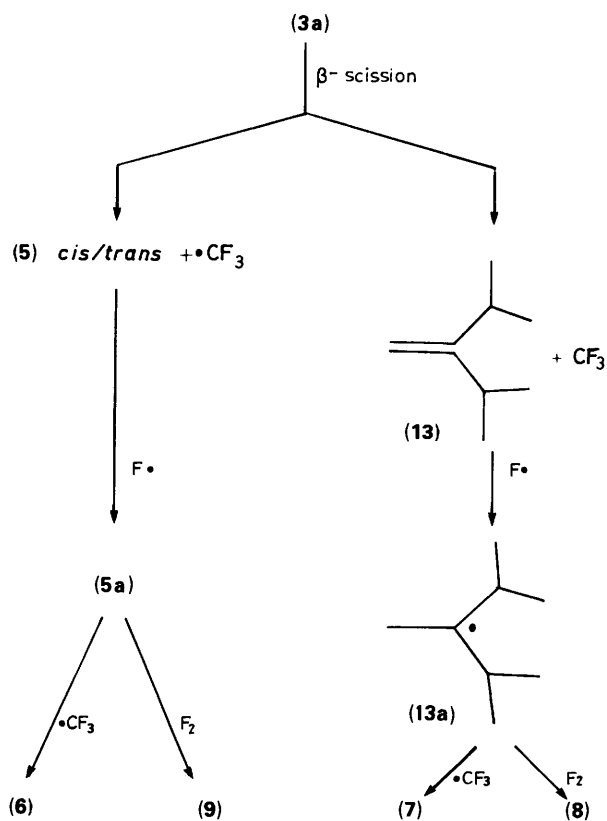
**Scheme 3.** Photoinduced fluorination of hexafluoropropene trimers: synthesis of branched perfluoroalkanes

Since both olefins (1) and (2) gave the same products even if they had different extinction coefficients, we thought that Scherer's radical could be again the common intermediate. In fact, pure (3) when isolated interacts with u.v. radiation in presence of fluorine to give the expected alkanes (7) and (8) (Scheme 4).

So the stable radical (3) can undergo an  $n \rightarrow \sigma^*$  transition of the unpaired electron to give a very unstable excited species (3a) which can rearrange in two ways: (i) the main pathway is the  $\beta$  elimination of  $\cdot CF_3$  from the  $CF_3CF_2$  group with formation of terminal alkene perfluoro-2-isopropyl-3-methylbut-1-ene (13), its reaction with  $F_2$  giving the intermediate perfluoro-2,3,4-trimethylpentan-3-yl (13a) which can react with  $F^\cdot$  or  $\cdot CF_3$  to



**Scheme 4.** Photoinduced fluorination of hexafluoropropene trimers: synthesis of branched perfluoroalkanes



**Scheme 5.** Photoinduced fluorination of hexafluoropropene trimers: synthesis of branched perfluoroalkanes






form compounds (8) and (7); (ii) the other is the  $\beta$  elimination of  $\cdot CF_3$  from the  $(CF_3)_2CF$  group with formation of the alkene (5), and reaction of the latter with  $F_2$  to give the intermediate perfluoro-3-isopropylpentan-3-yl (5a); this can then react with  $F^\cdot$  or  $\cdot CF_3$  to form compounds (9) and (6) (Scheme 5). For the olefin (1), which has a significant extinction coefficient (see Table 2), we cannot exclude at present that the 'hot' radical (3a)

**Table 1.** Photoinduced fluorination

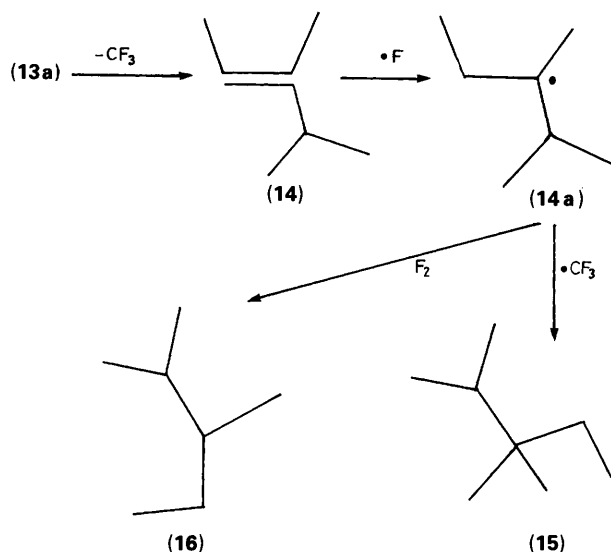
Run	Starting Compd.	Conc. <sup>a</sup> (mol l <sup>-1</sup> )	F <sub>2</sub> (dm <sup>3</sup> h <sup>-1</sup> )	Temp. (°C)	Yield of products (%)						
					(16)	(15)	(9)	(8)	(4)	(6)	(7)
1	(1)	0.56	0.9	15	5.1	<1.0	14.3	32.9	—	5.1	38.0
2	(1)	1.10	0.9	15	5.3	<1.0	11.0	25.7	—	7.3	49.0
3	(1)	1.78	0.9	15	1.1	<1.0	17.1	42.8	4.5	3.8	24.0
4	(1)	3.34	0.9	15	—	<1.0	12.6	33.6	15.2	4.6	26.0
5	(1)	1.10	0.9	5	4.4	<1.0	14.2	33.6	—	4.6	42.0
6	(1)	1.10	0.9	30	1.3	<1.0	16.8	44.1	3.4	3.7	25.9
7	(1)	1.10	0.7	15	13.0	9.7	3.0	6.7	—	6.0	55.0
8	(1)	1.10	0.4	15	12.4	16.7	2.8	4.7	—	7.1	46.0
9	(2)	0.48	0.9	15	—	—	—	—	98.0	—	—
10	(2)	0.67	0.4	5	12.0	8.9	8.9	8.9	5.2	10.1	42.0
11	(4)	0.45	0.4	5	1.6	<1.0	11.0	54.0	4.5	5.0	15.5

<sup>a</sup> Solvent: Fomblin Y 06/6.<sup>9</sup> Charged olefin: 0.1–0.7 mol. <sup>b</sup> Determined by quantitative g.l.c. analysis. Conversion of olefin is quantitative. Not detected 2–10% of very volatile products (CF<sub>4</sub>, C<sub>2</sub>F<sub>6</sub>, etc.).

**Table 2.** U.v. absorptions of branched fluoro-olefins<sup>a</sup>

Olefin					
$\lambda_{\max.}/\text{nm}$	—	—	296.2	320.4	296.6
$\Sigma/\text{mol}^{-1} \text{cm}^{-1}$	—	—	0.14	0.17	1.82

<sup>a</sup> Perfluoro-2-methylpentane as solvent.

**Scheme 6.** Photoinduced fluorination of hexafluoropropene trimers: synthesis of branched perfluoroalkanes

comes from reaction of an excited state of (1) ( $\pi \rightarrow \pi^*$  transition) with fluorine instead of reaction of (1) with fluorine to form (3) and then interaction with u.v. light.

This hypothetical mechanism is supported by isolation of the intermediates (5) (*cis-trans* isomers)<sup>4</sup> and (13), and can satisfactorily explain the experimental results. It follows that (i) the concentration of fluorine in solution is low enough to allow rearrangements of intermediate carbon radicals through elimination–readdition of •CF<sub>3</sub> groups without excessive loss by reaction with F<sub>2</sub>; (ii) rearrangement of (3a) is faster than its reaction with F• and •CF<sub>3</sub>; (iii) the rate of reaction of F• and •CF<sub>3</sub> with (5a) or (13a) is comparable with the rate of reaction of •CF<sub>3</sub> with F• or another •CF<sub>3</sub>.

According to this mechanism we can qualitatively explain the following experimental results. If fluorine is fed in very slowly [runs 7 and 8, Table (1)] we decrease the amounts of all products arising from F reactions, *i.e.* (4), (8), (9) while branched products deriving from •CF<sub>3</sub> group reactions, (6) and (7), increase. It is interesting to note that the new perfluoroalkane 2,3,3-trimethylpentane is now formed by further arrangement of (13a) (Scheme 6). There is a  $\beta$  scission of (13a) to form •CF<sub>3</sub> and the alkene (14), the latter reacting with fluorine to give (14a): this last intermediate can react with F• or •CF<sub>3</sub> to give respectively (16) and (15). We observed that although (16) is always present as a product (see Table 1) (15) is formed only in significant amounts when the rate at which fluorine is fed in very slow; this is because the rate at which •CF<sub>3</sub> groups couple to (14a) becomes competitive with F• coupling.

The olefin (2) is more reactive than (1) toward fluorine:<sup>4</sup> when F<sub>2</sub> is fed in at 0.9 l h<sup>-1</sup> and 15 °C (run 9, Table 1) we find only compound (4) because the concentration of (3) is high enough to react directly with F<sub>2</sub>. When we decrease both the temperature and the rate at which F<sub>2</sub> is fed in (run 10, Table 1) we allow, instead, formation of (3) and its rearrangement too, before reaction with F<sub>2</sub>. The influence of temperature and concentration of starting olefin on product distribution is quite difficult to explain even in qualitative terms: the overall reaction is very complex and final products are the result of several, probably opposing reaction parameters effects.

Since the main product of reaction, *i.e.* (7), is highly branched with two symmetrical bonds between the quaternary and tertiary carbon atoms, it decomposes at much lower temperatures than already known perfluoroalkanes.<sup>5</sup> In fact, at temperatures of *ca.* 140 °C homolytic scission of the most hindered C–C bond occurs to give a (CF<sub>3</sub>)<sub>2</sub>CF• radical (not detected) and a perfluoro-2,3-dimethylbutyl radical, detected and fully characterized by e.s.r. spectroscopy. Therefore (7) has potential as a new initiator for vinylic polymerization, which is both useful at low temperature and easily handled and stored.<sup>7</sup>

## Experimental

<sup>19</sup>F N.m.r. spectra were recorded on Varian 200 MHz spectrometer with CHCl<sub>3</sub>/CDCl<sub>3</sub> as solvent and CFCl<sub>3</sub> as internal standard; resolution-enhanced spectra, obtained with the application of Lorentzian-Gaussian weighting functions to the f.i.d.s. prior to Fourier transformation, show that the broad singlets relative to almost all fluorine atoms present in the perfluoroalkanes involved are actually complex multiplets due to through-bond and through-space scalar couplings. Such signals are indicated as multiplets (m).

Mass spectra were obtained on a Finnigan-MAT 8400 double focusing reverse geometry mass spectrometer equipped with a SuperIncos data system. Electron Capture Chemical Ionization spectra were recorded (negative ions) using isobutane as reagent gas at a pressure of 0.4–0.5 bar. Fragmentations are selective and highly informative: for the structural determination, the lack of certain peaks in a spectrum was as meaningful as the peaks effectively present.<sup>8</sup>

Irradiations were carried out with Hanau TQ 150 high-pressure mercury lamps. G.l.c. analyses were performed with a Hewlett Packard 5830 instrument equipped with thermo-conductivity detectors [4.5 m columns packed with 10% Fomblin Y R<sup>9</sup> on Chromosorb W HP (60–80 mesh), injection temperature 150 °C]. U.v. spectra were obtained on a Shimadzu u.v. 160 spectrophotometer.

**Fluorination of Perfluoro-3-ethyl-2,4-dimethylpent-2-ene (1) and perfluoro-3-isopropyl-4-methylpent-2-ene (2): General Procedure.**—In a cylindrical reactor of 300 ml capacity (15 cm high), fitted with a magnetic stirrer, a reflux condenser (–78 °C), and a central immersion lamp, undiluted fluorine was bubbled from the bottom into the solution of alkene and Fomblin Y 06/6<sup>9</sup> until conversion was quantitative (followed by g.l.c. analysis on reaction sample). The reactor was connected to a cold trap (–78 °C) to collect off-products. Experimental details are reported in Table 1.

The crude mixture was washed with a 10% aqueous NaOH to remove fluorine and then distilled at reduced pressure on a Spaltror Fischer automatic instrument (60 plates column) to separate pure components. As an example, we report the distillation relative to run 2, Table 1 (starting olefin 104 g, products recovered after exhaustive fluorination 105 g); fractional distillation was performed starting at 760 mmHg and with an increase in the temperature until the head temperature was 40 °C to eliminate residual volatile compounds (CF<sub>4</sub>, C<sub>2</sub>F<sub>6</sub>, C<sub>3</sub>F<sub>8</sub>, total recovered 1.05 g). Then we gradually reduced the pressure to 200 mmHg and began to separate the products. We obtained with high purity (>98%): (16) (5.3 g), b.p. 45 °C at 200 mmHg; (8), (10.6 g), b.p. 67 °C at 200 mmHg; (9) (24.2 g), b.p. 69 °C at 200 mmHg; (6) (5.1 g), b.p. 80 °C at 130 mmHg; (7) (49.4 g), b.p., 83 °C at 130 mmHg.

Perfluoro-2,3,3,4-tetramethylpentane (7) (CF<sub>3</sub>)<sub>2</sub>CFC(CF<sub>3</sub>)<sub>2</sub>CF(CF<sub>3</sub>)<sub>2</sub>: δ<sub>F</sub> 55.5 (6 F, m, 2-F), 65.8 (12 F, m, 1-F), and 161.9 (2 F, m, 3-F); *m/z* 488 (0.1%), 319 (100%), and 169 (0.1%).

Perfluoro-2,3,4-trimethylpentane (8) (CF<sub>3</sub>)<sub>2</sub>CF<sub>2</sub>CF(CF<sub>3</sub>)CF(CF<sub>3</sub>)<sub>2</sub>: δ<sub>F</sub> 69.2 (3 F, m, 2-F), 70.1 (12 F, m, 1-F), 170.5 (1 F, m, 3-F), and 171.5 (2 F, m, 4-F); *m/z* 269 (100%), 169 (0.5%).

Perfluoro-2-isopropyl-3-methylbut-1-ene (13) [(CF<sub>3</sub>)<sub>2</sub>CF]<sub>2</sub>C=CF<sub>2</sub>: δ<sub>F</sub> 58.6 (2 F, septet, *J*<sub>13</sub> 22.3 Hz, *J*<sub>12</sub> <1 Hz not resolved, 1-F), 77.5 (12 F, d, 3-F), and 179.8 (2 F, m, 2-F).

Perfluoro-2,3,3-trimethylpentane (15) (CF<sub>3</sub>)<sub>2</sub>CFC(CF<sub>3</sub>)<sub>2</sub>CF<sub>2</sub>CF<sub>3</sub>: δ<sub>F</sub> 58.7 (6 F, m, 3-F), 67.1 (6 F, m, 1-F), 78.5 (3 F, m, 5-F), 102.8 (2 F, m, 4-F), and 166.9 (1 F, m, 2-F); *m/z* 369 (1.8%), 319 (100%), and 269 (54%).

Perfluoro-2,3-dimethylpentane (16) (CF<sub>3</sub>)<sub>2</sub>CF<sub>2</sub>CF(CF<sub>3</sub>)CF<sub>2</sub>CF<sub>3</sub>: δ<sub>F</sub> 70.0 (6 F, m, 1-F), 70.7 (3 F, m, 4-F), 80.4 (3 F, m, 6-F), 114.0 (2 F, AB system *J*<sub>F,F</sub> 280 Hz, 5-F), 176.7 (1 F, m, 3-F), and 181.0 (1 F, m, 2-F); *m/z* 388 (100%), 369 (0.5%), 269 (25%), 219 (11%), and 169 (1.3%).

**Photochemical Isomerization of (1) and (2).**—In a cylindrical

reactor of 300 ml equipped with a central immersion lamp a mixture of (1) and (2) (ratio 96:4; 300 g, 0.67 mol) were charged and irradiated whilst being stirred for 260 h at 35 °C. G.l.c. shows full conversion into perfluoro-3-ethyl-2,4-dimethylpent-1-ene (10) and perfluoro-2-isopropyl-3,3-dimethylbut-1-ene (11) in a 4:1 ratio. These terminal olefins were very difficult to purify by fractional distillation and were characterized by <sup>19</sup>F n.m.r. spectroscopy on the basis of an enriched mixture of both olefins.

Perfluoro-3-ethyl-2,4-dimethylpent-1-ene (10)\* (CF<sub>3</sub>)<sub>2</sub><sup>6</sup>CF<sub>3</sub>CF(CF<sub>2</sub>CF<sub>3</sub>)<sub>2</sub>C(CF<sub>3</sub>)=CF<sub>2</sub>: δ<sub>F</sub> 54.0–55.3 (3 F, m, 2-F), 57.0–60.0 (2 F, m, 1-F), 69.3–71.6 (6 F, m, 7-F), 79.5–80.5 (3 F, m, 5-F), 112.5–119.0 (2 F, m, 4-F), and 177.0–182.0 (2 F, m, 3-F and 6-F).

Perfluoro-2-isopropyl-3,3-dimethylbut-1-ene (11) (CF<sub>3</sub>)<sub>3</sub>CC-[CF<sub>2</sub>(CF<sub>3</sub>)<sub>2</sub>]=CF<sub>2</sub>: δ<sub>F</sub> 49.3 (1 F, septet of doublets, *J*<sub>1,3</sub> 30.1 Hz, 1'-F), 50.6 (1 F, dectet of doublets, *J*<sub>1,1'</sub> 7.5 Hz, 1-F), 60.8 (9 F, t, *J*<sub>4,1</sub> = *J*<sub>4,2</sub> 26.4 Hz, 4-F), 73.4 (6 F, d, 3-F), 171.5 (1 F, nonet, 2-F).

**Fluorination of (10) and (11).**—In a cylindrical reactor of 80 ml capacity, containing a solution of (10) and (11) (ratio 65:35; 40 g, 8.88 mmol) in Fomblin Y 06/6 (45 ml), undiluted fluorine at 0.9 dm<sup>3</sup> h<sup>-1</sup> was bubbled from the bottom, at 5 °C for 7 h. The reactor, 12 cm high, equipped with a magnetic stirrer and reflux condenser (–78 °C) was connected to a cold trap (–78 °C) to collect volatile products. The crude mixture was washed with 10% aqueous NaOH and then distilled *in vacuo*. We obtained 35 g of products and 6 g from the cold trap (95% total recovered). From g.l.c. analysis on the whole solution we found (12) (34%), (4) (10%), perfluoro-2-methylpentane (35%), perfluoro-2,3-dimethylbutane (15%), and 6% of unassigned products.

Perfluoro-2,2,3,4-tetramethylpentane (12) (CF<sub>3</sub>)<sub>3</sub>CCF(CF<sub>3</sub>)<sub>2</sub>CF(CF<sub>3</sub>)<sub>2</sub>: δ<sub>F</sub> 57.7 (9 F, m, 1-F), 66.2 (6 F, m, 5-F), 70.8 (3 F, m, 3-F), 159.5 (1 F, m, 2-F), and 162.5 (1 F, m, 4-F); *m/z* 488 (0.5%), 419 (1.5%), 319 (1.7%), 269 (0.5%), 219 (100%), and 169 (1.22%).

## Acknowledgements

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\* All signals are split in doublets due to the presence of stable rotamers at room temperature.<sup>10</sup>