

in these systems. Also, the substantial difference in magnetic properties between this adduct and anhydrous copper(II) trifluoroacetate<sup>12</sup> reinforces the view<sup>11-13</sup> that the anhydrous material does not possess the bridged dimeric structure.

Finally, we note that the general difficulty of preparing dimeric copper(II) trifluoroacetate adducts and the strong tendency of this complex to undergo hydrolysis are consistent with the observation that the bridged dimeric structure tends to be destabilized as the strength of the parent carboxylic acid increases. This appears to be a well-established trend and may be rationalized in a number of ways. The great lability of  $[\text{Cu}(\text{O}_2\text{CCF}_3)_2(\text{quin})]_2$  to hydrolysis suggests that it could be of interest to investigate its reactions with other ligands in the absence of water. It is conceivable that such reactions could afford a route for preparation of novel bridged dimeric species which are not readily obtainable from the more stable copper(II) acetate dimers.

**Acknowledgments.** We are grateful to the National Science Foundation for support of this work and to Dr. David Jeter for numerous helpful conversations.

**Supplementary Material Available.** A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24X reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D.C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.00 for microfiche, referring to code number JACS-75-508.

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## Synthesis of Structurally Unusual Fluorocarbons by Direct Fluorination

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**Abstract:** The reaction of elemental fluorine with structurally unusual hydrocarbon starting materials has been carefully controlled so that structurally analogous perfluorocarbons have been successfully obtained. The syntheses by direct fluorination of perfluoroneopentane, perfluorohexamethylethane, perfluoronorborene, 1-hydroxoundecafluoronorborene, perfluorocyclooctane, and monohydropentadecafluorocyclooctane are reported.

New techniques for controlling the reactions of elemental fluorine<sup>2</sup> have recently been discovered which are of significant utility in both inorganic<sup>3-5</sup> and organic<sup>3,6</sup> synthesis. Hydrocarbons, hydrocarbon polymers,<sup>7</sup> and other hydrocarbon derivations with functional groups, particularly those containing oxygen,<sup>8</sup> have been previously studied in this

laboratory. The synthesis of structurally unusual (see Figure 1) fluorocarbons in our laboratory was undertaken because the delicate structures were a challenge to the technique and because many of the perfluorocarbons prepared are also of interest. This task has led to the development of new techniques and apparatus<sup>3,8</sup> to overcome difficulties as

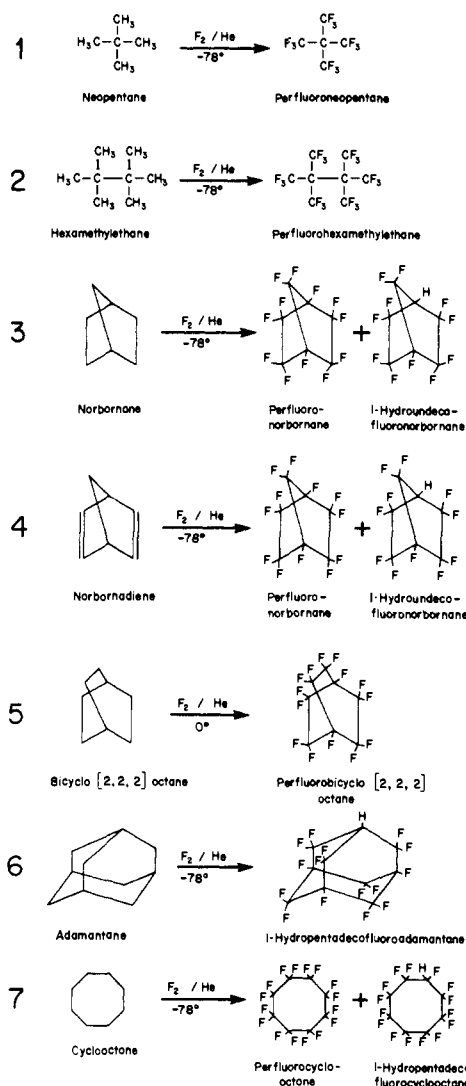


Figure 1.

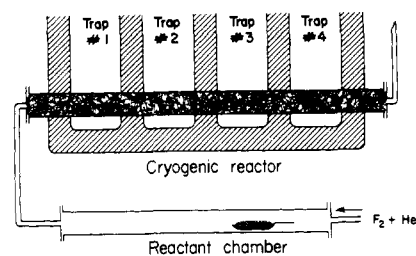
sociated with the fluorination of these materials. In the case of the syntheses of compounds such as perfluoronorbornane and perfluorobicyclo[2.2.2]octane, we are able to compare the results obtained by direct fluorination with those recently obtained by Tatlow and coworkers<sup>9,10</sup> using the more established cobalt trifluoride fluorination technique. Thus, insight can be gained into the relative merits of this new method with those of the cobalt trifluoride fluorination. In several other cases, such as the fluorination of neopentane, hexamethylethane, adamantane, and cyclooctane, the synthesis of the perfluorocarbon analogs by the cobalt trifluoride method, electrochemical fluorination, or other fluorination techniques has not been reported or, in some cases, has not been successful.

### Experimental Section

Mass spectra were measured on a Hitachi RMU 6D mass spectrometer at 70 eV. Nmr spectra were taken on a Perkin-Elmer R20-B spectrometer, at 60 Hz for protons and 56.4 MHz for fluorine, and a Bruker HFX 90 with Fourier transform capabilities. Gas chromatography was done on a Varian or Bendix gas chromatograph equipped with a cryogenic controller and thermal conductivity detector. Columns were made of 10% SE-30 on Chromosorb P and 13% fluorosilicone on Chromosorb P. Both columns were 10 ft  $\times$  0.25 in. Analyses were done by Schwarzkopf Microanalytical Laboratory. Infrared data were collected on a Beckman IR 20A instrument.

The two types of reactor systems used are illustrated in Figure 2. System A was used for the fluorination of neopentane, hexamethy-

### A. Cryogenic reactor system



### B. Bucket reactor system

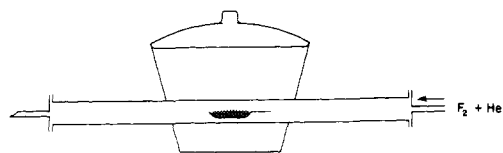


Figure 2.

lethane, norbornane, norbornadiene, and cyclooctane. The reaction chamber was made from a nickel tube and was 18 in. long and 1.5 in. wide. It was connected with 0.25 in. copper tubing to the cryogenic reactor. The cryogenic reactor consisted of a nickel tube 24 in. long and 1.5 in. wide, tightly packed with fluorinated copper turnings. It was enclosed by a stainless steel cold box of overall depth of 9 in. and width of 6 in. The individual compartments were 4  $\times$  4  $\times$  8 in. and were insulated with urethane foam. The general method for introducing compounds into the cryogenic reactor was as follows; the solid or liquid reactant was placed in a nickel boat in the reactant chamber, a helium flow was then used to carry the vapor over and condense it into the first zone of the cryogenic reactor which was cooled to the temperature needed to freeze the reactant. The individual zones of the cryogenic reactor can be cooled to 0° with ice, -78° with Dry Ice-solvent sludges, or to any temperature between 0 and -150° using a liquid nitrogen temperature controller. The reactant was vaporized slowly down the reactor by successive warming and cooling of zones. The more highly fluorinated material was more volatile than the partially fluorinated material and moved through the zones more quickly, thus providing a fresh surface for further fluorination. The zones may also be heated above room temperature with an immersion heater. Alternatively, a liquid can be introduced by directly syringing it into the copper turnings by way of a Swagelok T joint just before the cold reactor.

Reactor B is a "bucket" reactor and consists of an 18  $\times$  1.5 in. nickel tube passing through a urethane ice bucket. This reactor was used for the fluorination of bicyclo[2.2.2]octane and adamantane. The reactant was placed in a nickel boat and the boat placed in the middle of the area cooled by the bucket. The bucket could be cooled to 0° with ice water or to -78° with an isopropyl alcohol-Dry Ice mixture.

**Fluorination of Neopentane.** A glass trap with ~1 g of NaF pellets was attached to the end of the four zone cold reactor system. The entire system was flushed with helium for 12 hr, then the glass trap cooled to -78°. The first two zones of the cold reactor were cooled to -78° and a 2.052-g ( $2.82 \times 10^{-2}$  mol) sample of neopentane condensed in the first zone. The fluorination conditions shown in Table I were used.

Table I

Zone (temp, °C)	He flow, cm <sup>3</sup> /min	F <sub>2</sub> flow, cm <sup>3</sup> /min	Time, hr
1, 2 (-78)	20	1.5	48
2, 3 (-78)	0	1.5	24
3, 4 (-78)	0	1.5	24
4 (-78)	0	1.5	24
1, 2, 3, 4 (RT) <sup>a</sup>	20	0	24

<sup>a</sup> RT = room temperature.

Table II

Zone (Temp, °C)	He flow cm <sup>3</sup> /min	F <sub>2</sub> flow cm <sup>3</sup> /min	Time, hr
1, 2, (-78)	20	1.5	15
2, 3, (-78)	20	1.5	9
2, 3, (-78)	8	1.5	24
3, 4, (-78)	0	1.5	32
1, 2, 3, 4, (RT) <sup>a</sup>	20	0	24

<sup>a</sup> RT = room temperature.

The glass trap was removed from the system, cooled in liquid nitrogen, and evacuated. The trap was then allowed to warm to room temperature and was shaken periodically for 12 hr. The volatile material was transferred into a liquid nitrogen cooled vial, diluted with CCl<sub>4</sub>, and subsequently separated by gas chromatography. A 10 ft × 0.25 in. column of 10% SE-30 on Chromosorb P was held at 0° for the separation. Perfluoroneopentane had a retention time of 3.5 min from injection. Perfluoroneopentane (0.849 g, 0.294 × 10<sup>-2</sup> mol) was obtained which corresponds to a 10.4% yield. The melting point was determined in a sealed capillary and found to be 72.5–73° in agreement with the reported value.<sup>11</sup> Anal. Calculated for C<sub>5</sub>F<sub>12</sub>: C, 20.84; F, 79.15. Found: C, 20.67; F, 79.23. The gas phase infrared spectrum contained three strong bands at 1300, 980, and 720 cm<sup>-1</sup> and a very weak band at 1190 cm<sup>-1</sup>, in agreement with the reported spectrum.<sup>12</sup> The <sup>19</sup>F nmr spectrum consisted of a singlet at -13.92 ppm from an external trifluoroacetic acid reference. A value of -13.8 ppm has been reported for perfluoroneopentane.<sup>13</sup> The mass spectrum of the compound at 70 eV does not contain a parent peak but exhibits a strong P - 19 peak at 269. The CF<sub>3</sub><sup>+</sup> ion is the most intense peak in the spectrum.

**Fluorination of Hexamethylethane.** In a typical experiment, a 0.4237-g (3.71 × 10<sup>-3</sup> mol) sample of hexamethylethane was placed in a nickel boat. The first two chambers of the cold reactor were filled with a Dry Ice-isopropyl alcohol slush (-78°) and allowed to reach the equilibrium temperature. The glass trap at the end of the cold reactor was filled with approximately 1 g of NaF and cooled to -78°. The system was flushed with helium for 0.5 hr. The fluorination conditions shown in Table II were used.

Twelve hours after the compartments had warmed, the stopcocks to the glass trap were closed, and it was removed from the system. The trap was immersed in liquid nitrogen and evacuated on a vacuum line. The trap was then warmed to room temperature, allowed to stand for 12 hr, and shaken periodically to allow the HF produced in the reaction to be absorbed by the NaF. The trap was reconnected to the vacuum line, and the volatile products were trapped with liquid nitrogen. Mixed fluorocarbons (0.6461 g) were obtained. This mixture was dissolved in CCl<sub>4</sub> and separated on a gas chromatograph at 20°. A 10 ft × 0.25 in. column of 10% SE-30 on Chromosorb P was used. A colorless, volatile crystalline material subliming at 108° and weighing 0.1525 g was isolated. A 9.3% yield was obtained based on the initial hexamethylethane. Anal. Calcd: C, 21.93; F, 78.06. Found: C, 21.94; F, 77.72. The <sup>19</sup>F nmr consisted of a very strong singlet at -22.0 ppm from an external trifluoroacetic acid reference. The gas phase infrared spectrum contained bands at 1285 (vs), 1260 (vs), 1245 (s), 1205 (s), 1135 (s), 880 (w), 850 (m), 735 (m), 715 (s), 535 (vw), and 5000 (vw) cm<sup>-1</sup>. The mass spectrum at 70 eV did not contain a parent peak, but a strong (P - 38)<sup>+</sup> (F<sub>2</sub>) peak is observed. The most intense peak in the spectrum was that of the CF<sub>3</sub><sup>+</sup> ion.

**Fluorination of Bicyclo[2.2.1]heptadiene (Norbornadiene).** The second zone of the cryogenic reactor was cooled to -78° with a Dry Ice slush. Norbornadiene (5 ml, 0.049 mol) (Chemical Samples Co.) was placed in a nickel boat in the reactant chamber. A helium flow of 60 cm<sup>3</sup>/min was initiated through the system to condense the norbornadiene in the first zone of the reactor which was at about -40°. The fluorination conditions shown in Table III were used.

The products were then taken to a vacuum line where the volatile material was condensed in a round-bottomed flask. This material was then dissolved in carbon tetrachloride, and the products were separated by cryogenic gas chromatography. The major products were perfluoronorbornane (1.261 g, 4.04 × 10<sup>-3</sup> mol, 8.22% yield) and monohydrundecafluoronorbornane (0.273 g, 9.29 × 10<sup>-3</sup> mol, 1.88% yield). The products were characterized by com-

Table III

Zone (Temp, °C)	He flow (cm <sup>3</sup> /min)	F <sub>2</sub> flow (cm <sup>3</sup> /min)	Time
1, 2 (-78)	30	0.5	48 hr
2 (-78)	30	0.5	48 hr
2 (-78)	30	1.5	24 hr
3 (-78)	15	1.5	12 hr
4 (-78)	15	1.5	12 hr
4 (-78)	0	1.5	12 hr
1, 2, 3, 4 (RT) <sup>a</sup>	0	1.5	4 days
1, 2, 3, 4 (RT) <sup>a</sup>	50	0	1 day

<sup>a</sup> RT = room temperature.

paring their physical properties with those reported in the literature.<sup>9,14</sup> Perfluoronorbornane, mp 106–106.5° (lit. 105–107°). Anal. Calcd for C<sub>7</sub>F<sub>12</sub>: C, 26.94; F, 73.05. Found: C, 26.69; F, 73.37. The mass spectrum shows a parent peak at *m/e* 312. Other prominent peaks in the spectrum were *m/e* 293 (C<sub>7</sub>F<sub>11</sub><sup>+</sup>), 243 (C<sub>6</sub>F<sub>9</sub><sup>+</sup>), 193 (C<sub>5</sub>F<sub>7</sub><sup>+</sup>), 162 (C<sub>4</sub>F<sub>6</sub><sup>+</sup>), 131 (C<sub>3</sub>F<sub>5</sub><sup>+</sup>), and 69 (CF<sub>3</sub><sup>+</sup>). The fluorine nmr showed three peaks at -42.85, -39.15, and +59.41 ppm from external C<sub>6</sub>F<sub>6</sub>. The peaks were in an integrated ratio of 4:1:1. The vapor phase ir gave bands at the following positions: 1315 (sh), 1290 (s), 1270 (vs), 1233 (s), 1010 (w), 970 (vs), 930 (s), 610 (w) cm<sup>-1</sup>.

1-Hydrundecafluoronorbornane, mp 94–95° (lit. 94–96°). Anal. Calcd for C<sub>7</sub>F<sub>11</sub>H: C, 28.58; F, 71.06. Found: C, 28.23; F, 70.65. The mass spectrum shows a parent peak at *m/e* 294. Other prominent peaks in the spectrum were *m/e* 275 (C<sub>7</sub>F<sub>10</sub>H<sup>+</sup>), 225 (C<sub>6</sub>F<sub>8</sub>H<sup>+</sup>), 175 (C<sub>5</sub>F<sub>6</sub>H<sup>+</sup>), 162 (C<sub>9</sub>F<sub>6</sub><sup>+</sup>), 113 (C<sub>3</sub>F<sub>4</sub>H<sup>+</sup>), and 69 (CF<sub>3</sub><sup>+</sup>). The <sup>1</sup>H nmr using C<sub>6</sub>F<sub>6</sub> as a solvent gives a broad, unresolved peak at 3.7 ppm from TMS. In CCl<sub>4</sub>, the peak is shifted to 1.8 ppm from TMS. The fluorine nmr shows a plethora of peaks (for the most part broad singlets of broad unresolved multiplets) from -42.9 to -37.9 ppm from C<sub>6</sub>F<sub>6</sub> and a broad singlet at +51.9 ppm from C<sub>6</sub>F<sub>6</sub>. The vapor phase ir gave bands at the following positions: 3020 (vww) 1365 (m), 1320 (vs), 1265 (vs), 1230 (vs), 1180 (m) cm<sup>-1</sup>.

**Fluorination of Bicyclo[2.2.1]heptane (Norbornane).** Norbornane (1.045 g, 0.1087 mol) (Chemical Samples Co.) was introduced into the cryogenic zone reactor in a manner similar to that described for norbornadiene. The conditions described in Table IV were then used. The products were worked up in the same way as the products from the norbornadiene reaction. The yield of perfluoronorbornane was 12.22% (0.414 g) and the monohydrundecafluoronorbornane was 8.14% (0.260 g).

**Direct Fluorination of Adamantane.** The bucket reactor was filled with a -78° bath (Dry Ice-isopropyl alcohol) and allowed to cool. Adamantane (0.723 g, 5.307 mmol) (Aldrich Chemical Co., Inc.) was placed in a boat and then in the reactor so the boat was in the middle of the area cooled by the -78° bath. See Table V for fluorination conditions. The glass trap (which had been cooled to -78° at the beginning of the run) was removed and taken to the vacuum line. The material was condensed into a 5-ml pear-shaped flask, dissolved with hexafluorobenzene, and separated on the gas chromatograph. A 4.4% (0.95 g) yield of monohydrundecafluoroadamantane was obtained.

It exhibits a mass spectrum consisting of the following peaks: 424 (C<sub>10</sub>F<sub>16</sub><sup>+</sup>), 406 (C<sub>10</sub>F<sub>15</sub>H<sup>+</sup>), 405 (C<sub>10</sub>F<sub>15</sub><sup>+</sup>), 205 (C<sub>6</sub>F<sub>7</sub><sup>+</sup>), 131

Table IV

Zone (Temp, °C)	He flow (cm <sup>3</sup> /min)	F <sub>2</sub> flow (cm <sup>3</sup> /min)	Time
1 (-78)	30	0.5	24 hr
2 (-78)	30	0.5	24 hr
2 (-78)	30	1.0	48 hr
2 (-78)	30	1.5	24 hr
3 (-78)	30	1.5	12 hr
3 (-78)	15	1.5	36 hr
3 (-78)	0	1.5	12 hr
4 (-78)	0	1.5	48 hr
1, 2, 3, 4 (RT) <sup>a</sup>	0	1.5	4 days
1, 2, 3, 4 (RT) <sup>a</sup>	50	0	1 day

<sup>a</sup> RT = room temperature.

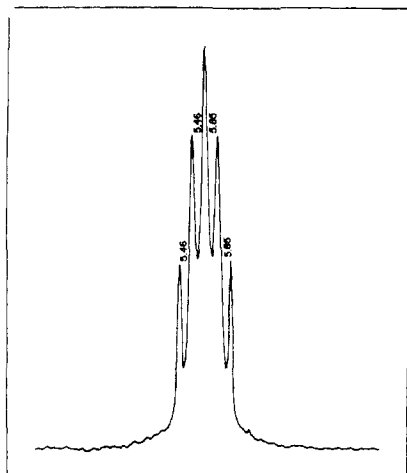


Figure 3.

( $C_3F_3^+$ ), 69 ( $CF_3^+$ ). Its melting point (sealed capillary) was 225–226°. Its gas phase infrared spectrum consisted of bands at 2911 (vw), 1305 (sh), 1285 (vs), 1080 (m), 970 (s), 745 (m), and 655 (w)  $cm^{-1}$ . The  $^{19}F$  nmr, taken in a solution of  $CCl_4$  and  $CFCl_3$  consisted of a quintet at 121.5 ppm and an unresolved peak at 223.6 ppm upfield from  $CFCl_3$ . The integrated ratio of the peaks was 3.95:1. The proton nmr showed a broad peak at 1.75 ppm downfield from TMS. (See Figure 3.)

In the  $^{19}F$  nmr of 1-hydropentadecafluoroadamantane, the coupling constants  $J_{CF_2-CF}$  and  $J_{CF_2-CF}$  are very similar while the chemical shifts of the two types of  $CF_2$  sites differ as expected. The methylene fluorine portion of the spectrum consists of an apparent pentet (ratio 1:3:4:3:1). (See Figure 3.)

The pentet results from two overlapping triplets. One triplet is due to six methylene fluorine coupled to two bridgehead fluorine. The other triplet is due to six methylene fluorine coupled to one bridgehead fluorine and one bridgehead proton. *Anal.* Calcd for  $C_{10}F_{15}H$ : C, 29.58; H, 0.29; F, 70.18. Found: C, 26.69; H, 0.49; F, 70.16.

**Direct Fluorination of Bicyclo[2.2.2]octane.** Bicyclo[2.2.2]octane (0.672 g, 6.1 mmol) (Chemical Samples Co.) was placed in the middle of a bucket reactor which had been cooled to 0° with ice. See Table VI for fluorination conditions. The glass trap (which had been cooled to –78° for the entire reaction) was removed and the volatile material condensed into a pear-shaped flask. It was then diluted with  $C_6F_6$ , and the products were separated on the gas chromatograph. The yield of perfluorobicyclo[2.2.2]octane was 3.5% (0.077 g). The product was characterized by comparing its physical properties with those reported in the literature.<sup>10</sup> *Anal.* Calcd for  $C_8F_{14}$ : C, 26.53; F, 73.46. Found: C, 26.45; F, 72.11.

The mass spectrum showed a ( $P - 19$ )<sup>+</sup> peak at  $m/e$  343. Other intense peaks in the spectrum were  $m/e$  293 ( $C_7F_{11}^+$ ), 243 ( $C_6F_9^+$ ), 193 ( $C_5F_7^+$ ), 162 ( $C_4F_6^+$ ), 119 ( $C_2F_5^+$ ), and 69 ( $CF_3^+$ ). The  $^{19}F$  nmr in  $C_6F_6$  showed a large doublet ( $J = 6.8$  Hz) at –41.3 ppm from  $C_6F_6$  and two small unresolved peaks at +55.07 and 57.6 ppm from  $C_6F_6$ . The ir contained peaks at 1285 (s), 1235 (vs), 1135 (m), 995 (s), and 950 (s)  $cm^{-1}$ .

**Fluorination of Cyclooctane.** Cyclooctane (1.67 g, 14.8 mmol) (Aldrich Chemical Co.), dried over Linde 4A molecular sieve, was

Table V

Reactor temp, °C	He flow (cm <sup>3</sup> /min)	F <sub>2</sub> flow (cm <sup>3</sup> /min)	Time
–78	60	0.5	31 hr
–78	30	0.5	24 hr
–78	30	1.0	31 hr
–78	15	1.0	24 hr
–78	15	1.5	50 hr
–78	0	1.5	20 hr
0	0	1.5	30 hr
RT <sup>a</sup>	0	1.5	84 hr
RT <sup>a</sup>	0	2.0	5 days
RT <sup>a</sup>	60	0	2 days

<sup>a</sup> RT = room temperature.

Table VI

Reactor temp, °C	He flow (cm <sup>3</sup> /min)	F <sub>2</sub> flow (cm <sup>3</sup> /min)	Time
0	25	0.5	24 hr
0	12.5	0.5	12 hr
0	12.5	1.0	12 hr
0	0	1.0	24 hr
RT <sup>a</sup>	0	1.0	6 days
RT <sup>a</sup>	0	1.5	4 days
RT <sup>a</sup>	0	2.0	3 days
RT <sup>a</sup>	0	2.5	2 days
RT <sup>a</sup>	0	2.5	7 days
RT <sup>a</sup>	50	0	1 day

<sup>a</sup> RT = room temperature

injected into the first zone of a four zone reactor whose last two zones had been cooled to 0° with ice water. The system was flushed with helium. See Table VII for fluorination conditions. The glass trap at the end of the system, which had been cooled to –78° during the entire reaction, was removed and attached to a vacuum line. The products were vacuum fractionated into –78 and –196° traps. The contents of the –196° trap (mostly  $SiF_4$ ) were discarded. The contents of the –78° trap were separated on the gas chromatograph using the fluorosilicone column. The reaction gives an 18.7% yield of perfluorocyclooctane and a 6.2% yield of monohydropentadecafluorocyclooctane.

Perfluorocyclooctane, mp 37.5°. The vapor phase mass spectrum exhibited the following intense peaks:  $m/e$  381 ( $C_8F_{15}^+$ ), 331 ( $C_7F_{13}^+$ ), 281 ( $C_6F_{11}^+$ ), 231 ( $C_5F_9^+$ ), 181 ( $C_4F_7^+$ ), 131 ( $C_3F_5^+$ ), 100 ( $C_2F_4^+$ ), 69 ( $CF_3^+$ ). The  $^{19}F$  nmr in  $CCl_4$  consisted of a singlet at 121.2 ppm from internal  $CFCl_3$  and the following bands: 1258 (sh), 1237 (s), 1188 (s), 1169 (sh), 1030 (w), 940 (s), 660 (w)  $cm^{-1}$ . *Anal.* Calcd: C, 24.02; F, 75.98. Found: C, 23.62; F, 76.44.

Monohydropentadecafluorocyclooctane, mp 26–28°. The mass spectrum showed the following intense peaks:  $m/e$  363 ( $C_8F_{14}H^+$ ), 313 ( $C_7F_{12}H^+$ ), 275 ( $C_7F_{10}H^+$ ), 263 ( $C_6F_{10}H^+$ ), 231 ( $C_5F_9^+$ ), 181 ( $C_4F_7^+$ ), 163 ( $C_4F_6H^+$ ), 131 ( $C_3F_5^+$ ), 133 ( $C_3F_4H^+$ ), 69 ( $CF_3^+$ ). The  $^{19}F$  nmr in  $CCl_4$  consisted of an unresolved multiplet centered at +119.0 ppm and a peak due to the lone fluorine at +214.5 ppm from internal  $CFCl_3$ . The vapor phase ir contained the following bands: 2930 (vw), 1382 (vw), 1360 (vw), 1290 (sh), 1254 (s), 1229 (vs), 1180 (s), 1149 (s), 1120 (m), 1100 (w), 1072 (w), 1032 (w), 1000 (m), 947 (s), 897 (s), 831 (w), 790 (vw), 720 (vw), 650 (w), 620 (w)  $cm^{-1}$ . *Anal.* Calcd: C, 25.15; F, 74.59; H, 0.26. Found: C, 23.18; F, 76.01; H, 0.76.

## Results and Discussion

Perfluoroneopentane is a compound which had long been of interest in fluorine chemistry. An extremely spherical molecule which has an outer sheath of fluorine atoms,  $(CF_3)_4C$  has very interesting physical properties. The synthesis of perfluoroneopentane by classical fluorination techniques had not been successful.<sup>6</sup> The only previously reported synthesis of perfluoroneopentane involved fluorocarbon starting materials.<sup>11</sup> Its successful synthesis by direct fluorination led to the successful preparation of related perfluoroanalogs such as perfluorohexamethylethane, which has a relatively weak carbon–carbon bond. Perfluorohex-

Table VII

Zone (T, °C)	He flow (cm <sup>3</sup> /min)	F <sub>2</sub> flow (cm <sup>3</sup> /min)	Time, hr
3, 4 (0)	10	0.5	24
3, 4 (0)	10	1.0	24
3, 4 (0)	10	2.0	24
3, 4 (0)	0	2.0	24
1 (+50), 3, 4 (–78)	40	2.0	24
1, 2 (+50), 3, 4 (–78)	20	2.0	24
2, 3 (+50), 4 (–78)	10	2.0	12
1, 2, 3, 4 (RT) <sup>a</sup>	0	2.0	24
1, 2, 3, 4 (RT) <sup>a</sup>	50	0.0	24

<sup>a</sup> RT = room temperature.

amethylethane had not been previously reported and its preparation demonstrates very effectively the sensitivity of this fluorination technique. The yield was 9.3%. Both perfluoroneopentane and perfluorohexamethylethane are colorless solids of very great volatility and both must be stored in sealed tubes in spite of their relatively high melting points (72.5 and 108°, respectively).

To compare this new fluorination process to the older  $\text{CoF}_3$  technique, the fluorination of bicyclo[2.2.1]heptadiene, bicyclo[2.2.1]heptane, and bicyclo[2.2.2]octane was undertaken.  $\text{CoF}_3$  fluorination of bicyclo[2.2.1]heptadiene gives a 0.09% yield of perfluorobicyclo[2.2.1]heptane and a 5.9% yield of 1*H*-undecafluorobicyclo[2.2.1]heptane.<sup>9</sup> The  $\text{CoF}_3$  fluorination of bicyclo[2.2.1]octane was not attempted on the hydrocarbon precursor but instead started with the partially fluorinated 1*H*-endo-2- and -3-carbomethoxyheptafluorobicyclo[2.2.2]oct-5-ene.<sup>10</sup> Using these partially fluorinated starting materials, both the perfluorobicyclo[2.2.2]octane and the 1*H*-tridecafluorobicyclo[2.2.2]octane were obtained in good yields by Tatlow and coworkers. All of these perfluoro and monohydro compounds are white, fairly volatile substances. As in the case of perfluoroneopentane and perfluorohexamethylethane, the volatility is much greater than normal for compounds of similar molecular weight.

Using direct fluorination, an 8.2% yield of perfluorobicyclo[2.2.1]heptane and a 1.9% yield of 1*H*-undecafluorobicyclo[2.2.1]heptane were obtained from bicyclo[2.2.1]heptadiene. Starting with bicyclo[2.2.1]heptane, the yield of perfluorobicyclo[2.2.1]heptane increased to 12.2% and that of 1*H*-undecafluorobicyclo[2.2.1]heptane increased to 8.1%.

It is not surprising that the saturated bicycloheptanes should give a better yield of both products than does the unsaturated starting material. The presence of double bonds on the starting material not only increases the number of radicals formed during the reaction but also facilitates the polymerization process itself.

The direct fluorination of bicyclo[2.2.2]octane gives a 3.5% yield of perfluorobicyclo[2.2.2]octane. In the case of the bicycloheptanes, 1*H*-undecafluorobicyclo[2.2.1]heptane was very volatile and leaves the reactor quickly before becoming perfluorinated. The 1*H*-tridecafluorobicyclo[2.2.2]octane, on the other hand, is less volatile and stays in the reactor, thus allowing more complete fluorination to occur. Under normal fluorination conditions, it is interesting that the only major product from the fluorination of adamantane is the 1*H*-pentadecafluoroadamantane. It is even less volatile than the bicyclooctane and should remain in the boat and be completely fluorinated to perfluoroadamantane. It is indeed surprising that perfluoroadamantane is not formed under these conditions. The lower yields of perfluorobicyclo[2.2.2]octane and 1-hydropentadecafluoroadamantane are in part due to the physical properties of the starting materials. The parent hydrocarbons are only very slightly volatile, and bicyclo[2.2.2]octane is a waxy solid. A consequence of the lack of volatility of the compounds is that they do not move through the reaction zone and constantly renew the surface when exposed to fluorine. In addition, the material is difficult to grind to a very fine powder and the diffusion of fluorine through the solid tends

to promote only surface fluorination.

Tatlow, *et al.*, have found that the proton on 1*H*-undecafluorobicyclo[2.2.1]heptane can be removed by  $\text{CH}_3\text{Li}$  in ether at  $-40^\circ$ .<sup>9,16</sup> The proton on 1*H*-tridecafluorobicyclo[2.2.2]octane can also be removed by  $\text{CH}_3\text{Li}$  at  $-78^\circ$ .<sup>10</sup> This technique is useful in the synthesis of perfluoroadamantane from 1*H*-pentadecafluoroadamantane.<sup>17</sup>

The direct fluorination of cyclooctane yields perfluorocyclooctane and monohydropentadecafluorocyclooctane. The preparation of perfluorocyclooctane, by the polymerization of tetrafluoroethylene under high pressure and temperatures over activated charcoal, had been previously reported,<sup>18</sup> but no successful fluorination of cyclooctane by any method has been reported. The monohydropentadecafluorocyclooctane has not been previously reported. Several new problems are posed in fluorination of cyclooctane. This hydrocarbon is a slightly volatile liquid at room temperature, so the reactor type and method of introduction of the compound becomes quite important. In this direct fluorination technique, the best results are obtained when the compound is fluorinated in the solid state. Simply placing the liquid cyclooctane in a boat and passing fluorine over it results in a very low yield of products and substantial decomposition. In the case of compounds such as norbornadiene, which have significant vapor pressures at room temperature, placing the reactant in a boat and using a helium flow to volatilize the material before condensing in the cryogenic reactor was possible. Cyclooctane is not volatile enough for this procedure. The technique developed for this compound involved syringing the material directly into the cooled copper turnings in the first zone of the cryogenic reactor.

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