during the addition. After addition, stirring was continued for 1 hr at 25°. Excess BrF_3 and Br_2 were decomposed by washing with 10% aqueous $NaHSO_3$. The fluorocarbon layer was water washed and dried ($MgSO_4$). The crude product (89%) was fractionated by gas chromatography. The following peaks were collected and identified.

Perfluoro-*trans*-2-bromohexene-2 (9%): ^{19}F nmr $\mathbf{CF_3}C{=}C$, ϕ 76.6, CF_3CF_2, 82.3, $CF_2C{=}$, 115.3, $CF_3\mathbf{CF_2}$, 125.4, $CF{=}$, 143.1; ir ($CFCl_3$) 7.45 (s), 7.7–8.6, (vs), 8.82 and 8.95 (doublet, m), 9.98 (m), 10.6 (s), 10.9 (s), 12.65 (s), 13.48 (m), 13.9 (s), 14.3 (s), 14.55 (w), 14.9 μ (m); mass spectrum *m/e* (relative intensity) ion 343, 341 (6.5, 6.0) $C_6H_{10}\,Br^+$; 243, 241 (2.9, 2.5) $C_4F_6Br^+$; 231 (0.7) $C_5F_9{}^+$; 219 (0.7) $C_4F_9{}^+$; 193, 191 (5.2, 4.9) $C_3F_4Br^+$; 181, 179 (24.3, 20.0) $C_4F_7{}^+$ and $C_2F_4Br^+$; 169 (2.9) $C_3F_7{}^+$; 150 (0.9) $C_3F_6{}^+$; 131, 129 (30.9, 8.8) $C_3F_5{}^+$ and CF_2Br^+; 119 (42.1) $C_2F_5{}^+$; 112 (1.9) $C_3F_4{}^+$; 100 (17.4) $C_2F_4{}^+$; 93 (14.8) $C_3F_3{}^+$; 81,79 (4.7, 4.3) Br^+; 69 (100) $CF_3{}^+$; 50 (19.8) $CF_2{}^+$; 31 (80.0) CF^+.

Perfluoro-*trans*-2-bromo-heptene-2 (4%): ^{19}F nmr $\mathbf{CF_3}C{=}C$, ϕ 76.6, $\mathbf{CF_3}CF_2$ 82.2, $\mathbf{CF_2}C{=}$, 114.6, $\mathbf{CF_2}CF_2C{=}$, 121.7, $CF_3\mathbf{CF_2}$, 127.7, $CF{=}$, 142.5; ir ($CFCl_3$) 7.4 (m), 7.6–8.5 (vs), 8.75 (s), 10.2 (w), 10.45 (w), 10.7 (m), 10.82 (m), 13.45 (m), 14.1 (m), 14.6 (m), 14.7 μ (sh); mass spectrum *m/e* (relative intensity) ion 393, 391 (7.0, 6.5) $C_7F_{12}Br^+$; 374, 372 (0.7, 0.6), $C_7F_{11}Br^+$; 293, 291 (1.5, 1.1) $C_5F_8Br^+$; 243, 241 (0.9, 0.8) $C_4F_6Br^+$; 231, 229 (3.4, 3.0) $C_3F_6Br^+$; 193, 191 (1.5, 1.3) $C_3F_4Br^+$; 181, 179 (31.6, 30.2) $C_2F_4Br^+$; 169 (18.9) $C_3F_7{}^+$; 162, 160 (2.6, 1.6) $C_4F_6{}^+$ and $C_2F_3Br^+$; 150 (1.3) $C_3F_6{}^+$; 131, 129 (55.2, 13.2) C_3F_5 and CF_2Br^+; 119 (36.3) $C_2F_5{}^+$; 112 (3.2) $C_3F_4{}^+$; 100 (43.9) $C_2F_4{}^+$; 93 (20.8) $C_3F_3{}^+$; 81, 79 (8.9, 3.9) $C_2F_3{}^+$ and Br^+; 69 (100) $CF_3{}^+$; 50 (20.5) $CF_2{}^+$; 31 (91.0) CF^+.

Perfluoro-2-bromoheptane (87%): bp 114–116°, $n^{20}{}_D$ 1.3036; ^{19}F nmr $\mathbf{CF_3}CFBr$, ϕ 76.0, $\mathbf{CF_3}CF_2$, 81.8, $\mathbf{CF_2}CFBr$, 113.9, $\mathbf{CF_2}CF_2CFBr$, 119.5, $CF_3CF_2\mathbf{CF_2}$, 123.1, $CF_3\mathbf{CF_2}$, 127.1, $C\mathbf{F}Br$, 141.2; ir 7.4 (m), 7.6–9.0 (s), 9.71 (m), 9.82 and 9.9 (doublet, m), 10.2 (m), 10.6 (m), 10.92 (s), 11.3 (m), 11.6 (w), 12.1 (w), 12.45 (m), 12.57 (m), 12.92 (m), 13.1 (w), 13.4 (s), 13.62 (s), 14.1 (s), 14.7 μ (s); mass spectrum *m/e* (relative intensity) ion 450, 448 (4.5, 4.0) $C_7F_{15}Br^+$ (parent ion); 431, 429 (0.9, 0.8) $C_7F_{14}Br^+$; 231, 229 (5.0, 4.3) $C_3F_6Br^+$; 219 (8.3) $C_4F_3{}^+$; 193, 191 (6.2, 5.7) $C_3F_4Br^+$; 181, 179 (45.2, 37.6) $C_2F_4Br^+$; 169 (13.1) $C_3F_7{}^+$; 162, 160 (3.6 1.9) $C_2F_3Br^+$; 150 (3.8) $C_3F_6{}^+$; 131, 129 (78.5, 14.3) $C_3F_5{}^+$ and CF_2Br^+; 119 (51.2) $C_2F_5{}^+$; 112 (4.3) $C_3F_4{}^+$; 100 (51.3) $C_2F_4{}^+$; 93 (21.4) $C_3F_3{}^+$; 81, 79 (9.5, 4.8) $C_2F_3{}^+$ and Br^+; 69 (100) $CF_3{}^+$; 50 (10.7) $CF_2{}^+$; 31 (73.8) CF^+.

Preparation of Perfluoroheptene-2.[7]—Perfluoroheptene-1 (100 g) was heated under reflux (80–76°) with powdered cesium fluoride (3 g) for 10 hr with stirring. The reaction mixture was washed with water, dried ($MgSO_4$), and distilled giving a fraction (83 g) which boiled at 75.5–76.5°. Vpc collections were carried out at 20°. Area determinations indicated the presence of perfluoro-*trans*-heptene-2 (74%), *cis* heptene-2 (16%), and unreacted perfluoroheptene-1 (7%).

Perfluoro-*trans*-heptene-2: ir 6.0 (C═C, w), 7.15 (m), 7.45 (s), 7.7–8.9 (vs), 9.5 (m), 9.78 (m), 10.15 (m), 10.65 (w), 10.8 (w), 11.2 (s), 12.1 (m), 12.3 (m), 12.5 (m), 13.39 and 13.45 (doublet, s), 13.8 (s), 14.0 (w), 14.4 (m), 14.7 μ (w); ^{19}F nmr $\mathbf{CF_3}C{=}C$, ϕ 70.0, $\mathbf{CF_3}CF_2$, 82.0, $\mathbf{CF_2}C{=}C$, 119.2, $\mathbf{CF_2}CF_2C{=}C$, 125.3, $CF_3\mathbf{CF_2}$, 127.2, $\mathbf{CF{=}CF}$, 158.3.

Perfluoro-*cis*-heptene-2: ir ($CFCl_3$) 5.9 (C═C, m), 7.5 (s), 7.9–8.7 (vs), 8.9 (s), 9.1 (m), 9.4 (m), 9.6 (m), 9.8 (w), 10.2 (m), 10.68 (m), 10.9 (w), 11.3 (w), 12.5 (s), 13.45 (m), 13.68 and 13.8 μ (doublet, s); ^{19}F nmr $\mathbf{CF_3}C{=}C$, ϕ 66.3, $\mathbf{CF_3}CF_2$, 81.9, $\mathbf{CF_2}C{=}C$, 116.9, $\mathbf{CF_2}CF_2C{=}C$, 124.1, $CF_3\mathbf{CF_2}$, 127.1, $CF_2\mathbf{CF}{=}$, 137.7, $CF_3\mathbf{CF}{=}$, 141.0.

Reaction of Perfluoroheptene-2 with Bromine Trifluoride and Bromine.—A mixture of *trans*- (82%) and *cis*- (18%) perfluoroheptenes-2 (35 g, 0.1 mol) was allowed to react with a solution of BrF_3 (5.5 g, 0.04 mol) and Br_2 (12.8 g, 0.08 mol) as described previously. The crude product contained about 10 g of the unreacted perfluoroheptenes-2 (*trans* 80% and *cis* 20%) and 26 g (58%) of a colorless liquid. Vpc analysis of the colorless liquid at 130° showed one large peak with a shoulder. The peak and shoulder were collected together and analyzed by ^{19}F nmr. Peak intensity ratios indicated that there were two components present in 50:50 ratio. They were identified as perfluoro-2 bromoheptane and perfluoro-3-bromoheptane. The individual peaks in the ^{19}F nmr spectra were assigned as follows: $\mathbf{CF_3}CFBr$, ϕ 76.0 (2-bromo), $\mathbf{CF_3}CF_2CFBr$, 78.8 (3-bromo), $\mathbf{CF_3}CF_2$, 81.8 (2-bromo + 3-bromo), $\mathbf{CF_2}CFBr$, 113.4 (3-bromo), $\mathbf{CF_2}CFBr$, 113.9 (2-bromo), $CF_3\mathbf{CF_2}CFBr$, 117.0 (3-bromo), $\mathbf{CF_2}CF_2CFBr$, 119.5 (2-bromo), $CF_3CF_2\mathbf{CF_2}$, 119.9 (3-bromo), $CF_3CF_2\mathbf{CF_2}$, 123.1 (2-bromo), $CF_3\mathbf{CF_2}$, 127.0 (2-bromo + 3-bromo), $C\mathbf{F}Br$, 139.4 (3-bromo), $CFBr$, 141.1 (2-bromo). The infrared spectrum of the mixture shows considerable band overlapping and the presence of the 3-bromo isomer could not be definitely established by this method. The mass spectrum of the mixture, except for peak intensities, was very similar to that obtained for the 2-bromo isomer with the $C_7F_{15}Br^+$ fragment being the highest fragment observed in the spectrum.

Reaction of Hexafluoropropene Dimer with Bromine Trifluoride in Bromine.—Hexafluoropropene dimer[9] C_6F_{12} (300 g, 1 mol) was added during 45 min to an ice-cooled solution of BrF_3 (46 g, 0.33 mol) in Br_2 (55 g, 0.33 mol). The product (340 g) contained the three isomers of C_6F_{12} (**1**, **2**, **3**), in different ratios (see text, Table I) and the two isomers of $C_6F_{13}Br$ (**4**, **5**). The monobromides were separated from the dimers by fractional distillation. The mixed bromides have the following physical constants: bp 97–100°, d^{21} 1.9220; $n^{20}{}_D$ 1.3049; calcd molar refractivity (MR) 37.5, found 39.1. The two bromides were further fractionated by gas chromatography and analyzed by mass spectroscopy and ^{19}F nmr.

4: mass spectrum *m/e* (relative intensity) ion 400, 398 (0.7, 0.6) $C_6F_{13}Br^+$ (parent ion); 381, 379 (0.3, 0.2) $C_6F_{12}Br^+$; 293, 291 (0.8, 0.7) $C_5F_8Br^+$; 243, 241 (0.1, 0.2) $C_4F_6Br^+$; 231, 229 (1.2, 0.7) 193, 191 (0.7, 0.3) $C_3F_4Br^+$ and $C_5F_7{}^+$; 181 (6.3) $C_4F_7{}^+$; 169 (0.2) $C_3F_7{}^+$; 162 (1.2) $C_2F_3Br^+$ and $C_4F_6{}^+$; 160 (0.9) $C_2F_3Br^+$; 131, 129 (8.8, 1.8) CF_2Br^+ and $C_3F_5{}^+$; 124 (0.4) $C_4F_4{}^+$; 119 (0.9) $C_2F_5{}^+$; 112 (1.2) $C_3F_4{}^+$; 100 (4.7) $C_2F_4{}^+$; 93 (5.1) $C_3F_3{}^+$; 81, 79 (2.6, 1.6) Br^+; 69 (100.0) $CF_3{}^+$; 50 (2.6) $CF_2{}^+$; 31 (17.6) CF^+; ir 7.6–8.5 (vs), 8.75 (s), 8.92 (s), 10.2 (s), 10.9 (s), 12.3 (s), 12.7 (m), 13.2 (s), 13.6 (s), 14.0 (w), 14.2 (s), 14.4 μ (s).

Anal. Calcd for $C_6F_{13}Br$: C, 18.06; F, 61.91; Br, 20.03. Found: C, 18.20; F, 61.66; Br, 20.13.

5: mass spectrum *m/e* (relative intensity) ion 400, 398 (0.1, 0.2) $C_6F_{13}Br^+$ (parent ion); 381, 379 (0.1, 0.1) $C_6F_{12}Br^+$; 293, 291 (0.3, 0.8) $C_5F_8Br^+$; 281, 279 (2.0, 1.7) $C_4F_8Br^+$; 243, 241 (0.1, 0.4) $C_4F_6Br^+$; 231, 229 (1.4, 0.8) 193, 191 (0.9, 0.3) $C_3F_4Br^+$ and $C_5F_7{}^+$; 181 (2.6) $C_4F_7{}^+$; 169 (0.4) $C_3F_7{}^+$; 162 (0.5) $C_2F_3Br^+$ and $C_4F_6{}^+$; 160 (0.3) $C_2F_3Br^+$; 131, 129 (7.8, 3.3) CF_2Br^+ and $C_3F_5{}^+$; 124 (0.4) $C_4F_4{}^+$; 119 (2.1) $C_2F_5{}^+$; 112 (0.9) $C_3F_4{}^+$; 100 (1.9) $C_2F_4{}^+$; 93 (6.1) $C_3F_3{}^+$; 81, 79 (1.4, 1.1) Br^+; 69 (100.0) $CF_3{}^+$; 50 (2.6) $CF_2{}^+$; 31 (8.5) CF^+; ir 7.6–8.5 (vs), 8.72 (s), 8.99 (s), 9.13 (s), 10.18 (s), 11.2 (s), 11.5 (m), 12.2 (m), 12.38 (m), 13.2 (m), 13.6 (s), 13.97 (s), and 14.3 μ (s).

Anal. Calcd for $C_6F_{13}Br$: C, 18.06; F, 61.91; Br, 20.03. Found: C, 18.07; F, 61.71; Br, 20.26.

Registry No.—Bromine trifluoride, 7787-71-5; perfluoroheptene-1, 355-63-5; perfluoro-*trans*-2-bromohexene-2, 24010-45-5; perfluoro-*trans*-2-bromoheptene-2, 24057-16-7; perfluoro-2-bromoheptane, 24010-68-2; perfluoro-*trans*-heptene-2, 24010-46-6; perfluoro-*cis*-heptene-2, 24010-47-7; **4**, 24010-48-8; **5**, 24057-17-8.

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Directing a Chlorination Reaction

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We have been able to modify the course of the reaction between chlorine and hexane by carrying out the reaction in a "molecular sieve." When hexane, absorbed at 150° in a synthetic zeolite, a Linde 13X Molecular Sieve, is treated with chlorine, the ratio of secondary to primary chlorination rate constants [R (calculated on an H-atom basis) = k_s/k_p] is 1.1–1.9 (the conversion of hexane being 1.0 and 8.3%, respectively). Pretreatment of the sieve with chlorine lowers the R value further, even though the chlorine is desorbed before absorbing the hexane.

Conversion of hexane, %	R
0.71–1.7	0.3–0.8
11.8	1.9
52	2.2

At 150°, the homogeneous gas-phase reaction between chlorine and hexane yielded an R value of 2.7–3.7 (1–42% conversion, 0.5–9-sec contact time, and a molar ratio range of chlorine to hexane of 1–7). A small quantity of dichlorinated products was also obtained (*e.g.*, less than 1% in the product at 15% conversion of hexane), but these were not detected for the sieve reactions. Values for R of 2.8–6.0 in the homogeneous gas phase have been reported for the same or similar reactions.[1–3]

The pore size of the sieve is critical. Openings of 5 Å are too small to permit recovery of the product from the sieve. Openings of 13 Å are satisfactory. Openings of 10 Å appear to be borderline in value.

The increase in the value of R as the conversion is increased may be attributable to desorption of hexane from the sieve followed by reaction in the homogeneous phase. From desorption experiments with pure hexane, we have estimated that a maximum of 10% of the hexane in the sieve could have reacted in the vapor phase when the total conversion exceeded 15%. Under these circumstances, the molar ratio of chlorine to hexane in the vapor phase would be greater than 100:1 so that reaction would be rapid.

Reviewers raised the question as to whether secondary chlorides which were formed may have been dehydrohalogenated selectively to give the low R values. While no complete material balance was obtained, the following experimental facts make such a possibility remote. (1) In the normal sieve reactions, no alkenes were found. The only by-product detected was hexachlorobenzene in very small quantities. The overall time of the sieve reactions was 1–4 min. 1-Chlorohexane, deposited on the 13X sieve at 150°, left there for 80 min, and removed with steam at 150°, yielded a mixture of alkenes and 1-chlorohexane. (2) When 5A sieves were used under normal reaction conditions, product recovery was not possible as mentioned above. When the chlorination reaction was continued for extended periods of time over 5A sieves without the introduction of steam, a mixture of chlorohexanes was collected with an R ratio of 3.7–3.9, probably as a result of gas-phase chlorination. If selective dehydrohalogenation of secondary chlorohexanes occurred over sieves, the R value would be abnormally low. (3) If dehydrohalogenation were the cause of low R values, the R value would not be the increasing function of conversion noted in the text.

Experimental Section

Analysis.—The products of the reaction were analyzed by vapor phase chromatography using a 14-ft column containing 20% Carbowax on Gas-Chrom P (column temperature of 200°, feed block at 275°, with a thermal detector). The concentrations were estimated from the recorder peak heights. Pure materials and their mixtures were used to calibrate the vpc instrument, but only one secondary monochloride was available in pure form. Occasional confirmation of the identity of the individual components was made *via* nmr. A single peak on the chromatograph included all of the secondary monochlorohalides. Any component which was present in an amount greater than 0.5% would have been detected by the chromatograph.

Materials.—Linde 5X, 10X, and 13X Molecular Sieves (Union Carbide Corp) with 5-, 10-, and 13-Å pores respectively, were used directly as received ($^1/_{16}$-in. pellets). n-Hexane was Matheson Coleman and Bell Spectroquality; Cl_2 was 99.965% minimum purity with less than 3 ppm of water; HCl was 99.0% minimum purity, dried over H_2SO_4 before use; the nitrogen has less than 15 ppm of water and less than 0.002% oxygen.

Absorption and Desorption of Hexane on the Sieves.—The sieves were placed in a 30-in.-long, 25-mm-i.d. Pyrex tube and dried at 350–370° for 2 hr and under a stream of nitrogen. Mixed vapors of hexane and nitrogen were passed through the bed which was held at 150°. The absorption data were obtained gravimetrically. For desorption studies, pure nitrogen was passed through the bed containing the absorbed hexane. The effluent from the Pyrex tube was trapped at 0 and −76° in a series of traps. The absorption data were in reasonable agreement with those of Allen.[4]

Reaction of n-Hexane and Chlorine in the Molecular Sieves.—The same apparatus was used as for absorption studies with the additional precaution of eliminating free space before the sieve bed by the insertion of a close-fitting sealed Pyrex tube. Water was removed from 65 to 72 g of sieves at 450–480°. Hexane was deposited on the sieve at 150° by absorption from a stream of nitrogen. A mixture of chlorine and nitrogen was passed over the sieve for a predetermined length of time (experimental range of 1–4 min). The reactor was swept briefly with nitrogen, and the hydrocarbon was displaced from the sieve with water vapor mixed with enough nitrogen to prevent a negative pressure from forming. The time delay between the introduction of the various streams was less than 3 sec. When the water was introduced, the effluent from the reactor was led through wet and Dry Ice traps in series. After separating and discarding the aqueous phase, the excess chlorine in the trapped liquid was allowed to bleed into the atmosphere at 25° before analyzing the product. Essentially all of the chlorinated product was trapped at 0°. Fresh sieves were used for each experiment to avoid the problem of reaction between HCl and the sieves, which reaction was shown to occur slowly.

Homogeneous Gas-Phase Reaction of Chlorine and Hexane.—A Pyrex tube of 25-cc free volume served as the reactor. Mixed preheated streams of nitrogen, hexane, and chlorine were fed to the reactor at 150°. The off-gases were trapped and analyzed as described above.

Registry No.—Hexane, 110-54-3.

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Perfluoro-*t*-butyl Alcohol and Its Esters

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Perfluoroalkylcarbinols are especially interesting because of the large electronegativity of the fluorine