Chlorotrifluoroethylene-derived fluids. I. Model compound synthesis

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Abstract

A series of chlorofluoroalkanes having chlorines on adjacent carbon atoms has been prepared, i.e. n-$C_5F_{11}CFClCCl_3$, n-$C_6F_{13}CFClCCl_3$, n-$C_5F_{11}CFClCFCl_2$, n-$C_6F_{13}CFClCFCl_2$, n-$C_5F_{11}CFClCF_2Cl$, n-$C_2F_5CFClCFClC_3F_7$ and n-$CF_3CFClCFClC_4F_9$, by a combination of halogen exchange, dehalogenation and chlorine addition reactions. An attempt to synthesize n-$C_6F_{13}CFClCF_2CFCl_2$ by the coupling of n-$C_6F_{13}CFClI$ with an excess of ICF_2CFCl_2 under UV radiation in the presence of Hg gave only n-$C_6F_{13}CFClCFClC_6F_{13}$ together with $CFCl_2CF_2CF_2CFCl_2$. Under parallel conditions from n-$C_6F_{13}CFClI$ and $CF_2ClCFClI$, n-$C_6F_{13}CFClCFClCF_2Cl$ was obtained in 48% yield.

Introduction

Telomers of chlorotrifluoroethylene of the general formula $Cl(CF_2CFCl)_xCl$ (with $x=3$, 4) offer potential as hydraulic fluids [1] in view of their non-flammability, relatively low vapor pressure, acceptable fluid ranges and ability to dissolve additives. The $Cl(CF_2CFCl)_xCl$ notation implies exclusive 'head-to-tail' arrangement; however, the telomerization process is not structure-specific. Thus, disregarding any rearrangements and the presence of diastereoisomers [2] in the case of, for example the trimer ($x=3$), up to four positional isomers are possible: $CF_2ClCFClCF_2CFClCF_2CFCl_2$, $CF_2ClCFClCF_2CFClCFClCF_2Cl$, $CF_2ClCFClCFClCF_2CF_2CFCl_2$ and $CFCl_2CF_2CF_2CFClCF_2CFCl_2$. Structures such as $R_fCF_2Cl_3$, $R_fCFClCl_3$ and $R_fCFClCFCl_2$ cannot be ignored since telogens incorporating a trichloromethyl unit have been utilized in the past [3, 4]. The effect of the chlorine numbers and positions on the properties of the fluids needed to be evaluated to provide the understanding necessary for structure/property development. The study reported here was centered on syntheses of compounds having chlorines on two adjacent carbon atoms. Both C_7 and C_8 chain materials were studied to obtain data on even and odd carbon atom compositions.

Experimental

General

Operations involving moisture or air-sensitive materials were carried out either in an inert atmosphere enclosure (Vacuum Atmospheres model HE-93B), under nitrogen bypass or *in vacuo*.

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Infrared spectra were obtained on neat (liquids) or as double mulls (solids, Kel-F oil No. 10 and Nujol) using a Perkin–Elmer Corp. model 1330 infrared spectrophotometer. ^{19}F NMR spectra were recorded on Varian VRX-200 and Nicolet NT-300 spectrometers in $CDCl_3$ with $CFCl_3$ as the standard. For mass spectrometric (MS) analyses a Du Pont 21-491B double focusing mass spectrometer attached to a Varian Aerograph model 2700 gas chromatograph (GC) equipped with a flame ionization detector was employed in conjunction with a Du Pont 21-094 data acquisition and processing system. The majority of the product mixture identifications were performed using combined gas chromatography/mass spectrometry (GC/MS). Gas chromatography was conducted employing a $10' \times 1/8''$ stainless-steel column packed with 4% OV-101 on 80/100 mesh Chromosorb G or an $8' \times 1/8''$ stainless-steel column packed with Porapak Q. In the case of the OV-101 column, the conditions used were 35–300 °C at 8 °C min^{-1}. In the case of Porapak Q, the upper temperature was 220 °C. All photochemical experiments were carried out by irradiating the reaction mixture, sealed in Vycor or Pyrex ampoules, with a 450 W Hanovia mercury arc lamp at a distance of 10–15 cm.

Materials

Zinc dust (Aldrich Chemical Co.) 325 mesh was activated by washing with 10% hydrochloric acid, water and acetone followed by drying at 100 °C under vacuum for 18 h. 1-Iodoperfluoro-n-heptane, 1,2-dichloro-1-iodoethane (PCR Inc.), 1-iodoperfluoro-n-octane (Du Pont), aluminum chloride (99.99%, Aldrich Chemical Co.) and chlorotrifluoroethylene (Aldrich Chemical Co.) were used as received. All solvents were vigorously dried and degassed (if used in reactions carried out *in vacuo*).

Preparation of 1,1,1-trichloroperfluoro-n-heptane

A stirred mixture of anhydrous aluminum chloride (33.4 g, 250 mmol) and 1-iodoperfluoro-n-heptane (50 g, 101 mmol) was heated for 16 h at 80 °C under nitrogen bypass. After cooling to room temperature, the product was extracted with Freon-113. Distillation gave 1,1,1-trichloroperfluoro-n-heptane (b.p., 158–160 °C; 22.7 g, 51.4% yield; purity >97%). Vacuum line fractionation using traps cooled to −15 °C and −196 °C resulted in the collection of $n\text{-}C_6F_{13}CCl_3$ (19.5 g, 44.2% yield; purity >99%) in the −15 °C cooled trap characterized by comparison of the infrared spectrum, mass spectrum and GC retention time with that of an authentic sample [5].

Preparation of 1,1,1-trichloroperfluoro-n-octane

A stirred mixture of $n\text{-}C_8F_{17}I$ (10 g, 183 mmol) and $AlCl_3$ (58 g, 435 mmol) was slowly heated to 75 °C. This temperature was maintained until the reaction started, as evidenced by the formation of iodine crystals. Heating at 75 °C was continued for another 1.5 h, followed by 1 h at 85 °C, 1 h at 95 °C and finally 24 h at 115 °C. Subsequently, the flask was cooled to room temperature and taken into a nitrogen-filled glove bag. The black paste-

like material was washed with 7×50 ml of Freon-113 and gravity filtered. Distillation removed Freon-113 and the major portion of the entrapped iodine. The residue was purified on the vacuum line by trap-to-trap distillation using traps cooled to −15 °C and −196 °C; n-$C_7F_{15}CCl_3$ (69.7 g, 77.5% yield; purity >99.8%) was collected in the −15 °C trap. The material was characterized by the comparison of its infrared spectrum, mass spectrum and GC retention time with that of an authentic sample [5].

Preparation of n-$C_5F_{11}CF{=}CCl_2$ (nc)

Under nitrogen bypass to a stirred mixture of activated zinc dust (3.3 g, 50.7 mmol) in 50 ml of anhydrous ether (dried and distilled directly from $LiAlH_4$) was added 1,1,1-trichloroperfluoro-n-heptane (17.0 g, 38.9 mmol). An exothermic reaction set in almost immediately; after it had subsided, the reaction mixture was refluxed for additional 3 h. Subsequently, the ether was removed *in vacuo* at room temperature. The product was collected under high vacuum in a −196 °C cooled trap by heating the solid residue to 100 °C. It was purified by distillation; b.p., 128–130 °C (7.80 g, 52.3% yield; purity 92%). Further purification was carried out by vacuum line fractionation using traps cooled to 0, −47 and −196 °C, respectively. In the −47 °C trap, n-$C_5F_{11}CF{=}CCl_2$, 6.90 g (purity >98.0%) was collected. IR (capillary film, cm^{-1}): 1365 (m), 1319 (m), 1240 (vs), 1205 (vs), 1149 (s), 1108 (m), 1029 (m), 1014 (m), 932 (w), 890 (m), 847 (s), 810 (m), 778 (m), 745 (m), 732 (m), 716 (m), 691 (m), 645 (s). MS (70 eV) *m/e* (relative intensity, ion): (only ^{35}Cl ions listed) 382 (26.8%, M), 363 (10.5%, M−F), 194 (10.3%, $CF_2CFCFCCl_2$), 163 (base, CF_2CFCCl_2), 131 (10.3%, C_3F_5), 119 (17.2%, C_2F_5), 109 (16.3%, CF_2CCCl).

Preparation of n-$C_6F_{13}CF{=}CCl_2$ (nc)

The procedure used for the synthesis of n-$C_6F_{13}CF{=}CCl_2$ from $C_6F_{13}CF_2CCl_3$ was essentially identical to that utilized for the preparation of $C_5F_{11}CF{=}CCl_2$. Yields of 68% of >99% purity material were realized; b.p., 148–149 °C. ^{19}F NMR: −81.6 (t, J=10.1 Hz, 3F, CF_3), −114.3 (m, 1F, =CF), −114.8 (t, J=12.7 Hz, 2F, CF_2), −122.9 (m, 2F, CF_2), −123.5 (m, 4F, $2CF_2$), −126.9 (m, 2F, CF_2) ppm. IR (capillary film, cm^{-1}): 1365 (m), 1297 (m), 1240 (vs), 1205 (vs), 1150 (vs), 1125 (m), 1065 (m), 1051 (m), 985 (m), 958 (w), 930 (w), 860 (w), 816 (w), 770 (m), 735 (m), 711 (m), 660 (m). MS (70 eV) *m/e* (relative intensity, ion): (only ^{35}Cl ions listed) 432 (38.9%, M), 413 (19.2%, M−F), 213 (16.0%, $CF_2CF_2CFCCl_2$), 194 (19.0%, $CF_2CFCFCCl_2$), 163 (base, CF_2CFCCl_2), 159 (16.8%, CF_2CF_2CCCl), 131 (40.7%, C_3F_5), 109 (43.4%, CF_2CCCl), 93 (47.2%, C_3F_3).

Preparation of 1,1,1,2-tetrachloroperfluoro-n-heptane (nc)

In vacuo onto n-$C_5F_{11}CF{=}CCl_2$ (7.0 g, 18.3 mmol) in an ~250 ml ampoule was condensed chlorine (5.1 g, 72.2 mmol). The sealed ampoule was heated at 60–70 °C for 3 d. Following opening to the vacuum system, the products were separated by pumping through traps cooled to 0, −78

and −196 °C, respectively; n-$C_5F_{11}CFClCCl_3$ (7.5 g, 90.4% yield; purity >99%) was collected in the 0 °C trap. IR (capillary film, cm^{-1}): 1357 (m), 1304 (w), 1240 (vs), 1205 (vs), 1174 (s), 1143 (s), 1111 (s), 1050 (w), 1026 (w), 970 (w), 958 (w), 935 (w), 912 (w), 898 (w), 847 (s), 795 (s), 780 (s), 747 (w), 735 (m), 710 (w), 636 (m). MS (70 eV) *m/e* (relative intensity, ion): (only ^{35}Cl ions listed) 417 (19.0%, M−Cl), 269 (15.1%, C_5F_{11}), 183 (15.2%, $CFClCCl_3$), 181 (18.5%, C_4F_7), 163 (30.7%, CF_2CFCCl_2), 119 (base, C_2F_5, $C^{35}Cl_2{}^{37}Cl$), 117 (64.2%, CCl_3).

Preparation of 1,1,1,2-tetrachloroperfluoro-n-octane (nc)

In a sealed 850 ml ampoule, n-$C_6F_{13}CF{=}CCl_2$ (30.0 g, 69.3 mmol) was heated with chlorine (5.8 ml, 138.9 mmol) for 4 d at 110 °C. After opening to the vacuum line, the volatiles were pumped through traps cooled to −63 °C and −196 °C. The residue was subjected to pumping *in vacuo* at room temperature for 6 h, followed by distillation to give n-$C_6F_{13}CFClCCl_3$ (27.5 g, 79% yield; purity >99%); b.p., 94–95 °C/2 mmHg. ^{19}F NMR: −81.4 (t, 3F, CF_3), −109.1 (AB pattern, 2F, CF_2), −118.9 (AB pattern, 2F, CF_2), −118.7 (m, 1F, CFCl), −122.1 (m, 2F, CF_2), −123.1 (m, 2F, CF_2), −126.6 (m, 2F, CF_2) ppm. IR (capillary film, cm^{-1}): 1366 (m), 1318 (w), 1240 (vs), 1208 (vs), 1186 (vs), 1150 (vs), 1116 (m), 1094 (m), 1072 (w), 1010 (m), 956 (m), 888 (m), 850 (s), 795 (s), 770 (w), 749 (w), 740 (w), 729 (w), 717 (w), 690 (w), 638 (s). MS (70 eV) *m/e* (relative intensity, ion): (only ^{35}Cl ions listed) 467 (48.0%, M−Cl), 319 (15.1%, C_6F_{13}), 183 (16.2%, $CFClCCl_3$), 169 (51.2%, C_3F_7), 163 (56.8%, CF_2CFCCl_2), 148 (33.2%, $CFClCCl_2$), 119 (base, C_2F_5, $C^{35}Cl_2{}^{37}Cl$), 117 (69.0%, CCl_3).

Preparation of 1,1,2-trichloroperfluoro-n-heptane (nc)

A stirred mixture of SbF_3 (3.2 g, 18.0 mmol), $SbCl_5$ (2.7 g, 9.0 mmol) and 1,1,1,2-tetrachloroperfluoro-n-heptane (5.0 g, 11.0 mmol) was heated under nitrogen bypass at 125 °C for 18 h. After cooling to room temperature, the volatiles were condensed *in vacuo* into a −15 °C cooled trap. The condensate was then taken up in ether (25 ml), washed with water, dried over sodium sulfate and fractionated *in vacuo* from a warming trap through traps cooled to 0, −23 and −47 °C, respectively. In the 0 °C trap n-$C_5F_{11}CFClCFCl_2$ (2.2 g, 45.6% yield; purity >98%) was collected. IR (capillary film, cm^{-1}): 1360 (m), 1309 (w), 1239 (vs), 1205 (vs), 1144 (s), 1120 (m), 1092 (m), 1050 (m), 1010 (w), 984 (m), 935 (w), 883 (s), 839 (m), 804 (m), 770 (w), 739 (w), 723 (w), 714 (w), 704 (w), 690 (w), 643 (m). MS (70 eV) *m/e* (relative intensity, ion): (only ^{35}Cl ions listed) 401 (41.6%, M−Cl), 269 (21.7%, C_5F_{11}), 235 (21.6%, $CF_2CF_2CF_2CF_2Cl$), 167 (42.2%, $CFClCFCl_2$), 163 (36.8%, $CFClCF_2Cl$), 147 (89.4%, C_3F_4Cl), 119 (base, C_2F_5), 101 (80.3%, $CFCl_2$).

Preparation of 1,1,2-trichloroperfluoro-n-octane (nc)

A stirred mixture of SbF_3 (43 g, 240 mmol), $SbCl_5$ (36 g, 120 mmol) and n-$C_6F_{13}CFClCCl_3$ (100.9 g, 200 mmol) was heated under nitrogen bypass

at 125–130 °C (oil bath temperature) for 24 h. After cooling, the liquid was decanted, taken up in ether (250 ml) and washed first with a saturated solution of sodium bicarbonate then water. Following drying over sodium sulfate, the ether was removed and the residual liquid was distilled giving n-$C_6F_{13}CFClCFCl_2$ (80 g, 82% yield; purity >99.5%); b.p., 126–127 °C/125 mmHg. ^{19}F NMR: −65.3 (m, 1F, CCl_2F), −81.5 (t, J=10.2 Hz, 3F, CF_3), −111.8 (AB pattern, 2F, CF_2), −119.5 (AB pattern, 2F, CF_2), −122.2 (m, 2F, CF_2), −123.2 (m, 2F, CF_2), −125.9 (m, 2F, CF_2), −126.7 (m, 2F, CF_2). IR (capillary film, cm^{-1}): 1369 (m), 1318 (m), 1243 (vs), 1210 (vs), 1189 (s), 1151 (s), 1090 (m), 1020 (w), 970 (m), 888 (m), 840 (m), 813 (w), 798 (w), 736 (w), 720 (w), 694 (w). MS (70 eV) *m/e* (relative intensity, ion): (only ^{35}Cl ions listed) 467 (11.6%, M−F), 451 (70.1%, M−Cl), 319 (15.0%, C_6F_{13}), 197 (19.8%, $CF_2CF_2CF_2CCl$), 181 (41.2%, C_4F_7), 169 (base, C_3F_7), 167 (62.0%, $CFClCFCl_2$), 163 (52.4%, $CFClCF_2Cl$), 147 (91.3%, C_3F_4Cl), 101 (98.3%, $CFCl_2$).

Oxidation of 1-iodoperfluoro-n-octane with oleum

Under nitrogen bypass to a stirred mixture of 1-iodoperfluoro-n-octane (12.5 g, 22.9 mmol), mercuric sulfate (0.35 g, 1.2 mmol) and mercurous sulfate (0.07 g, 0.14 mmol) was added oleum (10 ml, 20% SO_3 in H_2SO_4) at 0 °C. After completion of the addition, the addition funnel was replaced by a condenser and the reaction mixture was slowly heated to 146 °C. Heating was maintained for 5 d. Subsequently, the temperature was raised to 178 °C and maintained there for 5 h. At the end of this period, the reaction mixture was cooled to 0 °C; methanol (10 ml) was added slowly via an addition funnel. Following the addition, the reaction mixture was allowed to stir at room temperature for 16 h. Two layers could be clearly seen in the reaction mixture. The bottom layer was separated out and washed several times with water. After drying over anhydrous sodium sulfate, 9.4 g (96% yield) of a pink liquid were obtained which consisted of n-$C_7F_{15}CO_2CH_3$ (78%) and $C_8F_{17}I$ (20%).

Oxidation of 1-iodoperfluoro-n-octane with chlorosulfonic acid and synthesis of $C_5F_{11}CF{=}CF_2$

A mixture of 1-iodoperfluoro-n-octane (25.0 g, 45.8 mmol) and chlorosulfonic acid (42.5 g, 363 mmol) was heated under nitrogen bypass for 20 h at 145–150 °C. At the end of this period, the reaction mixture was cooled in an ice bath, and methanol (100 ml) was added dropwise via an addition funnel attached to the top of the condenser. This arrangement helped to wash down all the perfluoro-n-octanoic acid that had sublimed into the condenser. After the addition was completed, the reaction mixture was once again refluxed for 4 h. Subsequently, to the cool mixture was added ice-cooled water (50 ml). The organic (bottom) layer was then separated out and washed several times with water and dried over anhydrous sodium sulfate, giving 18.5 g (94%) of a slightly pink liquid consisting of n-$C_7F_{15}CO_2Me$ (89%), n-$C_8F_{17}Cl$ (5%) and n-$C_8F_{17}I$ (6%). Hydrolysis of the methyl ester

with 10% NaOH at room temperature, followed by 3– 4 h at 40 °C, gave the free acid which was isolated by filtration after acidification with concentrated hydrochloric acid. From the acid the sodium salt was obtained by titration with 2 N NaOH solution. The water and any volatile impurities were then removed *in vacuo* at 80–100 °C following the procedure of Brice *et al.* [6]. Yields of n-$C_7F_{15}CO_2Na$ were 70–75% based on the n-$C_8F_{17}I$ used. The pyrolysis of the sodium salt was carried out at 210–300 °C [7]. The olefins were obtained in 85–95% yields; the terminal olefin n-$C_5F_{11}CF{=}CF_2$ comprised 90–98% of the product.

Preparation of 1,2-dichloroperfluoro-n-heptane (nc)

A mixture of the olefin (45.1 g, 128.9 mmol) prepared above and chlorine (5.0 ml, ~120 mmol) was sealed *in vacuo* and stirred at room temperature for 3 d. Under these conditions addition of chlorine to the internal olefins does not occur. Fractionation from a warming trap through −23 °C and −78 °C held traps into a −196 °C cooled trap gave 45.5 g (91.0% yield; purity 99.5%) of 1,2-dichloroperfluoro-n-heptane collected in the −23 °C cooled trap; b.p., 132 °C. ^{19}F NMR: −64.0 (AB pattern, 2F, CF_2Cl), −81.5 (t, J=10.1 Hz, 3F, CF_3), −114.8 (AB pattern, 2F, CF_2), −119.8 (AB pattern, 2F, CF_2), −123.0 (m, 2F, CF_2), −126.6 (m, 2F, CF_2), −131.7 (m, 1F, CFCl) ppm. IR (capillary film, cm^{-1}): 1364 (m), 1314 (m), 1244 (vs), 1210 (vs), 1150 (s), 1130 (m), 1070 (m), 1055 (m), 1041 (m), 997 (m), 959 (m), 908 (w), 836 (w), 745 (w), 734 (w), 719 (w), 694 (w). MS (70 eV) *m/e* (intensity, ion): (only ^{35}Cl ions listed) 385 (2.7%, M−Cl), 285 (23.7%, $C_5F_{10}Cl$), 219 (23.3%, C_4F_9) 201 (16.0%, $CF_2CFClCF_2Cl$), 197 (17.1%, $CF_2CF_2CF_2CFCl$), 169 (23.8%, $CF_3CF_2CF_2$), 151 (14.9%, $CFClCF_2Cl$), 85 (base, CF_2Cl).

Isomerization of perfluoro-n-heptene-1 with cesium fluoride in the presence of dimethylformamide

In vacuo in a 50 ml ampoule were sealed cesium fluoride (3.0 g, 20 mmol), dry dimethylformamide (5 ml) and $C_5F_{11}CF{=}CF_2$ (7.0 g, 20 mmol). The ampoule was then shaken for 18 h at room temperature. Subsequently, it was opened to the vacuum line and subjected to distillation through traps cooled to −15 °C and −196 °C. The −15 °C trap contained only dimethylformamide. In the −196 °C trap, two layers were present. The top layer consisted of dimethylformamide; the bottom layer (7.0 g), based on IR, GC and GC/MS, consisted of 99% of the internal olefin. ^{19}F NMR spectroscopy showed 78% $CF_3CF_2CF{=}CFCF_2CF_2CF_3$ *trans*, **1** and 22% $CF_3CF{=}CFCF_2CF_2CF_2CF_3$ *trans*, **2**; −69.8 (d of d, 3F, CF_3 in **2**), −81.8 (t, J=8.8 Hz, 3F, CF_3 in **1**), −81.9 (t, J=9.0 Hz, 3F, CF_3 in **2**), −85.5 (s, 3F, CF_3 in **1**), −119.2 (m, 2F, CF_2 in **2**), −119.9 (m, 2F, CF_2 in **1**), −122.4 (m, 2F, CF_2 in **1**), −125.2 (m, 2F, CF_2 in **2**), −127.1 (m, 2F, CF_2 in **2**), −129.0 (m, 2F, CF_2 in **1**), −155.3 (AB pattern, 2F, CF=CF in **1**), −157.6 (AB pattern, 2F, CF=CF in **2**) ppm. IR (capillary film, cm^{-1}): 1712

(w), 1395 (w), 1340 (vs), 1275–1210 (vs), 1192 (vs), 1145 (vs), 1125 (vs), 1102 (s), 1041 (s), 961 (s), 926 (m), 891 (w), 851 (w), 832 (w), 794 (m), 753 (m), 731 (s), 721 (s), 701 (m), 669 (m). MS (70 eV) *m/e* (intensity, ion): 350 (21.3%, M), 331 (27.9%, M−F), 231 (base, $CF_2CFCFC_2F_5$, $CF_2CF_2CFCFCF_3$), 181 (87.4%, C_4F_7), 131 (56.5%, C_3F_5).

Preparation of 2,3- and 3,4-dichloroperfluoro-n-heptanes (nc)

In an ~800 ml ampoule, the olefins $CF_3CF_2CF{=}CF(CF_2)_2CF_3$ and $CF_3CF{=}CF(CF_2)_3CF_3$ (26.4 g, 76.1 mmol) were sealed *in vacuo* together with chlorine (10 g, 141 mmol) and heated at 60 °C for 48 h. Following opening to the vacuum system, fractionation from a warming trap through traps held at −15 °C and −196 °C gave 30.9 g (96.7% yield; purity 99.7%) of the chlorinated product; b.p., 128–129 °C. IR (capillary film, cm^{-1}): 1342 (s), 1328 (m), 1255–1180 (vs), 1132 (s), 1096 (s), 1025 (s), 975 (m), 955 (m), 926 (m), 858 (m), 830 (m), 788 (w), 780 (w), 768 (w), 740 (m), 719 (m), 702 (m), 674 (w), 640 (w), 588 (w). MS (70 eV) *m/e* (intensity, ion): (only ^{35}Cl ions listed) 401 (5.1%, M−F), 301 (16.2%, $C_3F_7CFClCFCl$), 285 (18.9%, C_4F_9CFCl), 251 (21.5%, $C_2F_5CFClCFCl$), 235 (92.1%, C_3F_7CFCl), 201 (18.1%, $CF_3CFClCFCl$), 185 (84.1%, C_2F_5CFCl), 169 (69.5%, C_3F_7), 119 (86.8%, C_2F_5), 69 (base, CF_3).

Preparation of 1-chloro-1-iodoperfluoroheptane (nc)

The sodium salt n-$C_6F_{13}CFClCO_2Na$ was obtained in 87% yield from n-$C_6F_{13}CFClCCl_3$ following the procedure of Paciorek and Lin [8]. To n-$C_6F_{13}CFClCO_2Na$ (11.5 g, 12.9 mmol) dissolved in water (50 ml) was added a solution of silver nitrate (12.9 g, 75.0 mmol) in water (50 ml). The resultant white precipitate was filtered, washed and dried to give 11.7 g (85% yield) of n-$C_6F_{13}CFClCO_2Ag$. Analysis: Calcd. for $C_8F_{14}ClO_2Ag$: Ag, 20.11%. Found: 20.07% (ammonium thiocyanate titration). IR (Nujol/Kel-F mull, cm^{-1}): 1605 (vs), 1385 (m), 1235 (s), 1207 (vs), 1166 (m), 1145 (vs), 1097 (w), 1003 (w), 955 (m), 876 (w), 785 (w), 761 (w), 717 (w).

A mixture of n-$C_6F_{13}CFClCO_2Ag$ (2.80 g, 5.2 mmol) and iodine (13.7 g, 53.9 mmol), ground together in an inert atmosphere enclosure, was heated in a tube fitted with an adaptor and an inlet for nitrogen bypass for 5 h at 140 °C followed by 1 h at 155–160 °C. After cooling to room temperature, the dark liquid was pipetted off, treated with copper bronze and distilled *in vacuo* from a warming trap through traps cooled at −23 °C and −196 °C. 1-Chloro-1-iodoperfluoroheptane (1.65 g, 62% yield) was collected in the −23 °C cooled trap; b.p., 158 °C. IR (capillary film, cm^{-1}): 1365 (m), 1312 (w), 1240 (vs), 1205 (vs), 1149 (s), 1092 (m), 1071 (w), 1049 (w), 980 (w), 959 (w), 877 (m), 829 (w), 811 (w), 789 (w), 736 (w), 718 (w), 687 (w), 632 (w). MS (70 eV) *m/e* (intensity, ion): (only ^{35}Cl ions listed) 512 (9.6%, M), 493 (10.5%, M−F), 477 (29.7%, M−Cl), 385 (base, M−I), 243 (7.7%, CF_2CFClI), 208 (20.4%, CF_2CFI), 193 (21.8%, $CFClI$), 127 (38.1%, I), 116 (25.9%, CF_2CFCl).

Coupling of 1-chloro-1-iodoperfluoro-n-heptane and 1,1-dichloro-2-iodotrifluoroethane

A typical reaction was carried out by sealing *in vacuo* the appropriate amounts of 1-chloro-1-iodoperfluoro-n-heptane, 1,1-dichloro-2-iodotrifluoroethane (prepared and purified by a literature procedure [9] and mercury in a Pyrex ampoule followed by irradiation with a UV lamp while being continuously shaken in a horizontal position. At the end of the irradiation period, the ampoule was re-attached to a vacuum manifold and products separated by pumping through traps cooled to −23, −78 and −196 °C, respectively. Volatile products collected in the cold traps were analyzed by GC and GC/MS. Nonvolatiles, if any, were extracted with Freon-113. The Freon extract was filtered and the solvent removed under vacuum. Residue, if any, was analyzed by GC and GC/MS. In none of the reactions attempted (see Table 1) was n-$C_6F_{13}CFClCF_2CFCl_2$ observed; the major product was n-$C_6F_{13}CFClCFClC_6F_{13}$ (nc); b.p., 233 °C. IR (capillary film, cm^{-1}): 1365 (m), 1312 (m), 1240 (vs), 1205 (vs), 1149 (s), 1092 (m), 1070 (m), 1049 (w), 970 (w), 959 (w), 877 (m), 827 (m), 812 (m), 789 (w), 735 (m), 718 (w), 686 (w), 633 (m). MS (70 eV) *m/e* (relative intensity, ion): (only ^{35}Cl ions listed) 751 (0.1%, M−F), 735 (0.3%, M−Cl), 681 (2.2%, M−2Cl−F), 451 (20.8%, $C_6F_{13}CFClCFCl$), 431 (20.4%, $CF_2CFCFC_6F_{13}$), 385 (63.7%, $C_6F_{13}CFCl$), 319 (18.2%, C_6F_{13}), 297 (14.6%, $(CF_2)_4CFCFCl$), 197 (24.8%, $CF_2CF_2CFCFCl$), 169 (88.8%, C_3F_7), 69 (base, CF_3).

TABLE 1

Exposure of $C_6F_{13}CFClI$ and ICF_2CFCl_2 to UV radiation

$C_6F_{13}CFClI$		ICF_2CFCl_2		Hg (mmol)	UV exp. (h)	I[a] (%)[c]	II[b] (%)[c]	ICF_2CFCl_2 (%)
g	mmol	g	mmol					
1.65	3.22	2.69	9.65	16.1	18	75	36	n.d.[d]
2.00	3.90	10.89	39.00	78.0	42	60	60	31
0.50	0.98	5.44	19.50	39.0	24	59	54	27

[a] I = $C_6F_{13}CFClCFClC_6F_{13}$.
[b] II = $Cl_2CFCF_2CF_2CFCl_2$.
[c] Percentage yield assuming only self-coupling.
[d] Not determined.

UV irradiation of n-$C_6F_{13}CFClI$ and $CF_2ClCFClI$ in the presence of mercury

A mixture of n-$C_6F_{13}CFClI$ (1.0 g, 2.0 mmol) and $CF_2ClCFClI$ (10.9 g, 39.0 mmol) together with mercury (16.0 g, 8.0 mmol), sealed *in vacuo* in a Pyrex tube, was shaken under UV radiation for 24 h. The ampoule was subsequently opened to the vacuum system and the volatiles were fractionated through traps held at −23 °C and −78 °C into a −196 °C cooled trap. All the fractions were analyzed by GC/MS. In the −23 °C cooled trap, 3.00 g were collected; the material consisted of n-$C_6F_{13}CFClCFClCF_2Cl$ (0.4 g, 36%

yield), $(CF_2ClCFCl)_2$ (2.3 g, 39.5% yield) and $CF_2ClCFClI$ (0.2 g, 2% recovery). In the −78 °C cooled trap, 4.1 g condensed; it consisted of n-$C_6F_{13}CFClCFClCF_2Cl$ (40. mg, 4% yield), $(CF_2ClCFCl)_2$ (2.59 g, 44% yield) and $CF_2ClCFClI$ (1.4 g, 13% recovery). From the involatile residue on extraction with Freon-113, 0.4 g of material was obtained which consisted of n-$C_6F_{13}CFClCFClCF_2Cl$ (0.1 g, 8% yield) and n-$C_6F_{13}CFClCFClC_6F_{13}$ (0.2 g, 29% yield). The total yield of $C_6F_{13}CFClCFClCF_2Cl$ (nc) was 48%. MS (70 eV) *m/e* (relative intensity, ion): (only ^{35}Cl ions listed) 501 (7.9%, M−Cl), 431 (16.2%, $C_6F_{13}CFCFCF_2$), 385 (53.4%, $C_6F_{13}CFCl$), 269 (24.3%, $CF_3CF_2CF_2CF_2CF_2$), 217 (47.1%, $CFClCFClCF_2Cl$), 197 (56.0%, $CF_2CFCFCF_2Cl$), 163 (50.8%, $CFClCClCF_2$), 151 (94.9%, $CFClCF_2Cl$), 147 (79.5%, CF_2CF_2CCl), 85 (base, CF_2Cl).

Results and discussion

The 1,1,1-trichloroperfluoroalkanes were of interest both in view of the presence of the CCl_3 group and as starting materials for other model compounds. 1,1,1-Trichloroperfluoro-n-heptane and 1,1,1-trichloroperfluoro-n-octane were obtained in >99% purity from the reaction of the perfluoroalkyl iodides with aluminum trichloride following essentially the procedure of Eapen *et al.* [5], i.e.:

$$C_7F_{15}CF_2I \xrightarrow{AlCl_3} C_7F_{15}CCl_3$$

Modifications to the procedure included the use of an open system (instead of an autoclave), stringent exclusion of air and moisture, and the workup which consisted either of distillation of the volatiles *in vacuo* at room temperature, followed by product separation from the co-distilled iodine, or extraction with Freon-113 and product separation by distillation. Based on our observations, in the aluminum trichloride reaction some intermediates are formed which on treatment with ether give hydrocarbon-substituted products, possibly $R_fC_2H_5$, as indicated by the mass spectral data. Consequently, protonated solvents were avoided in the product isolation. It should be mentioned that in the preparation of n-$C_7F_{15}CCl_3$, extreme care needs to be exercised in the initial stages of reaction. Rapid heating must be avoided to prevent a sudden exothermic reaction. These problems were not encountered in the case of n-$C_6F_{13}CCl_3$. It is believed that this behavior has to do with the solubility of aluminum trichloride in the iodides. Another aspect is the necessity of using aluminum trichloride of a very high purity.

For the preparation of $R_fCFClCCl_3$ and $R_fCFClCFCl_2$, the sequence depicted below was utilized:

$$R_fCF_2CCl_3 \xrightarrow{Zn} R_fCF{=}CCl_2 \xrightarrow{Cl_2} R_fCFClCCl_3 \xrightarrow{SbF_3/SbCl_5} R_fCFClCFCl_2$$

The dehalogenation reaction was found to be extremely sensitive to moisture, purity of the starting materials and the type of solvent. Depending on the conditions, a spectrum of by-products resulted. The major by-products were two $C_5F_{11}C_2FClH$ olefins, most likely *trans* and *cis* isomers, and the

saturated product $C_5F_{11}CF_2CCl_2H$. The formation of hydrogen-containing by-products in zinc dehalogenations was reported in the early investigations by Haszeldine [10] and Henne and Finnegan [11], as well as by others. Production of these side-products was eliminated by using activated zinc dust in dry ether with stringent exclusion of moisture and by conducting the final decomposition of the zinc complex after removal of ether.

Chlorination of n-$C_6F_{13}CF{=}CCl_2$, using elemental chlorine, did not proceed as smoothly as that of n-$C_5F_{11}CF{=}CCl_2$, which took place readily at 60–70 °C. At 60 °C the extent of reaction was very low, but raising the temperature to 100 °C gave >90% yield of the adduct in 24 h.

The partial fluorination of n-$C_5F_{11}CFClCCl_3$ and n-$C_6F_{13}CFClCCl_3$ to n-$C_5F_{11}CFClCFCl_2$ and n-$C_6F_{13}CFClCFCl_2$, respectively, proceeded readily using $SbF_3/SbCl_5$ at 125–130 °C. Under these conditions only one of the terminal chlorines was replaced by fluorine. These compounds are isomers of the corresponding R_fCCl_3 materials, 1,1,1-trichloroperfluoroalkanes.

The olefin n-$C_5F_{11}CF{=}CF_2$ provided the starting material for the 1,2- and internal-dichloro compounds. The commercially available material is admixed with branched isomers; accordingly, the olefin employed under this program was prepared by pyrolysis of sodium perfluoro-n-octanoate following essentially the procedure of La Zerte *et al.* [7]. Perfluoro-n-octanoic acid was obtained from 1-iodoperfluoro-n-octane by oxidation with chlorosulfonic acid; this process was found to be much less cumbersome and to proceed in a better yield than the oleum oxidation.

Chlorination of the terminal olefin n-$C_5F_{11}CF{=}CF_2$ proceeded to completion at room temperature. Under these conditions, the chlorine did not add to the internal olefins. Consequently, following the chlorination step, any of the internal olefins originally present could be readily separated from the desired product. 1,2-Dichloroperfluoro-n-heptane was characterized by infrared spectral analysis, ^{19}F NMR spectroscopy and mass spectrometry.

To prepare the isomeric dichloro compounds, namely 2,3- or 3,4-dichloroperfluoro-n-heptane, required first the isomerization of the double bond followed by chlorine addition, e.g.:

$$\text{n-}C_5F_{11}CF{=}CF_2$$

$$\downarrow$$

$$\text{n-}C_4F_9CF{=}CFCF_3 + \text{n-}C_3F_7CF{=}CFC_2F_5$$

$$\downarrow \; Cl_2$$

$$\text{n-}C_4F_9CFClCFClCF_3 + \text{n-}C_3F_7CFClCFClC_2F_5$$

In the absence of solvent, cesium fluoride failed to effect the isomerization; in dimethylformamide the process occurred readily. The isomerized product was characterized by infrared spectral analysis, GC/MS and ^{19}F NMR spectroscopy. Based on ^{19}F NMR spectral analysis, the material consisted of 78% $CF_3CF_2CF{=}CFCF_2CF_2CF_3$ and 22% $CF_3CF{=}CFCF_2CF_2CF_2CF_3$. The two isomers could not be separated by GC methods.

The internal alkenes did not add chlorine at room temperature. However, at 60 °C the reaction proceeded readily. 2,3- and 3,4-Dichloroperfluoroheptanes could not be separated by GC. Their GC retention time, however, differed from that of the 1,2-dichloroperfluoro-n-heptane. The composite mass spectrum of the two internal-dichloro compounds exhibited definite differences from that of the 1,2-dichloro isomer. Most significant were the $[M-F]^+$, $[C_3F_7CFClCFCl]^+$ and $[C_2F_5CFClCFCl]^+$ ions. These were not observed in the mass spectrum of 1,2-dichloroperfluoro-n-heptane. The relative intensity of the ions such as *m/e* 235 $[C_3F_7CFCl]^+$ and *m/e* 185 $[C_2F_5CFCl]^+$ versus *m/e* 285 $[C_4F_9CFCl]^+$ and *m/e* 135 $[CF_3CFCl]^+$ reflects the relative ratios of the two isomers in the mixture.

Limited investigations were carried out on the synthesis of model compounds such as $R_fCFClCF_2CCl_3$ (precursor to $R_fCFClCF_2CFCl_2$ and $R_fCFClCF_2CF_2Cl$) and $R_fCFClCFClCF_2Cl$. One of the routes studied was the reaction of n-$C_6F_{13}CFClI$ with ICF_2CFCl_2 performed under UV radiation in the presence of mercury. The compound n-$C_6F_{13}CFClI$ was obtained from n-$C_6F_{13}CFClCCl_3$ by the sequence given below:

$$\text{n-}C_6F_{13}CFClCCl_3 \xrightarrow[CH_3OH,\ NaOH]{HSO_3Cl,} \text{n-}C_6F_{13}CFClCO_2Na \xrightarrow[I_2]{AgNO_3} \text{n-}C_6F_{13}CFClI$$

Several attempts were made to couple $C_6F_{13}CFClI$ with ICF_2CFCl_2. These are summarized in Table 1. Although up to a 20-fold excess of 1,1-dichloro-2-iodotrifluoroethane (reaction 3) was employed, the cross-coupled compound n-$C_6F_{13}CFClCF_2CFCl_2$ was not formed. The major products observed were n-$C_6F_{13}CFClCFClC_6F_{13}$ and n-$CFCl_2CF_2CF_2CFCl_2$, which arise from self-coupling of n-$C_6F_{13}CFClI$ and $CFCl_2CF_2I$, respectively. Apparently, the CFCl—I bond being weaker than the CF_2—I bond it dissociates much more readily; the iodine is removed by mercury and the radicals thus formed couple. Once n-$C_6F_{13}CFClI$ is exhausted, ICF_2CFCl_2 starts to couple with itself. This mechanism agrees with the recovery of unreacted ICF_2CFCl_2. Subsequently, n-$C_5F_{11}CFClCF_2CCl_3$ was prepared by reaction of n-$C_5F_{11}CF{=}CF_2$ with carbon tetrachloride [12].

It is of interest that the coupling of n-$C_6F_{13}CFClI$ with a 10-fold excess of $CF_2ClCFClI$ gave n-$C_6F_{13}CFClCFClCF_2Cl$ in 48% yield, supporting the above postulations. It is noteworthy that n-$C_6F_{13}CFClCFClCF_2Cl$ offers a model for the three-chlorine arrangement potentially present in the chlorotrifluoroethylene trimers as discussed earlier.

The number and position of the chlorine atoms in these model compounds were found to affect both their physical properties and chemical reactivity [13, 14] as well as their physiological activity [15].

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