riodic strong agitation. The test tube was cooled and opened. The solvent was evaporated and the residue was fractionated to give 1.72 g (42%) (IIa), bp 71°C (90 mm),  $n_D^{22}$  1.4390. Found, %: C 19.28, H 2.31, F 37.90. C4H6ClF5OS. Calculated, %: C 19.35, H 2.41, F 38.61. <sup>19</sup>F NMR spectrum ( $\delta$ , ppm, relative to CF<sub>3</sub>CO<sub>2</sub>H): -143.9 d (S-F<sub>A</sub>), -159.4 pent (S-F<sub>B</sub>, J<sub>FA</sub>-F<sub>B</sub> = 148.3 Hz, A:B = 1:4). PMR spectrum ( $\delta$ , ppm, relative to TMS): 4.1 m (CH), 3.4 m (CH<sub>2</sub>), 3.3 s (CH<sub>3</sub>, 1:2:3 intensity ratio). IR spectrum,  $\nu$ , cm<sup>-1</sup>, neat on KBr): 3015 w, 2970 m (CH), 1755 s (C=O), 1500-1410 s, 1220 s, 850 s, 775 s, 615 w, 565 m (S-F).

Under analogous conditions, 4 g (0.075 mole) (Ib) gave 3 g of an unidentified solid and 1.3 g (32.5%) (IIb), bp 36°C (10 mm),  $n_D^{20}$  1.4738. Found, %: C 15.9, H 1.1, N 6.4, F 43.9, S 13.9.  $C_3H_3ClF_5NS$ , Calculated, %: C 16.7, H 1.3, N 6.5, F 44.1, S 14.8. <sup>19</sup>F NMR spectrum ( $\delta$ , ppm): 132.2 d (S-F<sub>A</sub>), -134.1 pent (S-F<sub>B</sub>). PMR spectrum ( $\delta$ , ppm): 3.8 m (CH), 2.9 m (CH<sub>2</sub>), intensity ratio 1:2. IR spectrum ( $\nu$ , cm<sup>-1</sup>, neat on KBr): 3080 s (CH), 2300 s (CN), 1830 m, 1290 s, 1100 w, 975 s, 890 m, 685 s, 604 w, 488 m (S-F).

# CONCLUSIONS

Sulfur pentafluoride chloride adds readily to acrylic acid derivatives to give derivatives of l-chloro-2-pentafluorothiopropionic acid.

## LITERATURE CITED

1. W. A. Sheppard and C. M. Sharts, Organic Fluorine Chemistry, W. A. Benjamin, New York (1969).

REACTION OF PERFLUORO-2-METHYL-2-PENTENE WITH DI-TERT-BUTYL PEROXIDE

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The reactivity of perfluoro-2-methyl-2-pentene (I) relative to nucleophilic reagents has been studied in detail [1]. In all cases, the nucleophilic attack was directed toward C<sup>3</sup>.



The reaction of perfluoroalkene (I) with free radicals has virtually not been studied. The free radical addition of methanol and ethanol to (I) has been described. The structures of the products obtained indicated that radical attack in both these cases is directed exclusively at  $C^3$  of the olefin [2].\*

We have studied the reaction of perfluorolefin (I) with di-tert-butyl peroxide (II), which is a source of electrophilic tert-butoxyl and nucleophilic methyl radicals [3, 4].

A spectrum for a radical species, corresponding to attack only at C<sup>2</sup> (A) upon the thermal (140°C) and photochemical (20°C) initiation in the probe of an EPR spectrometer, was recorded. This spectrum is characterized by coupling of the unpaired electron with one  $\alpha$ -fluorine atom ( $a^{F-\alpha} = 63.3$  Oe, doublet), two equivalent  $\beta$ -fluorine atoms ( $a^{F-\beta} = 35.4$  Oe, triplet), and with nine equivalent  $\gamma$ -fluorine atoms ( $a^{F-\gamma} = 2.6$  Oe, decet)<sup>†</sup> (Fig. 1).

\*The intermediate free radical species were not determined. <sup>†</sup>The lifetime of this radical is several minutes. A reduction in the temperature to -120°C does not lead to cessation of the rotation of the perfluorethyl group.

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Fig. 1. EPR spectrum of 2-methylperfluoro-2-methyl-3-pentyl free radical.

The nature of the species, which adds at the double bond, in radical (A) was established as follows. The photolysis of a mixture of (I) and (II) at -50°C, when the tert-butoxyl radical does not decompose to a significant extent to give  $CH_3$  and acetone, does not lead to radical (A) but this radical is readily formed upon the irradiation of alkene (I) in the presence of MeI [5]. Thus, methyl radicals are active in this reaction.

In order to identify the final products, we carried out the reaction of fluorolefin (I) and peroxide (II) on a preparative scale: a 2:1 mixture of (I) and (II) was heated in an autoclave for 17 h at 140°C. The conversion of the alkene was 82%. A 1:4 mixture of 3-hydro-2-methyl-(III) and 2-hydro-3-methylperfluoro-2-methylpentanes (IV) formed as a result of the abstraction of a hydrogen atom by radicals (A) and (B), respectively, was obtained in 30% yield.



RH is a hydrogen donor.

A complex mixture of products with unestablished structure, containing hydrogen and oxygen in addition to carbon and fluorine, is obtained in addition to (III) and (IV).

These results indicate significantly greater stability of secondary radical (A) in comparison with tertiary radical (B), which supports the proposal of Probst et al. [6] on the stabilizing effect of the fluorine atoms in the  $\gamma$ -position to the radical site [nine  $\gamma$ -fluorine atoms in (A) and two  $\gamma$ -fluorine atoms in (B)]. Fluoroalkane (IV), which predominates in the isomer mixture, could not be detected by EPR spectroscopy from more reactive radical (B).

# EXPERIMENTAL

The EPR experiments were carried out in a Varian E-12A radiospectrometer. The photolysis was carried out by the focused irradiation of a DRSh-250M lamp in evacuated quartz ampuls.

The preparative gas-liquid chromatography on a Perkin-Elmer F-20 chromatograph was run using a 4 m  $\times$  20 mm column packed with 20% K-352 on Inerton AW.

The chromato-mass spectra were obtained on a Varian MAT CH-8 instrument at 70 eV using a 25 m capillary column packed with OY-101. The <sup>19</sup>F and <sup>1</sup>H NMR spectra were taken on a Bruker WP-200 spectrometer. The <sup>19</sup>F NMR spectra were taken at 188.3 MHz and the <sup>1</sup>H NMR spectra were taken at 200 MHz.

<u>3-Hydro-2-methyl- (III) and 2-Hydro-3-methylperfluoro-2-methylpentanes (IV).</u> A mixture of 7.3 g (0.05 mole) (II) and 30 g (0.1 mole) (I) was maintained for 17 h in a 50 ml steel

autoclave at 140°C. Distillation and preparative gas-liquid chromatography gave 7.9 g of a 1:4 mixture of (III) and (IV) [30% yield relative to consumed (I)], bp 91-94°C. Found, %: C 26.79, H 1.27, F 72.13. C<sub>7</sub>H<sub>4</sub>F<sub>12</sub>. Calculated, %: C 26.59, H 1.28, F 72.13. Mass spectra, m/z (intensity, % (>1%) relative to the strongest ion peak for (III)/for (IV)):  $[M - F]^+$ : 297(1.5/-),  $[M - HF - F]^+$ : 277(14.1/13.5)  $[C_7F_9H_2]^+$ : 257(3.8/2.6),  $[M - CF_3]^+$ : 247(9.6/-),  $[C_6F_9H_2]^+$ : 245(-/1.7),  $[M - CF_3 - HF]^+$ : 227(9.1/3.2),  $[C_5F_8H]^+$ : 213(1.3/1.9]),  $[C_6F_7H_4]$ : 209(2.8/-),  $[C_6F_7H_2]^+$ : 207(4.7/2.3),  $[M - C_2F_5]^+$ : 197(21.5/11.5),  $[C_5F_7H_2]^+$ : 195(1.4/-),  $[C_6F_6H_3]^+$ : 189(1.8/-),  $[M - C_2F_5 - HF]^+$ : 177(31.7-),  $[C_4F_6H_3]^+$ : 165(6.1/10.2),  $[C_4F_6H]^+$ :  $163(6.7/1.7), \ [C_5F_5H_4]^+: \ 159(15.2/2.6), \ [C_5F_5H_2]^+: \ 157(4.5/1.3), \ [C_3F_6H]^+: \ 151(9.2/-),$  $[C_{4}F_{5}H_{2}]^{+}$ : 145(19.4/6.9),  $[C_{5}F_{4}H_{3}]^{+}$ : 139(3.1/-),  $[C_{5}F_{4}H]^{+}$ : 137(1.0/-),  $[C_{3}F_{5}H_{2}]^{+}$ : 133- $(1.3/-), [C_3F_5H]^+: 132(4.1/2.2), [C_4F_4H_3]^+: 127(43.1/-), [C_2F_5]^+: 119(9.8/2.8), [C_3F_4H_3]^+:$ 115(10.1/2.2),  $[C_3F_4H]^+$ : 113(20.2/8.7),  $[C_4F_3H_4]^+$ : 109(24.0/4.7),  $[C_2F_4H]^+$ : 101(2.5/-),  $[C_2F_4]^+: 100(2.6/1.3), [C_3F_3H_2]^+: 95(20.7/10.4), [C_3F_3]^+: 93(1.5/-), [C_4F_2H_3]^+: 89(5.1/2)$ 2.5), [C<sub>2</sub>F<sub>3</sub>H]<sup>+</sup>: 82(6.6/-), [C<sub>3</sub>F<sub>2</sub>H<sub>3</sub>]<sup>+</sup>: 77(21.4/10.7), [C<sub>3</sub>F<sub>2</sub>H]<sup>+</sup>: 75(5.4/1.2), [CF<sub>3</sub>]<sup>+</sup>: 69-(100/38.2),  $[C_2F_2H_3]^+$ : 65(6.4/100),  $[C_2F_2H_2]^+$ : 64(1.3/1.7),  $[C_3FH_4]^+$ : 59(4.0/1.3),  $[C_3-100/38.2)$ FH<sub>2</sub>]<sup>+</sup>: 57(3.7/1.5), [CF<sub>2</sub>H]<sup>+</sup>: 51(45.4/8.9), [C<sub>2</sub>FH<sub>4</sub>]<sup>+</sup>: 47(1.3/-), [C<sub>2</sub>FH<sub>2</sub>]<sup>+</sup>: 45(-/1.1). <sup>19</sup>F NMR spectra in CDCl<sub>3</sub>( $\delta$ , ppm, relative to CF<sub>3</sub>CO<sub>2</sub>H as the external standard, J, Hz): (III): -9.4 q. d. q ( $CF_3^a$ , J = 10.3, 5.5, 1.3), -7.9 q.d ( $CF_3^b$ , J = 10.3, 5.5), 5.6 d ( $CF_3^c$ , J = 15.0), 41.6, 52.5 ( $CF_2^{AB}$ ,  $J_{AB} = 280.0$ ), 126.0 m (CF); (IV): -17.1 m ( $CF_3^a$ ,  $CF_3^b$ ), 1.3 d  $(CF_3^c, J = 16.5), 43.1, 45.3 (CF_2^{AB}, J = 281.0), 85.0 m (CF).$  PMR spectrum in CDCl<sub>3</sub> ( $\delta$ , ppm, relative to HMDS at the external standard, J, Hz): (III): 1.63 d. hept (CH<sub>3</sub>, J = 0.9, 0.9), 5.13 d.d.d (CH, J = 42.5, 22.0, 1.0); (IV): 1.91 d (CH<sub>3</sub>, J = 24.0), 3.85 hept, d (CH, J =  $\frac{1}{2}$ 7.9, 1.9).

## CONCLUSIONS

1. The reaction of perfluoro-2-methyl-2-pentene with di-tert-butyl peroxide gives a 4:1 mixture of 2-hydro-3-methyl- and 3-hydro-2-methylperfluoro-2-methylpentanes.

2. Only the 2-methylperfluoro-2-methyl-3-pentyl free radical was detected by EPR spectroscopy upon thermal and photochemical initiation.

## LITERATURE CITED

- 1. N. Ishikawa and M. Maruta, J. Synth. Org. Chem. Jpn., <u>39</u>, 51 (1981).
- 2. N. Ishikawa, A. Nagashima, and S.-I. Hayashi, J. Chem. Soc. Jpn., No. 7, 1240 (1974).
- 3. L. F. Fieser and M. Fieser, Reagents for Organic Synthesis, Vol. 1, Wiley, New York (1967).
- J. M. Tedder, Angew. Chem. Int. Ed., <u>21</u>, 401 (1982); B. Giese, Angew. Chem. Int. Ed., <u>22</u>, 753 (1983).
- 5. B. L. Tumanskii, A. N. Degtyarev, N. N. Bubnov, et al., Izv. Akad. Nauk SSSR, Ser. Khim., No. 11, 2627 (1980).
- 6. A. Probst, K. Raab, K. Ulm, and K. von Werner, J. Fluor. Chem., <u>37</u>, 223 (1987).