$CF_2]_{4\ av.})_2$, was isolated as the fraction boiling mainly at 215–225° at *ca.* 0.1 mm., $n^{40}D$ 1.383, solid at room temperature. The yield and conversion were 54%.

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[CONTRIBUTION FROM THE ORGANIC RESEARCH DEPARTMENT, PENNSALT CHEMICALS CORP.]

Thermal Syntheses of Telomers of Fluorinated Olefins. III. Perfluoropropene Telomer Bromides[1]

BY MURRAY HAUPTSCHEIN, MILTON BRAID AND ARNOLD H. FAINBERG

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By the thermal reaction of CF_3Br, CF_2Br_2 and $CF_3CFBrCF_2Br$ with perfluoropropene, the telomer bromides, $R[CF_2CF(CF_3)]_nBr$, where R = CF_3, CF_2Br and CF_3CFCF_2Br, and n = 1–*ca.* 6 have been prepared. Several correlations of infrared absorption data for the series $R[CF_2CF(CF_3)]_nX$ are presented. A strong band at 10.19 ± 0.03 μ, which is attributed to a skeletal vibration characteristic of the repeated $-CF_2CF(CF_3)-$ unit, has been found without exception for 46 members of this series.

The formation of telomer iodides of the formula $R[CF_2CF(CF_3)]_nI$ by reaction of primary and secondary fluorocarbon iodides with the difficultly polymerizable olefin perfluoropropene under thermal conditions has been described previously.[2] Stabilizations of the telomer iodides have been carried out by means of chlorination, fluorination, coupling, etc.[3]

Since telomer bromides of the formula $R(CH_2CF_2)_nBr$ have been synthesized by the thermal reactions of CF_2Br_2 and $CF_3CFBrCF_2Br$ with 1,1-difluoroethylene,[4] an olefin of intermediate polymerizability, it was of interest to investigate the possibility of synthesizing telomer bromides of perfluoropropene by purely thermal means. These novel telomer bromides without further transformation should be relatively stable fluorocarbon derivatives having high densities and large temperature coefficients of viscosity. In addition, infrared studies of the telomer bromides $R[CF_2CF(CF_3)]_nBr$ were expected to be particularly useful in furthering the correlation of absorption data with structure for the polyperfluoropropene system, including the iodides, chlorides and fluorides, $R[CF_2CF(CF_3)]_nX$ were X = I, Cl or F, previously reported.[3]

We have now found that the telomer bromides of formula $R[CF_2CF(CF_3)]_nBr$[5] may be prepared by the thermal reaction of fluorocarbon bromides with perfluoropropene. It is particularly noteworthy that CF_3Br as well as CF_2Br_2 and $CF_2BrCFBrCF_3$ has been employed successfully as a reactant bromide since it was certainly not obvious that these bromides, and particularly the less reactive primary fluorocarbon monobromide, would undergo thermal reaction with perfluoropropene. Indeed, while temperatures of 245 and 255° were sufficient for reaction with perfluoropropene for CF_2Br_2 and $CF_2BrCFBrCF_3$, respectively, no reaction was observed for CF_3Br until a temperature of 260° was attained. Olefin to bromide molar ratios of 4–5:1 were used in all three cases and telomers $R[CF_2CF(CF_3)]_nBr$ having values of n = 1–*ca.* 6 were formed. It is apparent that, inasmuch as the temperature required to produce the bromine adduct of perfluoropropene lies well below that required for the formation of telomers, the synthesis where R = $CF_2BrCF(CF_3)-$ is most conveniently carried out by merely heating a mixture of bromine and an excess of perfluoropropene up to the optimum temperature (and pressure) necessary to produce telomers. It should be pointed out that although theoretically $CF_2BrCFBrCF_3$ may add to $CF_2{=}CFCF_3$ to give either $CF_2BrCF(CF_3)[CF_2CF(CF_3)]_nBr$ or $CF_3CFBrCF_2[CF_2CF(CF_3)]_nBr$, the former structure is favored, since less energy is required to dissociate a secondary C–Br bond than a primary C–Br bond. This is supported by the fact that the primary fluorocarbon bromide, CF_3Br, did not react noticeably at the temperature at which $CF_2BrCFBrCF_3$ did undergo reaction.

It is noted that since the temperatures and pressures used in all these syntheses (245–260° and 4000–9000 p.s.i.) were sufficiently high to cause the dimerization of perfluoropropene,[6] the bromine-free fluorocarbon, perfluoro-(dimethylcyclobutane),[6] was produced concurrently. It was not possible to separate this dimer, b.p. 45°, from the adduct of CF_3Br and $CF_2{=}CFCF_3$, 2-bromoperfluorobutane, b.p. 45°. It was necessary, therefore, to prepare the latter by the thermal bromination at 125–150° of 2-iodoperfluorobutane.

Infrared Absorption Spectra Correlations.—In Table I are listed the infrared bands characteristic of each of the three series of telomer bromides reported in this paper, as well as those of a closely related series, $CF_3[CF_2CF(CF_3)]_nI$, previously re-

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[1] The work herein reported was carried out under contract between the Office of Naval Research and the Pennsylvania Salt Manufacturing Co. Reproduction in whole or in part is permitted for any purpose of the United States Government.

[2] M. Hauptschein, M. Braid and F. E. Lawlor, THIS JOURNAL, **79**, 2549 (1957).

[3] M. Hauptschein, M. Braid and F. E. Lawlor, *ibid.*, **79**, 6248 (1957).

[4] M. Hauptschein, M. Braid and F. E. Lawlor, *ibid.*, **80**, 846 (1958).

[5] A fluorocarbon radical, R·, attacks the CF_2 group of perfluoropropene. See ref. 2 and references cited therein.

[6] M. Hauptschein, A. H. Fainberg and M. Braid, THIS JOURNAL, **79**, 842 (1957).

TABLE I

CHARACTERISTIC INFRARED BANDS[a] IN MICRONS

$CF_3(CF_2\overset{CF_3}{\overset{\vert}{C}}F)_nI$	$CF_3(CF_2\overset{CF_3}{\overset{\vert}{C}}F)_nBr$	$CBrF_2(CF_2\overset{CF_3}{\overset{\vert}{C}}F)_nBr$	$Br(CF_2\overset{CF_3}{\overset{\vert}{C}}F)_nBr$
Range of n			
1 to *ca.* 6	1 to *ca.* 6	1 to *ca.* 6	1 to *ca.* 6
	7.24 ± 0.01(m)[b]	7.25 ± 0.01(m)	
7.48 ± 0.02(s)			
8.1 ± .1	8.10 ± .02[b]	8.1 ± 0.1	8.14 ± .04[b]
8.62 ± .02[b]	8.59 ± .01[b]	8.53 ± .03	8.59 ± .02[b]
	8.90 ± .02	8.91 ± .01	8.92 ± .01[b]
9.01 ± .03			
		9.12 ± .03	
9.23 ± .02(s)	9.21 ± .01(s)		
9.30 ± .01(s)[b]	9.29 ± .02(s)		
		9.63 ± .01(m)[b]	
		9.89 ± .04(s)	
10.19 ± .03	10.18 ± .02[b]	10.18 ± .01[b]	10.18 ± .02[b]
	10.49 ± .01(s)[b]	10.52 ± .04(s)[b]	
10.72 ± .01(s)	10.70 ± .04(s)[b]		
	10.92 ± .02[b]	10.92 ± .01	10.90 ± .03
11.21 ± .03	11.17 ± .03(s)[b]		
11.34 ± .01[b]			
		13.35 ± .01[b]	
		13.52 ± .02[b]	13.50 ± .02[b]
	13.69 ± .03[b]		
	14.26 ± .03[b]		14.22 ± .05
14.40 ± .03[b]			

[a] Bands listed are vs (very strong) unless otherwise noted as s(strong) or m (medium). [b] Not present for $n = 1$ compound.

ported.[2,3] Certain of the bands which are not shown by the first member of the series are suitably footnoted.

Seven or more very strong bands are characteristic of each of these series of compounds. These similarities in spectra furnish strong support for the telomer nature of the structures.

The three telomer bromide series have the following characteristic bands in common for $n > 1$: 8.1 ± 0.1, 8.57 ± 0.07, 8.91 ± 0.02, 10.18 ± 0.02 and 10.90 ± 0.04 μ.

All of the compounds thus far prepared in this Laboratory which have the repeating unit $[-CF_2CF(CF_3)-]_n$, $n > 1$, show the following characteristic bands: 8.1 ± 0.1, 8.57 ± 0.07 and 10.19 ± 0.03 μ. These compounds include not only 20 representative members of the four series listed in Table I but also 26 compounds in the series $CF_3CF_2CF_2[CF_2CF(CF_3)]_nCl$, n = 2 to *ca.* 9; $CF_3CF_2CF_2[CF_2CF(CF_3)]_nF$, n = 3 to *ca.* 9; $CF_3CF_2CF_2[CF_2CF(CF_3)]_nI$, n = 2 to *ca.* 10; $CF_3[CF_2CF(CF_3)]_n[(CF_3)CFCF_2]_nCF_3$, n = 2,3; and $CF_3CF_2CF_2[CF_2CF(CF_3)]_n[(CF_3)CFCF_2]_nCF_2CF_2CF_3$, n = 1 to 4.

The bands at 8.1 and 8.57 μ are probably associated with C–F stretching, and have no special significance since many highly or fully fluorinated compounds show strong bands in these regions.

The band at 10.19 ± 0.03 μ, however, which is attributed to a skeletal vibration associated with the repeating $-CF_2CF(CF_3)-$ unit, is of considerable diagnostic value since most perfluoroalkanes and perfluoroalkyl halides, which do not have this recurring unit, do not have absorption bands at this wave length.

Each of the series of secondary halides $R[CF_2CF(CF_3)]_nX$, is characterized by the following bands[3]: 10.45 ± 0.02 μ for the chlorides, 10.91 ± 0.03 μ for the bromides, and 11.31 ± 0.03 μ for the iodides. These bands thus appear to be characteristic of $-CF_2CFXCF_3$ and may be a skeletal vibration of this group.

Experimental

Thermal Reaction of Perfluoropropene with 1,2-Dibromoperfluoropropene.—Into a 300-ml. Monel autoclave containing 100 g. (0.32 mole) of 1,2-dibromoperfluoropropane and cooled to −75°, 224 g. (1.49 moles) of perfluoropropene was condensed *in vacuo*. The autoclave was sealed and heated at a temperature of 255°[7] with shaking for 560 hours. The pressure dropped from 4100 to 1675 p.s.i. during this time. From this reaction there were recovered, by condensation in refrigerated receivers during venting of the autoclave, 40 g. of the olefin, and, by careful fractionation of the less volatile reaction products, 55 g. of the reactant dibromide and 120 g. of a bromine-free fluorocarbon, b.p. 44–45°, perfluoro-(dimethylcyclobutane).[6] By means of fractional distillation of the remaining liquid reaction products, the telomer bromides, $CF_2BrCF(CF_3)[CF_2CF(CF_3)]_nBr$, were obtained in the following respective conversions and yields: 30% and 60% where n = 1, a liquid (45 g.) middle cut, b.p. 80° at 100 mm., $n^{26}D$ 1.3448 (*Anal.* Calcd. for $C_6F_{12}Br_2$: C, 15.7; F, 49.7. Found: C, 15.8; F, 50.2); 15% and 30%, where n = 2, a liquid (30 g.); middle cut, b.p. 78° at 9 mm., $n^{25}D$ 1.3435 (*Anal.* Calcd. for $C_9F_{18}Br_2$: C, 17.8; F, 56.2. Found: C, 17.8; F, 56.6); 5% and 10% where n = 3.5 av. (containing n = 3–5), a moderately viscous liquid (15 g.) middle cut, b.p. 48–49° at *ca.* 0.1 mm., $n^{25}D$ 1.3423 (*Anal.* Calcd. for $C_{13.5}F_{27}Br_2$: C, 19.4; F, 61.5. Found: C, 19.5; F, 61.5); a small residue (n = 6 estd.) remained undistilled.

Thermal Reaction of Perfluoropropene with Dibromodifluoromethane.—Forty-two grams (0.20 mole) of dibromodifluoromethane and 151 g. (1.01 moles) of perfluoropropene were condensed *in vacuo* in a 140-cc. Monel autoclave cooled in Dry Ice. The autoclave was sealed and heated at a temperature of 245°[7] for 10 days while shaking. During this period the pressure dropped from 4000 to 1700

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(7) Lowest temperature at which the pressure dropped noticeably after one hour.

p.s.i., about one-half of the drop occurring during the first day.

From this reaction there were recovered by venting through refrigerated receivers 75 g. of perfluoropropene, 4 g. of dibromodifluoromethane and 4 g. of perfluoro-(dimethylcyclobutane).[6] The remaining liquid products were rectified in a small Vigreux still. The resulting fractions were shown by their infrared spectra to consist entirely of telomer bromides, $BrCF_2[CF_2CF(CF_3)]_nBr$, which may be regarded as homologs of the telomer bromide series $Br[CF_2CF(CF_3)]_nBr$ derived from $CF_2BrCFBrCF_3$ described previously. Thus, with values of n estimated by comparison with the latter series, the composition of the remaining products was found to be 20 (weight) % $n = 1$ av., b.p. mainly 40–50° (100 mm.), n^{25}D 1.350; 20% $n = 2$ av., b.p. mainly 93–95° (100 mm.)., n^{25}D 1.346; 20% $n = 3$ av., b.p. mainly 80–87° (8 mm.), n^{25}D 1.345; 15% $n = 4$ av., b.p. mainly 45–55° (*ca.* 0.1 mm.), n^{25}D 1.344; and 10% $n = 5$ av. (containing $n = 4$–6) b.p. 55–124° (*ca.* 0.1 mm.), n^{25}D 1.343. For an intermediate fraction, b.p. 87–114° (8 mm.), n^{25}D 1.344, $n = 3.5$ av., the following values were determined: viscosities, 13.46 cs. (centistokes) at 78.4°F., 7.3 cs. at 100°F. (extrapolated), 4.33 cs. at 123.8°F., 1.48 cs. at 197.6°F. and 1.3 cs. at 210°F. (extrapolated); ASTM slope[8] (78–198°F.), 1.26; d^{26}_4 2.1312. For a fraction, b.p. 78–124° (*ca.* 0.1 mm.), $n = 5+$ av., viscosities were 13,190 cs. at 78.4°F., 1400 cs. at 100°F. (extrapolated), 240 cs. at 123.8°F., 11.8 cs. at 197.6°F. and 8.6 cs. at 210°F. (extrapolated), ASTM slope (78–198°F.), 1.29.

Thermal Reaction of Perfluoropropene with Bromotrifluoromethane.—A 300-cc. Monel autoclave was cooled to −75° and evacuated; 75 g. (0.50 mole) of bromotrifluoromethane and 300 g. (2.0 moles) of perfluoropropene were condensed in the autoclave by gaseous transfer. The reaction mixture was shaken and heated finally at a temperature of 260°[7] for 296 hours. During this time the pressure dropped from 9000 to 5600 p.s.i. After cooling to room temperature, the autoclave was vented slowly through a series of refrigerated receivers at atmospheric pressure. Recovered from the Dry Ice-cooled receivers were 60 g. of bromotrifluoromethane and 110 g. of perfluoropropene. Collected from the brine-cooled receivers and the autoclave were 200 g. of higher boiling liquid which was carefully fractionated. By this means there were obtained 155 g. of perfluoro-(dimethylcyclobutane)[6] and about 10 g. of $CF_3CF_2CFBrCF_3$ (estimated by vapor–liquid partition chromatography). A fraction (11 g.), b.p. 119–121°, middle cut 121°, colorless liquid, n^{30}D 1.3044, was $CF_3[CF_2CF(CF_3)]_nBr$ where $n = 2$. *Anal.* Calcd. for $C_7F_{15}Br$: F, 63.5; Br, 17.8. Found: F, 63.3; Br, 17.0. The telomer bromide where $n = 3$ was collected as a fraction (10.5 g.) middle cut, b.p. 93° at 50 mm., colorless liquid. n^{23}D 1.3139. *Anal.* Calcd. for $C_{10}F_{21}Br$: C, 20.1; F, 66.6; Br, 13.3. Found: C, 20.6; F, 67.1; Br, 12.7. The remaining fraction (5 g.), b.p. 51–160° at *ca.* 0.1 mm., was $n =$ *ca.* 5.5 av. (estimated) containing $n = 4$–7. The last portion of this fraction became solid at room temperature. Finally, a residue of higher telomer, 1 g., remained undistilled.

Thermal Reaction of 2-Iodoperfluorobutane with Bromine.—A 75-cc. heavy-wall Pyrex ampoule containing 15 g. (0.043 mole) of 2-iodoperfluorobutane and 15 g. (0.094 mole) of bromine was sealed *in vacuo* and heated while shaking. No change in the appearance of the contents was noted after 1.5 hr. at 125°, one hr. at 140° and one hr. at 150°. The tube was cooled in Dry Ice and opened, and volatiles were transferred *in vacuo* to a small Vigreux still. By distillation there was obtained 14 g., b.p. up to 56°. This fraction was washed with 15% aqueous sodium thiosulfate solution and then water (some handling losses occurred). The organic layer, 9 g., was dried with Drierite and distilled. The distillate was a colorless liquid, b.p. entirely 44–45°, n^{20}D 1.292. *Anal.* Calcd. for C_4F_9Br: C, 16.1. Found: C, 15.9.

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[8] The viscosity values lie on a nearly straight line when plotted on an ASTM (D341-43) viscosity chart. The ASTM slope is the slope of this line showing the temperature dependence of viscosity.

[CONTRIBUTION FROM THE ORGANIC RESEARCH DEPARTMENT, PENNSALT CHEMICALS CORP.]

Synthesis of Perfluoro-(2,4-dimethyl-2,4-di-n-butyl-1,3-dithiacyclobutane), a Fluorocarbon –C–S–C–S Heterocycle, and Related Reactions[1]

BY MURRAY HAUPTSCHEIN AND MILTON BRAID

RECEIVED MARCH 25, 1957

A novel fluorocarbon heterocyclic, $C_{12}F_{24}S_2$, of probable structure IIIb has been synthesized by (a) the thermal reaction of 2-iodoperfluorohexane with mercuric sulfide and (b) the thermal reaction of perfluoro-2-hexyl polysulfides in the presence of mercuric sulfide. Under less vigorous thermal conditions and by ultraviolet irradiation 2-iodoperfluorohexane interacted with mercuric sulfide to give almost entirely the linear di- and polysulfides, which have been demonstrated to be at least one of the precursors of perfluoro-(2,4-dimethyl-2,4-di-n-butyl-1,3-dithiacyclobutane). Mercuric sulfide and 1-iodoperfluoropropane when exposed to ultraviolet irradiation produced exclusively perfluoro-n-propyl disulfide.

Reactions of primary fluorocarbon iodides with elemental sulfur under thermal conditions where the products are the corresponding perfluoroalkyl disulfides and polysulfides have been described.[2,3] Recently, the conversion of a secondary fluorocarbon iodide, 2-iodoperfluorohexane, to perfluoro-2-hexyl polysulfides by a relatively less vigorous thermal reaction with sulfur was reported.[4]

It has now been found that primary and secondary perfluoroalkyl iodides are smoothly converted to their di- and polysulfides by reaction with mercuric sulfide under ultraviolet irradiation. Thus perfluoro-n-propyl disulfide was the sole product isolated from the photochemical reaction of n-C_3F_7I with mercuric sulfide while a mixture of perfluoro-2-hexyl di- and polysulfides was obtained from $C_4F_9CFICF_3$ under similar conditions.

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[1] The work herein reported was carried out under contract between the Office of Naval Research and the Pennsylvania Salt Manufacturing Co. Reproduction in whole or in part is permitted for any purpose of the United States Government.

[2] M. Hauptschein and A. V. Grosse, THIS JOURNAL, **73**, 5461 (1951).

[3] G. R. A. Brandt, H. J. Emeléus and R. N. Haszeldine, *J. Chem. Soc.*, 2198 (1952).

[4] M. Hauptschein, M. Braid and F. E. Lawlor, THIS JOURNAL, **79**, 6248 (1957).