Thermal Syntheses of Telomers of Fluorinated Olefins. II. 1,1-Difluoroethylene[1]

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Received March 25, 1957

The formation of telomers of 1,1-difluoroethylene of formula $R(CH_2CF_2)_nI(Br)$ where RI or RBr = CF_3I, C_3F_7I, CF_2-$ClCFClI$, $CF_2ClCFICF_3$, $C_2F_5CFICF_3$, $C_4F_9CFICF_3$, CF_2Br_2 and $CF_3CFBrCF_2Br$ and $n = 1$ to > 8 has been accomplished under thermal conditions. A study of the effect of the end groups on the liquid range of the telomers and their coupling products has been carried out, and has been successful in providing a means of obtaining liquid polymers of useful viscosity ranges based on 1,1-difluoroethylene. The prediction that such liquid polymers would have greatly improved viscosity–temperature properties has been verified. The preparation and properties of various coupling products, $R(CH_2CF_2)_n(CF_2$-$CH_2)_nR$ are presented. Certain infrared data are recorded.

The previous paper in this series described the stepwise syntheses of telomers of a relatively non-polymerizable olefin, perfluoropropene, by purely thermal means.[2] The present report is concerned with the application of the method of thermal synthesis to 1,1-difluoroethylene, an olefin of intermediate polymerizability.

Solid homopolymers of 1,1-difluoroethylene are readily prepared.[3-5] Although characterizations and properties of liquid polymers of this olefin had not been reported previously, we predicted that such polymers would have viscosity–temperature properties superior to any other liquid fluorohydrocarbons of comparable fluorine content as well as the expected high thermal stability characteristics.[6] Consequently, these materials should have special utility as hydraulic fluids and lubricants.

The influence of fluorine distribution as well as fluorine content on the temperature coefficient of viscosity has been noted for fluorine-containing diesters.[7] In the present case it was reasoned that the viscometric properties of oils based on

$$-\left[\begin{array}{c} H\ \ F \\ -C-C- \\ H\ \ F \end{array}\right]_n-$$
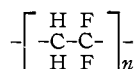
in which alternating $-CH_2$ "spacers" allow freer rotation, would be less markedly affected by temperature than those based on the isomeric structure in which rotation should be more restricted, i.e.

$$-\left[\begin{array}{c} F\ \ F \\ -C-C- \\ H\ \ H \end{array}\right]_n-$$
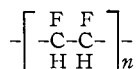
Although the polymerization of 1,1-difluoroethylene by the usual radical type of initiation affords exclusively solid polymers, it was considered likely that a telomerization based on thermal synthesis would provide the most practical method for forming the low molecular weight polymers required for oils of desired viscosity ranges. It was soon found, however, that chains containing

$-(CH_2CF_2-)_n-$ recurring units tend to give crystalline solids even for low n-values,[8] e.g., the coupling product of $CF_3(CH_2CF_2)_2I$, $CF_3CH_2CF_2CH_2$-$CF_2CF_2CH_2CF_2CH_2CF_3$, is a solid, melting at 38–40°. It was felt that liquids of useful viscosities could be prepared by introducing, through choice of telogens, appropriate end groups. The latter by preventing the too close approach of the molecular layers might lessen the tendency for crystallization.[9] A study of the effect of end groups on the liquid range of the telomers and their coupling products therefore was initiated.

The photochemical reactions of 1,1-difluoroethylene with trifluoroiodomethane[10] and pentafluoroiodoethane[11] in equimolar ratios were first described by Haszeldine and Steele who obtained mostly the addition products $CF_3(CH_2CF_2)_nI$ and $C_2F_5(CH_2CF_2)_nI$ where $n = 1$ with some evidence for the formation of small amounts where $n = 2$. In a single thermal reaction in which equimolar amounts of pentafluoroiodoethane and 1,1-difluoroethylene were heated 10 hours at 220° only $C_2F_5CH_2CF_2I$ (95%) was reported.[11] One-to-one and 2:1 addition products have been obtained from the peroxide-catalyzed reactions of 1,1-difluoroethylene with CF_2ClBr,[12] CF_2Br_2[13] and CF_2-$BrCFClBr$[14] using molar ratios of bromide to olefin of 1.9, 4.3 and 2, respectively.

We have now found that 1,1-difluoroethylene does react under thermal conditions with CF_3I, C_3F_7I, $CF_2ClCFClI$, $CF_2ClCFICF_3$, $C_2F_5CFICF_3$, $C_4F_9CFICF_3$, CF_2Br_2 and $CF_3CFBrCF_2Br$ to produce telomer iodides and bromides of the general formula $R(CH_2CF_2)_n$ $I(Br)$ in which n may range from 1 to >8 (see Tables I and II). The reaction may be controlled by varying the ratio of olefin to iodide or bromide from nearly equimolar to >5:1 and adjusting the reaction time to give telomers of desired narrow molecular weight ranges. In gen-

(8) It is likely that these chains have a greater tendency to orient, i.e., as $-CH_2CF_2CH_2CF_2CH_2CF_2-$ due to a type of hydrogen bonding

$-CF_2CH_2CF_2CH_2CF_2CH_2-$

and thus more readily crystallize.

(9) Another method for preparing oils of useful viscosity ranges would be to make telomers of a modified difluoroethylene in which one fluorine is replaced by a perfluoroalkyl group. Thus, the thermal synthesis in this Laboratory of $C_3F_7[CH_2CF(CF_3)]nI$ by reaction of C_3F_7I with $CH_2=CFCF_3$ afforded almost entirely oils of wide viscosity ranges.

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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.

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TABLE I

NEW TELOMER IODIDES

	B.p.,					Carbon		Analysis, %[b] Hydrogen		Fluorine	
	°C.	Mm.	$n^t D$	t, °C.	ϵ^a	Calcd.	Found	Calcd.	Found	Calcd.	Found
$CF_3(CH_2CF_2)_nI$											
$n = 2$	67	50	1.3815	26	304	18.5	18.8	1.2	1.5	41.1	41.1
$n = 3$	109–110	50	1.385	26	315	21.7	21.8	1.6	1.7	44.1	43.8
$C_3F_7(CH_2CF_2)_nI$											
$n = 1$	55	101	1.3502	23	318	16.7	16.9	0.56	0.65	47.5	47.6
$n = 2$	100	101	1.360	22	324	19.8	20.2	0.95	1.2	49.3	49.8
$n = 3$	111	19	1.3668	24	274	22.2	22.4	1.2	1.2	50.6	50.9
$n = 4$	88	ca. 0.1	1.3707	23	287	23.9	23.8	1.5	1.5		
$C_2F_5(CF_3)CF(CH_2CF_2)_nI$											
$n = 1$	67	100	1.3501	25	331	17.6	17.9	0.49	0.69		
$n = 2$	109	100	1.3573	25	333	20.3	20.0	0.85	0.94		
$n = 3$	96	8	1.3630	28	..	22.3	22.6	1.1	1.2		
$n = 4$	127	8	1.3671	28	..	23.9	24.2	1.3	1.3	53.7	53.4
$C_4F_9\overset{\overset{CF_3}{\mid}}{C}F(CH_2CF_2)_3I$	116.5–117.5	10	1.358	19	359	22.6	22.5	0.95	0.63		
$CF_3ClCFCl(CH_2CF_2)_nI$											
$n = 1$	92	75	1.4343	23	356	14.0	14.0	0.59	0.63		
$n = 2$	128	75	1.4252	23	353	17.7	17.9	0.99	0.69		
$n = 3$	54	ca. 0.1	1.420	25	362	20.4	20.0	1.3	1.4		
$n = 4$	94.5–95.5	ca. 0.1	1.415	23	329	22.5	23.1	1.5	1.7		
$CF_2Cl\overset{\overset{CF_3}{\mid}}{C}F(CH_2CF_2)_nI$											
$n = 1$	68–69	72	1.387	26	331	16.0	16.9	0.54	1.1		
$n = 2$	112	72	1.3880	26	323	19.1	19.1	0.92	1.2		
$n = 3$	114–115	9	1.387	31	335	21.4	21.9	1.2	1.4		
$n = 4$	145	6	1.3892	29	336	23.2	23.4	1.4	1.4		
$n = 5$	112	ca. 0.1	1.389	30	318	24.7	25.2	1.6	1.8		
$n = 6$	131	ca. 0.1	1.390	30	317	25.9	26.4	1.7	1.8		

[a] Molar extinction coefficients for absorption maxima at 270 ± 2 mμ in the ultraviolet spectra taken in isoöctane. [b] Analyses were performed by the Analytical Department, Pennsylvania Salt Manufacturing Co., and the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.

TABLE II

THERMAL TELOMERIZATIONS IN SHAKING AUTOCLAVE

Mole ratio CH_2CF_2: iodide	Time, hours	Temp., °C.	Pressure, p.s.i. Initial	Final	Conversion,[a] %	Yield, $R(CH_2CF_2)nI$, % $n = 1$	$n = 2$	$n = 3$	$n = 4$	$n = 5$	$n > 5$ (av. n-value)
CF_3I											
1.02[b]	22	188	4000	1675	ca. 80	80	10	5	5 ($n = 4.5$ av.)[c]		
C_3F_7I											
2.31	28	185	3800	350	89	41	34	15	6	4[d]	
3.79	23	181	4000	1300	82	31	32	23	9	5[d]	
$CF_2ClCFClI$											
5.01	26	180–182	6700	1700	95	16	17	32	24	8	3 (6)
$CF_2ClCFICF_3$[f]											
4.05	23	185–188	3500	700	96	18	29	26	16	7	4 (6)
4.05	65.5	180	4350	400	96	6	20	25	21	17	8 (6) 3 (8)[e]

[a] Conversion of iodide, RI, to telomer, $R[CH_2CF_2]_nI$. [b] From another run using 4.53 olefin:iodide ratio, heated at 185° for 113 hr., the product consisted mainly, 87 wt. %, of solid telomer, m.p. 60–72°. [c] Average n-value for telomer iodide, boiling point range 60–117° at ca. 0.1 mm., contains $n = 4$–6; highest boiling fraction was a solid, m.p. 37–39°. [d] Average n-value for telomer iodide, boiling point range 90–158° at ca. 0.1 mm.; contains $n = 4$–7. [e] $n = 7$–10 (est). [f] Prepared by the addition of iodine monochloride to perfluoropropene; P. Tarrant, private communication.

eral, temperatures of 180–190° were sufficient to carry out the reactions with the iodides. Although CF_2Br_2 reacted with 1,1-difluoroethylene at 190°, a temperature of 220° was necessary to achieve significant reaction when $CF_2BrCFBrCF_3$ was used as the telogen.[15] Good conversions of iodide to telomers of low molecular weight range were

(15) In a single experiment using CF_3Br as the telogen significant reaction occurred at 280° to produce mostly high molecular weight solid telomer bromides.

realized for reaction times of 19 to 28 hours with a substantial amount of reaction occurring during the first few hours as gauged by the pressure drop. Longer times were required by the bromides.

The liquid range of the telomer iodides, R-$(CH_2CF_2)_nI$, appeared to increase with increasing structural complexity (e.g., side chains) of the R group. Where R = CF_3 or C_3F_7, $n = 1$ to 3 were mobile liquids; where R = $CF_2ClCFCl$, $n = 1$ to 5 were liquids of low to moderate viscosity; where R = $CF_3CF(CF_2Cl)$, $n = 1$ to 6 were light to viscous oils; where R = $CF_3CF_2CF(CF_3)$, $n = 1$ to 6 (est.), and where R = $CF_3CF_2CF_2CF_2CF(CF_3)$, $n = 1$ to 7 (est.), were light to viscous oils.

The iodine atom of the primary $-CF_2I$ group in the telomer iodides can be replaced by chlorine by direct chlorination.[16] Lithium aluminum hydride or catalytic hydrogenation converts the telomer iodide to the hydride.[17] The coupling of perfluoroalkyl iodides by means of irradiation with ultraviolet light in the presence of mercury[16] has now been extended to the $-CH_2-CF_2I$ group of the present telomer iodides.

Some initial viscometric data taken on selected fractions of telomer coupling products have shown, as predicted, that the viscosity-temperature properties are much improved over fluorocarbon oils. For example, the coupling products of telomers of perfluoropropene were noteworthy for exceptionally high temperature coefficients of viscosity (ASTM slopes of ca. 1.3–1.4),[16] whereas coupled telomers of 1,1-difluoroethylene in the viscosity range of about 40 to 250 centistokes at 124°F. have ASTM slopes ranging from 0.71 to 0.87.

Moreover, the data indicate that to a first approximation the slope decreases as the ratio of the weights of the 1,1-difluoroethylene units to the weights of the end groups; i.e., $n(CH_2CF_2)/2R$ for the coupled telomer, $\{R[CH_2CF_2]_n\}_2$, increases. Thus the slope for $\{C_4F_9CF(CF_3)[CH_2CF_2]_{3.5}$ av.$\}_2$ where $n(CH_2CF_2)/2R = 0.702$ is 0.87, while for $\{CF_3CF(CF_2Cl)[CH_2CF_2]_{4.9}$ av.$\}_2$ in which there is a greater relative contribution from 1,1-difluoroethylene, i.e., $n(CH_2CF_2)/2R = 1.69$, the slope is 0.71.

Table III presents the infrared absorption maxima typical of the 1,1-difluoroethylene telomer iodide and coupling products series. Common to all of the spectra are bands at 3.34 ± 0.01 μ and 3.38 ± 0.01 μ in the C–H stretching region, and at 7.02 ± 0.03 μ. Common to all where $n > 1$ are bands at 7.19 ± 0.04, 8.1 − 8.5, 10.44 ± 0.08 and 11.30 ± 0.08 μ. Common to all of the spectra of the telomer iodides where $n > 1$, but not to the coupling products, is a band at 10.85 ± 0.05 μ.

The infrared spectra of the telomer bromide series, $CF_2Br(CH_2CF_2)_nBr$, where $n = 1$–4, have all of the characteristic bands listed above for the 1,1-difluoroethylene telomer iodide series with the exception of the bands (where $n > 1$) at 10.44 and 10.85 μ. A strong band, however, at 10.67 ± 0.01 μ is present.

(16) M. Hauptschein, M. Braid and F. E. Lawlor, This Journal, **79**, 2549 (1957).

(17) M. Hauptschein, A. J. Saggiomo and C. S. Stokes, ibid., **78**, 680 (1956).

Experimental

General Procedure.—A Monel autoclave (approximately 300 ml.) was charged with the fluoroalkyl iodide and cooled in liquid nitrogen. 1,1-Difluoroethylene was admitted to the cooled autoclave by gaseous transfer in vacuo. After warming to room temperature, the autoclave was shaken and heated for the period of reaction and then allowed to cool. Unreacted olefin was recovered by condensation in refrigerated receivers and the remaining products were distilled in small Vigreux units to effect separation of the individual telomer fractions. New compounds, physical constants and analytical data are listed in Table I. Experimental data and results of various runs are presented in Table II and below.

In a typical experiment, 160 g. (0.54 mole) of 1-iodoperfluoropropane and 131 g. (2.04 moles) of 1,1-difluoroethylene (3.8 molar ratio of olefin:iodide) were heated at 181° while shaking for 23 hours. The pressure dropped from 4000 to 1300 p.s.i. during the heating period, nearly half of the drop occurring during the first three hours. There were recovered 73 g. of 1,1-difluoroethylene and 8 g. of 1-iodoperfluoropropane. The remaining 197 g. of products was collected and characterized as summarized in the tables.

In all of these experiments free iodine rarely was observed and only to the extent of a few tenths of a gram, indicating the absence of significant side reactions under the experimental conditions used. During these procedures precautions were taken to exclude oxygen to prevent reactions with the iodides.

The Thermal Reaction of 2-Iodoperfluorobutane with 1,1-Difluoroethylene.—A 1-l. 316 stainless steel autoclave was charged with 402 g. (1.17 mole) of 2-iodoperfluorobutane and 228 g. (3.56 moles) of 1,1-difluoroethylene and heated at 175–190° with shaking for 19 hours; 75 g. of olefin was recovered. The remaining products after distillation under reduced pressure comprised the telomer iodides C_2F_5CF-$(CF_3)[CH_2CF_2]_nI$ where $n = 1$, 101 g. (see Table I for physical constants and analysis); where $n = 2$, 200 g.; where $n = 3$ av., 155 g.; where $n = 4$ av., 40 g. These products ranged from light to viscous oils at room temperature.

The Thermal Reaction of 2-Iodoperfluorohexane with 1,1-Difluoroethylene.—A 300-ml. Monel autoclave was charged with 170 g. (0.38 mole) of 2-iodoperfluorohexane and 139 g. (2.17 moles) of 1,1-difluoroethylene and heated at 188 to 191° with agitation for 64 hours; the pressure dropped from 3600 to 1000 p.s.i.; 35 g. of olefin was recovered and none of the reactant iodide was isolated. The remaining product was fractionally distilled under reduced pressure. The first fraction boiling up to 97° at 10 mm. (25 g.) contained $C_4F_9CF(CF_3)[CH_2CF_2]_nI$ where $n = 1$–2 mostly; a fraction (45 g.), middle cut, b.p. 116.5–117.5° at 10 mm., was the telomer iodide where $n = 3$ (see Table I). The succeeding fractions were estimated from boiling point ranges, refractive indices and molar extinction coefficients (ϵ) to be $n = 4$–5 (65 g.), b.p. 131–160° at 10 mm., $n^{19}D$ 1.363; $n = 5.5$ av. (82 g.), b.p. 160° at 9 mm. to 200° at 8 mm., $n^{19}D$ 1.369 (mol. wt. 800 based on $\epsilon = 350$ in isooctane for λ_{max} 270 mμ). These materials were all liquids at room temperature; viscosities for the last fraction were 68.15 cs. (centistokes) at 78.4°F., 16.05 cs. at 123.8°F., 31.8 cs. at 100°F. (extrapolated), 4.30 cs. at 197.8°F., and 3.64 cs. at 210°F. (extrapolated); ASTM slope (78–198°F.), 0.96.[18]

Finally, 35 g., mostly distillable solids, were collected, b.p. 156° to >225° at 0.1 mm., where the value of n is about 8 av. containing $n = 7$–9.

The Thermal Reaction of Dibromodifluoromethane with 1,1-Difluoroethylene.—A 300-ml. Monel autoclave was evacuated, cooled in liquid nitrogen and charged by gaseous transfer in vacuo with 332 g. (1.58 moles) of dibromodifluoromethane and 100 g. (1.56 moles) of 1,1-difluoroethylene. The autoclave was heated at 200° for about 45 hours with shaking. During this time the pressure dropped from 8000 to 3000 p.s.i., most of the drop occurring during the first day. From this reaction there were recovered 40 g. of 1,1-difluoroethylene and 243 g. of dibromodifluoromethane. The remaining products were fractionated in a small stainless steel helices-packed column to effect the separation of the telomer dibromides $CF_2Br(CH_2CF_2)_nBr$ of various

(18) 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.

TABLE III

INFRARED ABSORPTION BANDS CHARACTERISTIC OF THE VARIOUS TELOMER SERIES; WAVE LENGTHS IN MICRONS

$CF_3(R^a)_nI$ $n = 2, 3$	$C_3F_7(R)_nI$ 1 to ca. 7	$C_2F_5\overset{CF_3}{C}F(R)_nI$ 1 to 4	$C_4F_9\overset{CF_3}{C}F(R)_nI$ 3 to ca. 5.5	$CClF_2\overset{CF_3}{C}F(R)_nI$ 1 to 6	$CClF_2CClF(R)_nI$ 1 to 4	$[C_3F_7(R)_n-]_2$ 2.8 to 4 av.	$[C_4F_9\overset{CF_3}{C}F(R)_n-]_2$ 3.5 av. to 5.5 av.	$[CClF_2\overset{CF_3}{C}F(R)_n-]_2$ 3.9 av. to 4.9 av.
3.32 ± 0.01	3.34 ± 0.01	3.33 ± 0.01	3.32 ± 0.01	3.34 ± 0.01	3.34 ± 0.01	3.34 ± 0.01	3.34 ± 0.01	3.33 ± 0.01
3.37 ± .01	3.38 ± .01[b]	3.37 ± .01[b]	3.37 ± .01[b,c]	3.38 ± .01	3.39 ± .01[b]	3.38 ± .01	3.38 ± .01	3.37 ± .01
		6.92 ± .02[b]						
7.03 ± .01[b]	7.02 ± .02	7.03 ± .01	7.02 ± .01	7.04 ± .02	7.04 ± .01	7.00 ± .01	7.01 ± .01	7.01 ± .01
7.17 ± .01	7.17 ± .01[c]	7.18 ± .02	7.17 ± .01	7.19 ± .04[c]	7.20 ± .02	7.16 ± .02	7.17 ± .01	7.17 ± .01
7.32 ± .01	7.38 ± .01	7.33 ± .01	7.36 ± .01			7.32 ± .01	7.42 ± .01	7.43 ± .01
7.92 ± .02				7.88 ± .02				
8.20 ± .04	8.15 ± .02	8.20 ± .04	8.14 ± .01	8.17 ± .01	8.11 ± .03	8.18 ± .03	8.17 ± .01	8.1 -8.55
8.47 ± .01	8.50 ± .02		8.41 ± .01	8.38 ± .05	8.47 ± .02	8.52 ± .03	8.42 ± .01	
9.09 ± .01							8.80 ± .01	
	9.23 ± .03[c]	9.28 ± .01						
9.61 ± .01	9.60 ± .01			9.56 ± .01	9.61 ± .02			9.51 ± 0.01
		10.16 ± .01						
10.42 ± .02	10.39 ± .04	10.49 ± .03	10.46 ± .01	10.44 ± .01	10.44 ± .04[c]	10.41 ± .01	10.45 ± .05	10.42 ± .01
						10.64 ± .01		
10.82 ± .01	10.82 ± .01[c]	10.86 ± .04	10.82 ± .01	10.83 ± .02	10.85 ± .01[b,c]			
					11.03 ± .02	11.05 ± .01[b]		
11.25 ± .01	11.31 ± .07	11.26 ± .02[c]	11.29 ± .02	11.31 ± .03[c]	11.26 ± .06[c]	11.35 ± .01	11.35 ± .04	11.32 ± .01
11.62 ± .02						11.97 ± .01		11.98 ± .01
			12.34 ± .01					
			12.66 ± .01					
13.11 ± .02		13.15 ± .03	13.13 ± .02	13.08 ± .02				13.05 ± .01
	13.47 ± .02	13.50 ± .01	13.57 ± .01[b]			13.44 ± .01		
13.62 ± .02	13.67 ± .03[c]	13.75 ± .02	13.76 ± .01			13.64 ± .01		13.70 ± .01
				14.04 ± .04				14.00 ± .01
		14.35 ± .03						
14.62 ± .03				14.68 ± .02[c]				
						15.12 ± .01		

[a] R = CH₂CF₂. [b] Shoulder. [c] Not present for $n = 1$.

values of n. There were collected first 24 g. where $n = 1$,[13] b.p. mainly 47° at 100 mm., n^{27}D 1.3969; and 26 g. where $n = 2$,[13] b.p. mainly 98° at 100 mm., n^{27}D 1.3964. *Anal.* Calcd. for $C_5H_4F_6Br_2$: C, 17.8; H, 1.2; F, 33.7; Br, 47.3. Found: C, 18.1; H, 1.2; F, 33.8; Br, 47.3.

The next fraction, 34 g., b.p. middle cut 44° at *ca.* 0.1 mm., 90° at *ca.* 10 mm., n^{28}D 1.3950, was the telomer dibromide where $n = 3$. *Anal.* Calcd. for $C_7H_6F_8Br_2$: C, 20.9; H, 1.5; F, 37.8; Br, 39.8. Found: C, 21.2; H, 1.5; F, 38.1; Br, 39.9.

There was collected next 14 g. where $n = 4$, b.p. mainly 77–79° at *ca.* 0.1 mm. A redistilled fraction, b.p. 124° at 10 mm., m.p. 31–32°, n^{27}D 1.3950, was analyzed. *Anal.* Calcd. for $C_9H_8F_{10}Br_2$: C, 23.2; H, 1.7; F, 40.8; Br, 34.3. Found: C, 23.3; H, 1.7; F, 40.8; Br, 34.3.

Finally, 27 g. of solid telomer dibromides of n values >4, b.p. >80° at *ca.* 0.1 mm., was obtained.

Similarly, from the reaction of 315 g. (1.50 moles) of dibromodifluoromethane and 96 g. (1.50 moles) of 1,1-difluoroethylene at 190° for 76.5 hours, pressure drop 4900 to 2575 p.s.i., there was recovered 324 g. of a mixture of the olefin and dibromodifluoromethane, and 80 g. of telomer bromides, which were distilled in a Vigreux unit. In addition to 25 g. of $CF_2Br(CH_2CF_2)_nBr$ where $n = 1$ and 20 g. where $n = 2$ there were collected 18 g. where $n = 4$ av., b.p. 97–144° at 10 mm., a colorless oil which had the following viscosities: 19.56 cs. at 32°F., 6.11 cs. at 78.4°F., 4.1 cs. at 100°F. (extrapolated), 2.97 cs. at 123.8°F. and 1.03 cs. at 197.8°F.; ASTM slope (32–198°F), 0.99; 12 g. where $n = 7$ av., b.p. 115–190° at *ca.* 0.1 mm., a white solid, m.p. 41–43° (*Anal.* Calcd. for $C_{15}H_{14}F_{16}Br_2$: C, 27.4; H, 2.1. Found: C, 27.5; H, 2.1); 3 g. where $n = 9$ av., b.p. 190–200° at *ca.* 0.1 mm., a light yellow solid, m.p. 80–84° (*Anal.* Calcd. for $C_{19}H_{18}F_{20}Br_2$: C, 29.0; H, 2.3. Found: C, 29.2; H, 2.3); and 1.5 g. of solid telomer dibromide, b.p. >200° at *ca.* 0.1 mm.

The Thermal Reaction of 1,2-Dibromoperfluoropropane with 1,1-Difluoroethylene.—A 300-ml. Monel autoclave was charged with 201.5 g. (0.65 mole) of 1,2-dibromoperfluoropropane and cooled with liquid nitrogen. By gaseous transfer *in vacuo*, 131 g. (2.05 moles) of 1,1-difluoroethylene was introduced into the autoclave which was then heated at 220° for 119 hours while shaking. The pressure dropped from 6200 to 1900 p.s.i. during this time; 70 g. of olefin and 95 g. of the reactant dibromide were recovered. The remaining products consisted of 116 g. (65 wt. %) of tan-colored solids and the following distilled fractions: 10 g. boiling up to 63° at 10 mm., clear colorless liquid; 4 g., b.p., 54–82° at *ca.* 0.1 mm., n^{24}D 1.3899, clear colorless oil; 4 g., b.p. 82–127° at *ca.* 0.1 mm., n^{29}D 1.3882, colorless oil (viscosities, 21.54 cs. at 78.4°F., 12.3 cs. at 100°F. (extrapolated), 7.37 cs. at 123.8°F., 2.46 cs. at 197.8°F. and 2.19 cs. at 210°F. (extrapolated), ASTM slope (78–198°F.) 1.0); 12 g., b.p. 127–195° at *ca.* 0.1 mm., solid, m.p., 25 to >35°; 13 g., b.p., 180–310° at <0.1 mm., solid, m.p. 50–55°. A residue (10 g.) remained undistilled at >310° at <0.1 mm.

Coupling of R[CH_2CF_2]$_n$I by Use of Ultraviolet Light and Mercury.—The general experimental procedure employed for coupling the telomer iodides in the sections below has been described previously for perfluoroalkyl iodides.[16]

(a) $CF_3[CH_2CF_2]_nI$.—Sixteen grams (0.062 mole) of $CF_3CH_2CF_2I$ and 8 ml. of clean dry mercury were sealed under a dry nitrogen atmosphere in a 50-ml. Vycor tube. After shaking for several days under ultraviolet irradiation, the tube was opened, 1,1,2-trichlorotrifluoroethane solvent was added, and the reaction mixture was filtered to remove mercury and solids. Several additional portions of solvent were used to wash the residue on the filter, and all the filtrates were combined. After removal of the solvent by distillation, the coupled product, $CF_3CH_2CF_2CF_2CH_2CF_3$, was obtained as a colorless oil, b.p. 83° at 760 mm. The yield and conversion were 49%.

Anal. Calcd. for $C_6H_4F_{10}$: C, 27.1; H, 1.5; F, 71.4. Found: C, 27.2; H, 1.97; F, 71.0.

By the above procedure, 18 g. (0.056 mole) of $CF_3[CH_2CF_2]_2I$ and 8 ml. of mercury were shaken and irradiated with ultraviolet light for two days. The tube was opened and, after the addition of 10 ml. of 1,1,2-trichlorotrifluoroethane solvent, resealed and irradiated with shaking for several additional days. The coupled product, $(CF_3[CH_2CF_2]_2)_2$, a white solid, m.p. 38–40°, was isolated by distilla-

tion, b.p. 100° at 25 mm. The yield and conversion were 54%.

Anal. Calcd. for $C_{10}H_8F_{14}$: C, 30.5; H, 2.1; F, 67.5. Found: C, 30.5; H, 2.4; F, 67.2.

Similarly, 13 g. (0.034 mole) of $CF_3(CH_2CF_2)_3I$ and 6 ml. of mercury were irradiated for two days. The tube was opened, 10 ml. of 1,1,2-trichlorotrifluoroethane was added, and tube was resealed and returned to the shaker for several additional days. The coupling product, $(CF_3[CH_2CF_2]_3)_2$, isolated by sublimation, was a white solid, m.p. 40–44°.

Anal. Calcd. for $C_{14}H_{12}F_{18}$: C, 32.2; H, 2.3; F, 65.5. Found: C, 31.9; H, 2.4; F, 65.3. The yield and conversion based on the product isolated were 29%; however, in this case as well as in the previous two examples efforts to separate all the product were not made. The actual conversions are estimated to be of the order of 80%.

(b) $C_3F_7[CH_2CF_2]_nI$.—Thirteen grams (0.027 mole) of $C_3F_7[CH_2CF_2]_{2.8 av.}I$, 8 ml. of mercury and 20 ml. of 1,1,2-trichlorotrifluoroethane in a Vycor tube were shaken and exposed to ultraviolet light for 4 days. The coupling product, $(C_3F_7[CH_2CF_2]_{2.8 av.})_2$, b.p. 105–140° at 10 mm., solid at room temperature, was obtained in 89% yield and conversion.

As described above, 9.3 g. (0.017 mole) of $C_3F_7[CH_2CF_2]_{4 av.}I$, 5 ml. of mercury and 15 ml. of 1,1,2-trichlorotrifluoroethane were allowed to react for 10 days. The coupling product $(C_3F_7(CH_2CF_2)_{4 av.})_2$ was a white solid boiling mainly at 75–150° at <0.1 mm. The yield and conversion based on product isolated were 40%, but additional solid products remained unextracted from the reaction mixture.

(c) $C_4F_9CF(CF_3)[CH_2CF_2]_nI$.—Eight milliliters of mercury, 12.6 g. (0.019 mole) of $C_4F_9CF(CF_3)[CH_2CF_2]_{3.5 av.}I$ and 10 ml. of 1,1,2-trichlorotrifluoroethane in a Vycor tube were shaken and exposed to ultraviolet irradiation for five days. The coupled product, $(C_4F_9CF(CF_3)[CH_2CF_2]_{3.5 av.})_2$, was an oil, b.p. 170–230° at *ca.* 0.1 mm., n^{29}D 1.333; viscosities: 318 cs. at 78.4°F., 58.7 cs. at 123.8°F., 10 cs. at 197.8°F.; ASTM slope (78 to 198°F.), 0.87. The conversion and yield were 83%.

By the same procedure, 14 g. (0.018 mole) of $C_4F_9CF(CF_3)[CH_2CF_2]_{5.5 av.}I$ and 8 ml. of mercury in 10 ml. of 1,1,2-trichlorotrifluoroethane were shaken and exposed to ultraviolet light for five days. The coupled product $\{C_4F_9CF(CF_3)[CH_2CF_2]_{5.5 av.}\}_2$, b.p. 180–260° at *ca.* 0.1 mm., n^{31}D 1.344, was an oil, partially solid at 25°; viscosities: 520 cs. at 100°F. (extrapolated), 204 cs. at 123.8°F., 26.5 cs. at 197.8°F., 21.8 cs. at 210°F. (extrapolated); ASTM slope (124–198°F), 0.77. The conversion and yield were 85%.

(d) $CF_3CF(CF_2Cl)[CH_2CF_2]_nI$.—Twenty grams (0.036 mole) of $CF_3CF(CF_2Cl)[CH_2CF_2]_{3.9 av.}I$, 8 ml. of mercury and 10 ml. of 1,1,2-trichlorotrifluoroethane were shaken in a Vycor tube under ultraviolet light for 4 days. The coupling product, $\{CF_3CF(CF_2Cl)[CH_2CF_2]_{3.9 av.}\}_2$, b.p. 153–240° at *ca.* 0.1 mm.; n^{28}D 1.361, was a heavy oil; viscosities: 455 cs. at 78.4°F., 181 cs. at 100°F. (extrapolated), 86.4 cs. at 123.8°F., 14.6 cs. at 197.8°F., 11.95 cs. at 210°F. (extrapolated); ASTM slope (78–198°F.), 0.79. The yield and conversion were 83%.

Twenty-two grams (0.035 mole) of $CF_3CF(CF_2Cl)[CH_2CF_2]_{4.9 av.}I$, 8 ml. of mercury and 10 ml. of 1,1,2-trichlorotrifluoroethane in a Vycor tube were exposed to ultraviolet while shaking for 6 days. The main fraction of coupled product, $\{CF_3CF(CF_2Cl)[CH_2CF_2]_{4.9 av.}\}_2$, b.p. 153–210° at <0.1 mm., was a heavy oil partially solid at 25°, n^{27}D 1.365, viscosities: 249 cs. at 123.8°F., 610 cs. at 100°F. (extrapolated), 34.6 cs. at 197.8°F., 28 cs. at 210°F. (extrapolated); ASTM slope (124–198°F.), 0.71. The yield and conversion were 70%.

(e) $CF_2ClCFCl[CH_2CF_2]_nI$.—By use of the previously described procedures, 10 g. (0.024 mole) of $CF_2ClCFCl[CH_2CF_2]_{2.2 av}I$ was converted to the coupling product, $(CF_2ClCFCl[CH_2CF_2]_{2.2 av.})_2$, an oil, b.p. 105–165° at *ca.* 0.1 mm., n^{40}D 1.380; viscosity 15.3 cs. at 123.8°F., in 61% conversion and yield after shaking in a Vycor tube with 9 ml. of mercury and 10 ml. of 1,1,2-trichlorotrifluoroethane under ultraviolet irradiation for 4 days.

Similarly, 10 g. (0.019 mole) of $CF_2ClCFCl[CH_2CF_2]_{4 av.}I$, 9 ml. of mercury and 10 ml. of 1,1,2-trichlorotrifluoroethane were shaken in a Vycor tube for 4 days while exposed to ultraviolet light. The coupling product, $(CF_2ClCFCl[CH_2-

CF$_2$]$_4$ $_{\text{av.}}$)$_2$, 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%.

Acknowledgment.—We wish to thank Mr. John J. Mullaney and Mr. Fred P. Curtis for technical assistance, Dr. Arnold Fainberg and Miss Ruth Kossatz for infrared spectroscopic work, and the Analytical Department of Pennsalt Chemicals Corporation.

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

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Received March 25, 1957

By the thermal reaction of CF$_3$Br, CF$_2$Br$_2$ and CF$_3$CFBrCF$_2$Br with perfluoropropene, the telomer bromides, R[CF$_2$CF-(CF$_3$)]$_n$Br, where R = CF$_3$, CF$_2$Br and CF$_3$CFCF$_2$Br, and $n = 1$–*ca.* 6 have been prepared. Several correlations of infrared absorption data for the series R[CF$_2$CF(CF$_3$)]$_n$X are presented. A strong band at 10.19 ± 0.03 μ, which is attributed to a skeletal vibration characteristic of the repeated –CF$_2$CF(CF$_3$)– unit, has been found without exception for 46 members of this series.

The formation of telomer iodides of the formula R[CF$_2$CF(CF$_3$)]$_n$I 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$_2$-CF$_2$)$_n$Br have been synthesized by the thermal reactions of CF$_2$Br$_2$ and CF$_3$CFBrCF$_2$Br 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$_2$CF(CF$_3$)]$_n$Br 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$_2$CF-(CF$_3$)]$_n$X were X = I, Cl or F, previously reported.[3]

We have now found that the telomer bromides of formula R[CF$_2$CF(CF$_3$)]$_n$Br[5] may be prepared by the thermal reaction of fluorocarbon bromides with perfluoropropene. It is particularly noteworthy that CF$_3$Br as well as CF$_2$Br$_2$ and CF$_2$BrCFBrCF$_3$ 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$_2$Br$_2$ and CF$_2$BrCFBrCF$_3$, respectively, no reaction was observed for CF$_3$Br 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$_2$CF(CF$_3$)]$_n$Br 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$_2$BrCF(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$_2$Br-CFBrCF$_3$ may add to CF$_2$=CFCF$_3$ to give either CF$_2$BrCF(CF$_3$)[CF$_2$CF(CF$_3$)]$_n$Br or CF$_3$CFBr-CF$_2$[CF$_2$CF(CF$_3$)]$_n$Br, 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$_3$Br, did not react noticeably at the temperature at which CF$_2$BrCFBrCF$_3$ 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$_3$Br 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$_2$CF(CF$_3$)]$_n$I, previously re-

(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).