acid and finding its sign of rotation. This acid is the isomer giving the most hindered transition state and, if the absolute configuration of the acid is known, the absolute configuration of the amine can often be deduced.

Coupling of the three amines with an excess of 2-phenylbutyric acid gave, in each case, recovered acid with a positive neat rotation and positive rotation in methanol. Since the structural changes among the three amines are not likely to alter group interactions in the 2-phenylbutyramides, 1-methylhexylamine and 1,4-dimethylpentylamine have the same absolute configuration as 1,3-dimethylbutylamine, namely *R*-(−) referred to neat rotations. As was mentioned above, in this series of amines *R* = L and taste turned out to be a reliable guide to absolute configuration.

Experimental Section

Elemental analyses were done under the direction of E. Zielinski and rotations under the direction of A. J. Damascus. Melting points were determined in a stirred bath and are uncorrected.

Resolutions.—1,3-Dimethylbutylamine (101 g, 1.0 mol) and 150 g (1.0 mol) of L-(+)-tartaric acid were dissolved in 600 ml of methanol, and the solution allowed to stand overnight at room temperature. The product (98.2 g) was crystallized three times from 2.5 parts of methanol to yield 41.2 g of the tartrate salt, mp 128–131°, $[\alpha]^{28}\mathrm{D}$ +21.0° (*c* 1, MeOH). *Anal.* Calcd for $C_{10}H_{21}NO_6\cdot{}^1/_3H_2O$: C, 46.68; H, 8.49; N, 5.44. Found: C, 46.91; H, 8.50; N, 5.46.

The above tartrate (30.2 g, 0.12 mol) was suspended in 150 ml of ether plus 50 ml of water. Sodium hydroxide (50%, 20 ml, 0.36 mol) was added and the mixture shaken vigorously. The ether layer was washed with 25 ml of 5 *M* potassium carbonate, and dried over anhydrous potassium carbonate; the ether was distilled. The residue was fractionated to yield 9.96 g (82%) of 1,3-dimethylbutylamine: bp 106–107°; $[\alpha]^{25}\mathrm{D}$ −11.2° (neat), +3.5° (*c* 1, MeOH) [lit.[9] −10.7° (neat)]. *Anal.* Calcd for $C_6H_{15}N$: N, 13.84. Found: N, 13.65.

1-Methylhexylamine tartrate had mp 109–110°; $[\alpha]^{26}\mathrm{D}$ +19.0° (*c* 1, MeOH). *Anal.* Calcd for $C_{11}H_{23}NO_6$: C, 49.80; H, 8.74; N, 5.28. Found: C, 49.53; H, 8.90; N, 5.12.

The free base had bp 140°; $[\alpha]^{25}\mathrm{D}$ −6.7° (neat), −0.8° (*c* 10, MeOH). *Anal.* Calcd for $C_7H_{17}N$: N, 12.16. Found: N, 12.21.

1,4-Dimethylpentylamine tartrate had mp 142–144°; $[\alpha]^{28}\mathrm{D}$ +19.5° (*c* 1, MeOH). *Anal.* Calcd for $C_{11}H_{23}NO_6$: C, 49.80; H, 8.74; N, 5.28. Found: C, 49.79; H, 8.90; N, 5.12.

The free base had bp 133°; $[\alpha]^{25}\mathrm{D}$ −7.2° (neat), −0.6° (*c* 10, MeOH). *Anal.* Calcd for $C_7H_{17}N$: N, 12.16. Found: N, 12.48.

N-*p*-Toluenesulfonyl-L-1,3-dimethylbutylamine.—L-Leucinol N-*p*-toluenesulfonamide O-*p*-toluenesulfonate[5] (8.50 g, 0.02 mol), mp 105–107°, $[\alpha]^{26}\mathrm{D}$ −54.1° (*c* 1, MeOH), was reduced with $LiAlH_4$ in refluxing ether. Crystallization of the crude product from *n*-pentane gave the desired amide, 3.29 g (65%), mp 65–67°, $[\alpha]^{25}\mathrm{D}$ +3.8° (*c* 1, MeOH); lit.[5] mp 62–63°, $[\alpha]^{18}\mathrm{D}$ +1.4° (*c* 0.8, EtOH).

Resolved 1,3-dimethylbutylamine (1.0 g, 0.01 mol) was treated with *p*-toluenesulfonyl chloride in pyridine. Crystallization of the crude product from *n*-pentane yielded the toluenesulfonamide, 2.03 g (80%), mp 65–67°, $[\alpha]^{28}\mathrm{D}$ +4.5° (*c* 1, MeOH).

Anal. Calcd for $C_{13}H_{21}NO_2S$: C, 61.14; H, 8.29; N, 5.49; S, 12.56. Found: C, 61.45; H, 8.14; N, 5.78; S, 12.73.

Asymmetric Syntheses.—Racemic 2-phenylbutyric acid (9.84 g, 0.06 mol) was dissolved in 50 ml of methylene chloride, and 4.04 g (0.04 mol) of resolved 1,3-dimethylbutylamine was added. The mixture was stirred in an ice bath and 8.24 g (0.04 mol) of dicyclohexylcarbodiimide in 40 ml of methylene chloride was added. After stirring 0.5 hr at room temperature, the dicyclohexylurea was removed by filtration and the methylene chloride distilled. The residue was dissolved in ether and extracted with 50 ml of 1 *N* sodium hydroxide. The basic extract was acidified with hydrochloric acid and the unreacted 2-phenylbutyric acid taken up in ether; the ether extract was washed twice with water, dried over sodium sulfate, and distilled. The residue was dried overnight at room temperature under vacuum. Recovered 2-phenylbutyric acid (3.40 g, 0.0207 mol) had $[\alpha]^{27}\mathrm{D}$ +7.4° (neat), +6.3° (*c* 10, MeOH).

When optically active 1-methylhexylamine was used, unreacted 2-phenylbutyric acid showed $[\alpha]^{26}\mathrm{D}$ +7.3° (neat), +5.7° (*c* 10, MeOH).

When optically active 1,4-dimethylpentylamine was used, unreacted 2-phenylbutyric acid had $[\alpha]^{27}\mathrm{D}$ +8.4° (neat), +6.5° (*c* 10, MeOH).

Registry No.—1-Methylhexylamine, 6240-90-0; 1-methylhexylamine tartrate, 24118-68-1; 1,4-dimethylpentylamine, 24110-97-2; 1,4-dimethylpentylamine tartrate, 24215-84-7; 1,3-dimethylbutylamine tartrate, 24118-69-2; 1,3-dimethylbutylamine toluene sulfonamide, 24118-70-5.

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[9] R. H. Holm, A. Chakravorty, and G. O. Dudek, *J. Amer. Chem. Soc.*, **86**, 379 (1964).

Reaction of Perfluoro Olefins with Bromine Trifluoride in Bromine

ELIZABETH S. LO,[1] JOSEPHINE D. READIO,[2]
AND HYMAN ISERSON

Research Department, Thiokol Chemical Corporation,
Trenton, New Jersey 08607

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Bromine trifluoride has been used as a source of BrF in organic reactions; however, the references are few.[3,4] Chambers, *et al.*,[5] have reported the addition of BrF to hexafluoropropene to give the 2-bromo derivative. No information is available concerning such reactions with more complex perfluoro olefins. The present investigation concerns the reactions of bromine trifluoride in bromine with some perfluoroheptenes and hexenes. Davis and Larsen,[6] using BrF_3 in the presence of a large excess of Br_2, have replaced Br by F in bromofluoroethanes. In the present study no perfluoroalkanes were found. The major products of the reactive olefins are the perfluoroalkyl monobromides.

Perfluoroheptene-1 gave almost exclusively perfluoro-2-bromoheptane (87%). Other fractions isolated in small amounts were perfluoro-*trans*-2-bromoheptene-2 (4%) and perfluoro-*trans*-2-bromohexene-2 (9%). Perfluoroheptane and 1-bromoheptane were absent in the crude product as shown by vpc analysis. Perfluoroheptene-2,[7] synthesized by treating perfluoroheptene-1 with cesium fluoride,[8] gave a mixture of 50:50 perfluoro-2-bromo- and -3-bromoheptanes.

The reaction of BrF_3 in Br_2 with the three isomeric

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[1] To whom inquiries should be addressed: 102 Maclean Circle, Princeton, N. J. 08540.

[2] Reaction Motors Division, Thiokol Chemical Corp., Denville, N. J.

[3] W. K. R. Musgrave, *Advan. Fluorine Chem.*, **1**, 12 (1960).

[4] E. T. McBee, V. V. Lindgren, and W. B. Ligett, *Ind. Eng. Chem.*, **39**, 378 (1947).

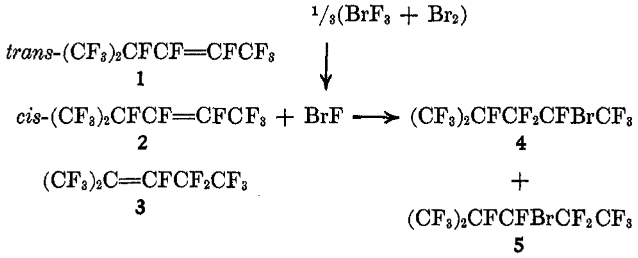
[5] R. D. Chambers, W. K. R. Musgrave, and J. Savory, *Proc. Chem. Soc. London*, 113 (1961).

[6] R. A. Davis and E. R. Larsen, *J. Org. Chem.*, **32**, 3478 (1967).

[7] W. T. Miller, Jr., *J. Amer. Chem. Soc.*, **82**, 3091 (1960), had probably synthesized perfluoroheptene-2; however, no attempt was made to identify it.

[8] R. N. Dresdner, F. N. Tlumac, and J. A. Young, *J. Org. Chem.*, **30**, 3524 (1965).

hexafluoropropene dimers[9] gave only two monobromides. No perfluorohexane was found in the product.



$$trans\text{-}(CF_3)_2CFCF{=}CFCF_3\ (\mathbf{1}) \xrightarrow{^1/_3(BrF_3 + Br_2)}$$

$$cis\text{-}(CF_3)_2CFCF{=}CFCF_3\ (\mathbf{2}) + BrF \longrightarrow (CF_3)_2CFCF_2CFBrCF_3\ (\mathbf{4}) + (CF_3)_2CFCFBrCF_2CF_3\ (\mathbf{5})$$

$$(CF_3)_2C{=}CFCF_2CF_3\ (\mathbf{3})$$

As was evident from the data in Table I, the formation of these products arose almost exclusively from the *trans* olefin **1**.

TABLE I

REACTION OF HEXAFLUOROPROPENE DIMER WITH BrF_3–Br_2

Structure	%[a] present before reaction	%[a] present after reaction
1	87.43	12.53
2	7.09	7.13
3	5.48	5.16
4	0	37.46
5	0	37.72

[a] Area measurement by gas chromatographic analysis.

The structures of the two perfluoro monobromides were assigned on the basis of the ^{19}F nmr results. The room temperature ^{19}F nmr data of structures **4** and **5** were given in Table II.

TABLE II

	4		5	
	ϕ	J	ϕ	J
$(CF_3)_2CF$–	72.2		69.4	
CF_3–	75.5		77.9	
CF_2–	98.2, 103.4 108.4, 113.7	296	109.5, 114.5 117.4, 122.4	283
CFBr–	142.1		137.7	
CF	180.8		171.5, 172.0	

The assignment of structure was based on chemical shifts, area measurements, and observed coupling patterns. The data are consistent with the conclusion that structurally related fluorines which are closest to the CFBr group in the above two compounds will be deshielded to the greatest extent. The deshielding effect of the perfluoroisopropyl group is likewise considered.

The high-resolution nmr spectrum of **4** shows complex multiplets for $(CF_3)_2CF$, CF_3CFBr, and $(CF_3)_2CF$ fluorines, while the CF_2 and CFBr nuclei appear as broad unresolved peaks. The $(CF_3)_2CF$ fluorines which give essentially one absorption at room temperature are seen as two distinct signals (71.7 and 79.8) at low temperature (−105°). The individual members of the AB quartet attributed to the CF_2 geminal fluorines are unaffected by variations in temperature. The chemical-shift difference, however, increases from 505 Hz at 24° to 568 Hz at −105°. Upfield shifts in the peak positions of the CFBr and $(CF_3)_2CF$ fluorines [CFBr, ϕ 145.0; $(CF_3)_2CF$, ϕ 181.4] occur with lowering of temperature. These observations reflect changes in conformer population. Studies from −105 to 80° indicate that at −105° interconversion between conformers has not been slowed sufficiently so that individual rotamers are observed.

The high-resolution room-temperature nmr spectrum of **5** shows the $(CF3)_2CF$ fluorines as an unsymmetrical multiplet. The CF_3CF_2 fluorines appear as a doublet of doublets (J = 6.6 Hz). The individual members of the AB quartet (chemical-shift difference = 340 Hz at 24°) due to the geminal CF_2 fluorines are broad as are the CFBr and CF fluorines. The latter shows doublet structure due to coupling with the adjacent CFBr. Spectra obtained at low temperature (−105°) show the following differences resulting from changes in conformer population. The isopropyl CF_3's are partially resolved (ϕ 69.4 and 70.0). The chemical-shift difference of the geminal CF_2 fluorines increases to 392 Hz. Both CFBr and $(CF_3)_2CF$ fluorines experience upfield shifts as the temperature is lowered [CFBr, 141.3; $(CF_3)_2CF$, 173.3 Hz]. As in the case of **4** no individual rotamers were observed.

The above results indicated that bromoperfluoro alkanes may be successfully prepared by the reaction of certain perfluoro alkenes with bromine trifluoride in bromine. In case of perfluoroheptene-1, the addition of BrF was stereospecific and yielded only the 2-bromo adduct. On the other hand, reactions involving additions to internal double bonds such as perfluoroheptene-2 and *trans*-perfluoro-4-methylpentene-2 (**1**) led to nearly equal amounts of the two possible adducts and thus proceeded with little selectivity. The apparent difference in reactivity between structures **1** and **2** and structures **2** and *cis*-perfluoroheptene-2 clearly resulted from the steric effect of the large perfluoroisopropyl group next to an internal double bond. This observation was further substantiated by the fact that the highly substituted double bonds of hexafluoropropene trimer[9] did not give BrF adducts under similar reaction conditions.

Experimental Section

The chromatographic preparative-scale separations for perfluoroheptenes and their bromides were performed on a Nester-Faust "Prepkro" unit using a column packed with 30% SF-96 on Chromosorb P (24 ft × $^3/_8$ in.). The chromatographic preparative scale separations for hexafluoropropene dimers and their bromides were performed on a Wilkens Autoprep Model A 700 utilizing a column at 60° packed with 30% SE-30 on Chromosorb W (20 ft × $^3/_8$ in.). The elemental analyses were performed by Schwarzkopf Microanalytical Laboratories, Woodside, N. Y. Infrared spectra were obtained with a Perkin-Elmer Model 137 double-beam spectrophotometer. The ^{19}F nmr spectra were obtained with a 60-MHz Varian DP-60 spectrometer. Spectra were calibrated by the side-band modulation technique using a Hewlett-Packard wide range oscillator. All ^{19}F chemical shifts were determined with $CFCl_3$ as an internal standard. Sample concentrations were approximately 20–40% by weight in $CFCl_3$. A Bendix time-of-flight mass spectrometer (Model 12-101) with source elements S14-107 was employed to record the mass spectra at 70 eV.

Reaction of Perfluoroheptene-1 with Bromine Trifluoride and Bromine.—Bromine trifluoride (0.06 mol) and bromine (0.12 mol) were placed in an ice-cooled flask equipped with a thermometer, a dropping funnel, a reflux condenser, and a stirrer. Perfluoroheptene-1[10] (0.143 mol) was added slowly to the BrF_3–Br_2 solution. The reaction was extremely exothermic. An ice bath was used to maintain the reaction temperature at 40–50°

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[9] Synthesized according to W. J. Brehm, *et al.*, U. S. Patent 2,918,501 (1959).

[10] Synthesized according to J. D. LaZerte, L. J. Hals, T. S. Reid, and G. H. Smith, *J. Amer. Chem. Soc.*, **75**, 4525 (1953).

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, $\mathbf{CF_3}CF_2$, 82.3, $\mathbf{CF_2}C{=}$, 115.3, $CF_3\mathbf{CF_2}$, 125.4, $\mathbf{CF}{=}$, 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, $\mathbf{CF}{=}$, 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°, $n^{20}\mathrm{D}$ 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, $\mathbf{CF}{=}\mathbf{CF}$, 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), CFBr, 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; $n^{20}\mathrm{D}$ 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

ELI PERRY

Monsanto Company, Central Research Department,
St. Louis, Missouri 63166

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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,