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Transformations of Polyfluoroalkyl Iodides[1]

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The coupling of primary and secondary perfluoroalkyl iodides has been achieved in high yield by the use of ultraviolet irradiation in the presence of mercury. Another novel method for coupling secondary fluorocarbon iodides by thermal reaction in the presence of mercuric oxide is reported. The syntheses and properties of the homologous series $R_f[CF_2CF(CF_3)]_n[(CF_3)CFCF_2]_nR_f$ where n = 1–4 and the series $C_3F_7[CF_2CF(CF_3)]_nX$ where X = Cl and F and n = 1–10 are described. The compounds $[C_4F_9CF(CF_3)]_2S_n$ where n = 2–5 have been prepared by interaction of 2-iodoperfluorohexane with sulfur and converted to perfluoro-2-hexylsulfenyl chloride by thermal chlorination. Related reactions of chlorofluoroalkyl iodides are presented. Certain correlations of the infrared absorption data are discussed.

The thermal synthesis of telomers of perfluoropropene gives products with a $-[CF_2CF(CF_3)]_n-$ chain and an iodine atom as one of the end groups.[2] This report deals with certain transformations and stabilization procedures[3] in which the iodine atoms in these telomers and certain related fluorocarbon iodides are replaced.

The iodides, $C_3F_7[CF_2CF(CF_3)]_nI$, where n = 1–10 were converted to the corresponding fluorides by conventional treatment with cobalt trifluoride and to the corresponding chlorides by reaction with chlorine at elevated temperatures.

The coupling of secondary perfluoroalkyl iodides has not been previously reported. Since the primary perfluoroalkyl iodide, $CF_3CF_2CF_2I$, has been shown to couple to n-C_6F_{14} by the use of either zinc and dioxane[4] or zinc and acetic anhydride–methylene chloride,[5] the latter method[5] was tried once on 2-iodoperfluorohexane. None of the expected coupling product $C_4F_9CF(CF_3)CF(CF_3)C_4F_9$ was produced; the only products detected were the two possible olefins formed by removal of iodine and fluorine from adjacent carbon atoms, $C_4F_9CF{=}CF_2$ and $C_3F_7CF{=}CFCF_3$.

In view of these findings, another method involving the use of mercury and ultraviolet light was tried. Haszeldine[6,7] has shown that good yields of coupling products are obtained by this procedure if the compound to be coupled contains a $-CFClI$ group, *e.g.*, $CF_2ClCFClI$, CF_3CF_2CFClI. Under similar conditions Emeléus and Haszeldine[8] had previously found that CF_3I and C_2F_5I gave principally CF_3HgI and C_2F_5HgI, with some reaction of the fluorocarbon radicals with the glass reaction vessels to form SiF_4 and CO_2. The simple coupling reaction leading to C_2F_6 or C_4F_{10} did not occur to any significant extent. The mercurial was rather easily decomposed by light, and, unless the shaking conditions caused the mercurial to be deposited in a section of the tube shielded from direct irradiation, the yields were low with increased formation of SiF_4 and CO_2.

It was, consequently, a welcome surprise to find that the above ultraviolet light–mercury method afforded exclusively the coupled products from secondary perfluoroalkyl iodides

$$2R_f[CF_2CF(CF_3)]_nI \xrightarrow[\text{u.v.}]{\text{Hg}} R_f[CF_2CF(CF_3)]_n[(CF_3)CFCF_2]_nR_f + HgI_2$$

where $R_f = CF_3$ and $CF_3CF_2CF_2$, and n = 1–4.

In view of these encouraging results, an attempt was made to couple the primary perfluoroalkyl iodide, n-C_3F_7I, by the mercury and ultraviolet light method. Quantitative conversion to n-C_6F_{14} was obtained. The reasons for the marked differences between the course of the reaction of n-C_3F_7I on the one hand and CF_3I or C_2F_5I[8] on the other hand are not clear. Although C_3F_7I may very well have coupled after the *in situ* formation of C_3F_7HgI,[9] the failure of this mercurial in contrast to C_2F_5HgI to decompose by ultraviolet light into SiF_4 and CO_2 and the quantitative nature of the reaction leading to n-C_6F_{14} were certainly not predictable.

In addition, the Hg–u.v. coupling method has been successfully extended to other compounds containing the primary $-CF_2I$ group, *e.g.*, $CF_3(CH_2CF_2)_nI \rightarrow CF_3(CH_2CF_2)_n(CF_2CH_2)_nCF_3$ (forthcoming communication).

An unusual method for coupling secondary perfluoroalkyl iodides by thermal reaction in the presence of mercuric oxide was discovered. Heating 2-iodoperfluorohexane and yellow mercuric oxide at 235° gave the coupling product, perfluoro-5,6-dimethyldecane, exclusively.

Other methods which afforded poor to moderate yields of coupling products from the $C_3F_7[CF_2CF(CF_3)]_nI$ (I) series included: (1) I + mercury + heat; (2) I + concentrated sulfuric acid + heat; (3) I + heat alone; (4) I + heat in the presence of excess perfluoropropene.

Among the reaction products of method 4 were *perfluoro*-(dimethylcyclobutane) and a perfluorohexane which was not the normal isomer. Although the origin of the latter compound was not established, it is likely that it was formed by the thermal degradation of a telomer iodide or of a coupling

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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] The term "stabilization procedures" refers to the replacement of the relatively reactive iodine atom of the telomer iodides by less reactive atoms such as fluorine or chlorine, or by a coupling reaction, to produce more stable transformation products, *i.e.*, "stabilized telomers."

[4] R. N. Haszeldine and E. G. Walaschewski, *J. Chem. Soc.*, 3607 (1953).

[5] A. L. Henne, THIS JOURNAL, **75**, 5750 (1953).

[6] R. N. Haszeldine, *J. Chem. Soc.*, 4423 (1952).

[7] R. N. Haszeldine and B. R. Steele, *ibid.*, 1592 (1953).

[8] H. J. Emeléus and R. N. Haszeldine, *ibid.*, 2948 (1949).

[9] Evidence was obtained (see Experimental) that the formation of the coupling products of both primary and secondary perfluoroalkyl iodides by the Hg–u.v. method proceeds at least to some extent *via* the intermediate formation of some type of perfluoroalkyl mercury compound, probably R_fHgI.

TABLE I

PHYSICAL CONSTANTS AND ANALYTICAL DATA OF STABILIZED TELOMERS

Formula	Conversion, %	B.p., °C.	B.p., Mm.	n^t_D	t, °C.	Pour point or f.p., °C.	Analyses, %[a] Carbon Calcd.	Carbon Found	Fluorine Calcd.	Fluorine Found
$C_3F_7[CF_2CF(CF_3)]_1Cl$	100	84	760	1.2826	26	<−80	20.3	20.0	69.7	69.8
$C_3F_7[CF_2CF(CF_3)]_2Cl$	89	134	760	1.299	22	<−80	21.4	21.7	71.5	71.8
$C_3F_7[CF_2CF(CF_3)]_3Cl$	98	75	8	1.3091	22	<−80	22.0	22.0	72.6	..
$C_3F_7[CF_2CF(CF_3)]_4Cl$	85	112	10	1.3169	20	*ca.* −15	22.4	22.3	73.2	73.8
$C_3F_7[CF_2CF(CF_3)]_{5av.}Cl$	81[b]	66-96	<0.1	1.3172	30	*ca.* 10	22.6	22.6	73.6	73.7
$C_3F_7[CF_2CF(CF_3)]_{6av.}Cl$	81[b]	96–117	< .1	1.3205	31	*ca.* 25	22.8	22.6	74.0	73.7
$C_3F_7[CF_2CF(CF_3)]_{8av.}Cl$	81[b]	117–150	< .1	....	..	38–42	23.1	23.1	74.4	74.4
$C_3F_7[CF_2CF(CF_3)]_{9av.}Cl$	81[b]	150–170	< .1	....	..	58–70	23.2	23.0	74.5	74.6
$C_3F_7[CF_2CF(CF_3)]_3F$	75[b]	115–116	98	1.290 (est.)	30	*ca.* −40[c]	22.6	22.7	77.4	77.6
$C_3F_7[CF_2CF(CF_3)]_4F$	75[b]	143–145	95	1.3003	30	*ca.* −10	22.9	22.8	77.1	77.3
$C_3F_7[CF_2CF(CF_3)]_5F$	75[b]	173	95	1.3067	30	*ca.* 15	23.0	22.8	77.0	77.1
$C_3F_7[CF_2CF(CF_3)]_{6av.}F$	75[b]	84–143	*ca.* 0.1	1.3112	29	*ca.* 20	23.2	23.0	76.8	76.9
$C_3F_7[CF_2CF(CF_3)]_{9av.}F$	75[b]	130–180	<0.1	....	..	58–64	23.5	23.5	76.5	76.7
$C_4F_9CF(CF_3)CF(CF_3)C_4F_9$	94	95	45	1.2945	21	<−80	22.6	22.4	77.4	77.8
$\{C_3F_7[CF_2CF(CF_3)]_2\}_2$	89	127	10	1.3079	28	*ca.* − 1[c]	23.0	23.3	77.0	76.7
$\{C_3F_7[CF_2CF(CF_3)]_{3av.}\}_2$	88	120–152	<0.1	1.3137	39	*ca.* 35	23.3	23.1	76.7	77.2
$\{C_3F_6[CF_2CF(CF_3)]_{4av.}\}_2$	76	159–168– 193	<0.1	....	..	42–48	23.5	23.5	76.5	76.2
$\{CF_3[CF_2CF(CF_3)]_2\}_2$	85	93	10	1.3040	25	*ca.* −26	22.8	22.9	77.2	76.9
$\{CF_3[CF_2CF(CF_3)]_3\}_2$	78	94–95	0.1	1.3152	26	*ca.* 15	23.1	22.8	76.9	76.8

[a] Microanalyses by Schwarzkopf Microanalytical Laboratory. In all cases % H was zero. [b] Over-all conversions or yields for the fluorinations and chlorinations of suitable mixtures of telomer iodides from which these individual products were isolated by subsequent rectification. [c] Pour points for $C_3F_7[CF_2CF(CF_3)]_{3av.}F$, b.p. 67–77° (9 mm.) = *ca.* −60°; for $C_3F_7[CF_2CF(CF_3)]_{2\,av.}[CF(CF_3)CF_2]_{2av.}\,C_3F_7$, b.p. 67–101° (<0.1 mm.) = *ca.* −20°.

product formed during the reaction. In this connection it should be mentioned that preliminary studies on the thermal stabilities of fluorocarbons have indicated a marked dependence upon their structural arrangements, the order of increasing stability being $-CF(CF_3)-CF(CF_3)- < -CF_2-CF(CF_3)-CF_2 < -CF_2-CF_2-$. Apparently, replacement of a fluorine atom by the larger trifluoromethyl group in a fluorocarbon chain creates increased strain, thus diminishing the carbon–carbon bond dissociation energy involved.

The secondary iodide 2-iodoperfluorohexane was converted in good yield to $[C_4F_9CF(CF_3)]_2S_n$ where $n = 2–5$, by reaction with sulfur at a lower temperature than was necessary for the corresponding reactions of the primary perfluoroalkyl iodides, trifluoroiodomethane and heptafluoroiodopropane. While $C_4F_9CFICF_3$ was converted to the polysulfide readily at 170–180° in either a Monel autoclave or in a sealed glass vessel, CF_3I gave low yields of disulfides at 205–210° in glass,[10] moderate yields in a stainless steel autoclave at 265°,[10] and good yields in a stainless steel autoclave at 310°.[11] C_3F_7I gave good yields and conversions in glass at 250°,[12] although it is reported[13] that in a steel autoclave little reaction occurred even at 350°, and 450° was necessary to achieve complete reaction of the iodide.

Although some of the above reaction conditions and yields of the primary perfluoroalkyl iodides, particularly C_3F_7I, are difficult to reconcile, it is nevertheless clear that the secondary perfluoroalkyl iodide linkage undergoes more facile reaction with sulfur. In general, it may be expected that the secondary $CF(CF_3)$–I bond will be more chemically reactive (less stable) than the primary CF_2–I bond.

The secondary perfluoro-2-hexyl polysulfides readily were converted to perfluoro-2-hexylsulfenyl chloride by thermal reaction with chlorine at 105°.

Certain related work on chlorofluoroalkyl halides is recorded here.

The coupling of $CF_2ClCFClCF_2CFClI$ to $(CF_2ClCFClCF_2CFCl)_2$[14] in 83% yield was accomplished by the use of zinc and an acetic anhydride–methylene chloride solvent pair. As might have been predicted, this yield is considerably higher than that obtained by Henne and Postelneck[15] with $CF_2ClCFClI$. The latter compound has a chlorine atom on the carbon alpha to the CFClI group, which increases the possibility of concurrent dechlorination.

1,1,2,3,4,4-Hexafluoro-1,2,3,4-tetrachlorobutane, the precursor of perfluorobutadiene, was obtained in low yield by heating 1,2-dichloro-2-iodo-1,1,2-trifluoroethane and mercuric oxide at 220 and 232°.

1,2-Dichloro-2-iodo-1,1,2-trifluoroethane and sulfur at 187° interacted to give mainly $(CF_2ClCFCl)_2S_n$ where $n = 2–5$.

Table I records the yields, analytical characterizations and some physical constants of the stabilized telomers prepared. Table II presents the kinematic viscosities of representative chlorides, fluorides and coupling products. The exceptionally high temperature coefficients of viscosity of these

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

[11] R. N. Haszeldine and J. M. Kidd, *ibid.*, 3219 (1953).

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

[13] R. N. Haszeldine and J. M. Kidd, *J. Chem. Soc.*, 3871 (1955).

[14] R. N. Haszeldine, *ibid.*, 4302 (1955), prepared this compound by the mercury-ultraviolet light method.

[15] A. L. Henne and W. Postelneck, THIS JOURNAL, **77**, 2334 (1955).

TABLE II

KINEMATIC VISCOSITIES (CENTISTOKES) OF STABILIZED TELOMERS

Formula	78.4°F.	141.4°F.	197.8°F.	100°F.^{a}	210°F.^{a}	ASTM slope^b
$C_3F_7[CF_2CF(CF_3)]_2Cl$	1.421	0.698	0.461	0.65	0.35	1.46
$C_3F_7[CF_2CF(CF_3)]_3Cl$	4.68	2.07	0.897	2.98	0.813	1.33
$C_3F_7[CF_2CF(CF_3)]_4Cl$	43.11	8.13	2.003	17.3	1.74	1.34
$C_3F_7[CF_2CF(CF_3)]_{5av.}Cl$	57.95^f	...	5.66	210	4.55	1.29
$C_3F_7[CF_2CF(CF_3)]_{6av.}Cl$	610.97^f	...	16.40	5100	11.9	1.34
$C_3F_7[CF_2CF(CF_3)]_{3av.}F^c$	3.58	1.47	0.79	2.55	0.45	1.34
$C_3F_7[CF_2CF(CF_3)]_{4+}F^d$	36.75	4.77	1.84	15.0	1.60	1.38
$C_3F_7[CF_2CF(CF_3)]_{6av.}F$	501.97^f		9.11	6300	6.5	1.64
$\{C_3F_7[CF_2CF(CF_3)]_2\}_2$	242.7	13.96	3.59	70	2.9	1.33
$\{C_3F_7[CF_3CF(CF_3)]_{2.8\ av.}\}_2^e$	.....	691.6	31.75 3.38^h	4650	20.02	1.38
$\{CF_3[CF_2CF(CF_3)]_2\}_2$	14.16 99.17^g	3.10	...	7.25	....	1.23
$\{CF_3[CF_2CF(CF_3)]_3\}_2$	.....	100.76	10.92 1.98^h	22.50	7.8	1.49

^{a} Extrapolated. ^{b} 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. ^{c} Distillation range 67–77° (9 mm.), pour point *ca.* −60°, $n^{28}D$ 1.292. ^{d} Distillation range 77–126° (9 mm.), pour point *ca.* −21°, $n^{25}D$ 1.3031. ^{e} Distillation range 118–138° (0.1 mm.), pour point *ca.* 20°, $n^{26.5}D$ 1.3170. ^{f} 123.8°F. ^{g} 32°F. ^{h} 291.2° F.

TABLE III

INFRARED ABSORPTION MAXIMA; WAVE LENGTHS IN MICRONS

$C_3F_7(R^a)_1I$	$C_3F_7(R)_2I$	$C_3F_7(R)_1Cl$	$C_3F_7(R)_2Cl$	$C_3F_7(R)_3F$	$C_3F_7(R)_4F$	$[C_3F_7(R)_1]_2$	$[C_3F_7(R)_2]_2$	$[CF_3(R)_2]_2$	$[C_3F_7(R)_2]S_2$	C_3F_7RSC
7.40	7.43	7.37	7.40	7.43	7.43	7.40	7.37	7.50^b	7.38	7.41
7.87	8.13	7.74	8.10	8.10	8.08	7.73	8.13	8.14	7.82	8.24
8.18	8.56	8.13	8.30^b	8.57	8.55	8.16	8.30^b	8.50^b	8.18	8.80
8.80	8.78	8.41	8.57	8.76	8.70	8.65	8.55	8.66	8.78	9.26
8.97	9.01	8.77	8.77	8.95	8.77	8.78	8.77	8.92^b	9.27	9.54
9.25^b	9.25	8.89	8.90^b	9.20	8.96^b	9.14^b	9.21	9.21	9.53	10.46
9.34	9.50	9.18	9.25	9.24	9.00^b	9.23	9.48	9.32	9.57	10.61
9.61	9.96	9.26	9.49	9.46	9.21	9.45	9.67	9.68	10.33	10.82
10.39	10.21	9.48	10.16	9.85	9.47	9.62	9.93	10.18	10.48	11.96
10.56	10.51	9.66	10.44	10.20	9.65^b	9.78	10.22	10.65^b	10.95	12.46
10.93	11.02^b	10.39	11.54	10.47^b	9.85	10.21	10.40	10.72	11.95	12.76
11.28	11.14^b	11.03	12.01^b	10.92	10.18	10.48	10.77	11.14	12.23^b	13.48
12.07	11.33	11.88	12.12	11.35	10.33	10.96	10.96	11.41	12.44	13.66
12.54	11.74	11.98^b	12.58	11.75	10.90	11.37	11.21	12.32^b	12.75	13.83
12.70	12.14	12.43	12.89	12.34	11.22	12.02	12.05	12.44	13.02	14.10
12.79	12.35	12.65	13.39	12.45	11.33	12.60	12.32	12.58^b	13.32	14.40
13.15	12.69	12.88	13.57	12.68	11.63	12.87	13.03	12.69	13.52	14.61
13.60	12.96	13.34^b	13.71	12.92	12.06	13.35^b	13.20	12.94	13.68	
13.83	13.11	13.45	13.91	13.33^b	12.62	13.55	13.50	13.28^b	13.82	
14.21	13.44	13.60	14.15	13.43	13.03	13.71	13.71	13.50	14.13	
14.82	13.60^b	13.82	14.48	13.52	13.32^b	14.00	14.00	13.60	14.43	
	13.73	14.03	14.77	13.68	13.46	14.27	14.33^b	13.85	14.65	
	13.94	14.14^b	15.12	13.89	13.68	14.95	14.67	14.00		
	14.45	14.47		14.10	13.95		15.08	14.49		
	14.57^b	14.69		14.57	14.12			14.85		
	14.95			15.12	14.26^b					
	15.24			15.35	15.10					

^{a} R = $CF_2CF(CF_3)$. ^{b} Shoulder.

branched chain perfluorocarbons and perfluoroalkyl chlorides are noteworthy.[16]

Table III presents the characteristic infrared absorption maxima of the lower members of the telomer iodides, chlorides, fluorides, coupling products, polysulfide series and of perfluoro-2-hexylsulfenyl chloride. Examination of these spectra in addition to all the other compounds shown in Table I and also ref. 2 revealed certain characteristic features of each series.

(a) $C_3F_7[CF_2CF(CF_3)]_nCl$ **Series.**—Previous studies on the infrared spectra of $CF_3(CF_2)_nCl$ where n = 1, 2 and 4[17,18] showed peaks in the general region of 10.2–10.6 μ. In the $C_3F_7[CF_2CF(CF_3)]_nCl$ series, where n = 1–9, all of the spectra are characterized by more or less strong absorption at 10.45 ± 0.02 μ (except n = 1 for which this band is at 10.39 μ). Another band at 10.19 ± 0.30 μ is a useful reference mark in studying this homologous

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[16] Viscometric properties of some of these materials and certain others in Table I are currently under more extensive study of C. M. Murphy and co-workers at the Naval Research Laboratory.

[17] M. Hauptschein, E. A. Nodiff and A. V. Grosse, THIS JOURNAL, **74**, 1347 (1952).

[18] M. Hauptschein, R. L. Kinsman and A. V. Grosse, *ibid.*, **74**, 849 (1952).

series. The 10.2 μ band, absent in $n = 1$, gradually increases in intensity as n is increased. The 10.4–10.45 μ band, very strong in $n = 1$ and 2, gradually decreases in intensity as n increases. At $n = 5$ the intensities of the two bands are approximately equal. At still higher values of n the 10.2 μ band becomes more intense than the 10.45 μ band. While the 10.2 μ band is characteristic of all members of the $-[CF_2CF(CF_3)]_n-$ series, the relative intensities of the bands at 10.2 and 10.45 μ may be used for diagnostic purposes.

(b) $C_3F_7[CF_2CF(CF_3)]_nI$.—In this series, where $n = 1$–10, all of the spectra are characterized by a band at 11.31 ± 0.03 μ.

(c) $C_3F_7[CF_2CF(CF_3)]_nF$.—In this series, where $n = 1$–9, a moderately strong band at 9.85 μ appears to be characteristic. Bands at 11.6–11.8 and 13.7 μ may also be useful in distinguishing fluorides from coupling products.

(d) $C_3F_7[CF_2CF(CF_3)]_n[(CF_3)CFCF_2]_nC_3F_7$.—In this series, where $n = 1$–4, a medium intense band at 9.6–9.7 μ appears to be characteristic. This is also true for the $CF_3[CF_2CF(CF_3)]_n[(CF_3)CF-CF_2]_nCF_3$ series.

(e) $C_4F_9CF(CF_3)$–S–S–$(CF_3)CFC_4F_9$.—In previous papers the C–S stretching vibrations in fluorinated thiolesters and in C_3F_7–S–S–C_3F_7 and C_3F_7–S_3–C_3F_7 were tentatively assigned to the bands at 14.1–14.42 μ in the thiolesters[19] and 14.71 and 14.72 μ in the perfluoro-*n*-propyl disulfide[12,19] and trisulfide.[12,19] A comparison of the spectrum of $C_4F_9CF(CF_3)(CF_3)CFC_4F_9$ with $C_4F_9CF(CF_3)$–S_2–$(CF_3)CFC_4F_9$, structurally similar in all respects except for the presence of the sulfur atoms, shows a similarity of absorption in this region, with the notable exception that only the disulfide has a maximum at 14.65 μ. This band is relatively weak, as was also the case for the other series, and thus provides additional evidence although not unequivocal proof for the correctness of the assignment for the C–S stretching vibrations.

Experimental

General Chlorination Procedure.—Chlorinations of telomer iodides $C_3F_7[CF_2CF(CF_3)]_nI$ in which the values of n were such that the products $C_3F_7[CF_2CF(CF_3)]_nCl$ ranged from light oils to friable solids were accomplished by use of the general procedure as illustrated by the following typical example:

A 300-ml. Monel autoclave was charged with 200 g. (0.335 mole) of $C_3F_7[CF_2CF(CF_3)]_2I$, sealed and cooled to −78°; 75 g. of chlorine (1.055 moles) was admitted to the autoclave which was then heated with shaking at 203° for 17 hours. Excess chlorine was vented from the autoclave and the remaining material was washed with water, 10% sodium hydroxide solution, and water, then dried with Drierite and distilled. (With higher telomer, 1,1,2-trichloro-1,2,2-trifluoroethane solvent was used to reduce the viscosity during washing, etc.) There was obtained 150 g. (0.297 mole) of chlorinated product $C_3F_7[CF_2CF(CF_3)]_2Cl$ representing an 89% yield and conversion.

As indicated in Table I the conversions obtained for the other chlorinated telomers ranged from 81–98%.

General Fluorination Procedure.—Fluorinated materials, $C_3F_7[CF_2CF(CF_3)]_nF$, ranging from light oils to clear brittle solids, were obtained from the corresponding iodo-compounds $C_3F_7[CF_2CF(CF_3)]_nI$ by reaction with cobalt trifluoride as illustrated by the following typical example.

Into a 2-l. Monel metal round-bottom flask equipped with a steel wire Hershberg stirrer and a copper, water-cooled condenser were charged 418 g. (0.350 mole) of a mixture of fluorocarbon iodides, $C_3F_7[CF_2CF(CF_3)]_nI$, where $n = 6$ average, and 395 g. (3.41 moles) of cobalt trifluoride. The mixture was heated with stirring to 190° for 1.5 hours and the temperature was maintained at 230–250° for several hours. The reaction mixture was then cooled, a fresh portion (100 g., 0.86 mole) of cobalt trifluoride was added, and heating was resumed at 230° for two additional hours. After cooling, a copper distillation head and receiver were substituted for the condenser, the flask was heated, and the pressure was reduced to *ca.* 0.1 mm. to allow the 291.5 g. of crude product (77%) to be distilled. The final pot temperature reached during this distillation was 275°. The crude product was taken up in 1,1,2-trichloro-1,2,2-trifluoroethane to reduce the viscosity and washed with dilute hydrochloric acid, dilute sodium hydroxide, and finally water then dried. Rectification through a Vigreux still was employed to separate components of various n values. The over-all yield of the purified products was 75%. The physical constants and analytical characterizations are listed in Table I.

General Procedure for Coupling $C_3F_7[CF_2CF(CF_3)]_nI$ and $CF_3[CF_2CF(CF_3)]_nI$ by Use of Ultraviolet Light and Mercury.—Enough clean dry mercury was admitted to a Vycor tube (No. 7900 or 7910) to extend the surface nearly the length of the tube in horizontal position. The telomer iodide together with an approximately equal volume of 1,1,2-trichloro-1,2,2-trifluoroethane, when necessary to decrease the viscosity of the reaction mixture, was added. After sealing *in vacuo* or under a high-purity dry nitrogen atmosphere the tube was mounted horizontally and shaken end to end while exposed to the ultraviolet irradiation of a Hanovia SH burner used without a filter.

The solids which began to form almost immediately increased in amount and underwent changes in color and texture from a red crystalline form which adhered tenaciously to the tube walls through orange, brown, and finally to finely dispersed black particles as the coupling proceeded to completion.

When the "black stage" was reached, generally after 72 to 160 hours exposure, the tube was cooled in Dry Ice to immobilize the remaining mercury, opened, and the liquid portion was decanted through a filter directly into the pot of a Vigreux distillation unit. The solids remaining in the tube were extracted in this fashion with several small portions of fresh 1,1,2-trichloro-1,2,2-trifluoroethane, and the extracts were added to the still-pot. After removal of the solvent by distillation at one atmosphere, the residue was fractionated under reduced pressure.

The distilled products were tested for complete coupling by further direct exposure to ultraviolet irradiation. Red or yellow mercuric iodide was precipitated by this treatment when coupling was incomplete, usually from the products isolated from reactions where irradiation was terminated prior to the "black stage." This evidence for the formation of some type of organomercurial through which the coupling reaction proceeds, at least to some extent if not entirely, was supported by the isolation of coupled fluorocarbons from some of the brown solids taken from an incomplete coupling reaction and exposed independently in 1,1,2-trichloro-1,2,2-trifluoroethane to ultraviolet irradiation.

The coupling products were clear, colorless oils or solids. Yields, physical constants and analytical characterizations are listed in Table I.

In a typical experiment 4.5 g. (0.010 mole) of 2-iodoperfluorohexane and 10 ml. of mercury were sealed in a Vycor 7910 tube under a dry nitrogen atmosphere and shaken end to end for 72 hours, while exposed to irradiation from the ultraviolet lamp at a distance of 5 inches. After working up, perfluoro-5,6-dimethyldecane (3 g., 94%) was isolated (Table I).

The Coupling of 1-Iodoperfluoropropane by Mercury and Ultraviolet Light.—1-Iodoperfluoropropane (29.6 g., 0.1 mole) and 10 ml. of mercury were sealed in a Vycor 7900 tube under a dry nitrogen atmosphere and shaken for 9 days while exposed to ultraviolet irradiation. The entire product was finally converted to a brown solid mass. 1,1,2-Trichloro-1,2,2-trifluoroethane was then added to the opened tube, which was resealed and irradiated for an additional 3 days when the solids were completely black. The cooled tube was then opened, the volatile contents were transferred *in vacuo* to a Vigreux unit and distilled. There were collected 33 g. of distillate, b.p. 42–44°, $n^{20}D$ 1.30. This

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[19] M. Hauptschein, C. S. Stokes and E. A. Nodiff, THIS JOURNAL, **74**, 4005 (1952).

material was analyzed spectroscopically and found to be a mixture of equal parts by weight of n-C_6F_{14} and $CF_2ClCFCl_2$ (probably an azeotrope). Thus the yield of n-perfluorohexane was 16.5 g. or 98%.

The Thermal Reaction of 2-Iodoperfluorohexane and Mercuric Oxide.—A mixture of 2-iodoperfluorohexane (5 g., 0.011 mole) and yellow mercuric oxide (3 g., 0.014 mole) was sealed in a heavy-walled Pyrex tube and heated first at 148° for 40 hours and then at 235° for 15 hours. (On initial mixing the pink iodine color was bleached and on gentle heating an exothermic reaction was observed.) The tube was then cooled and opened. The 1.5 g. of product which could be transferred *in vacuo* (with warming of the tube) was shown to be perfluoro-5,6-dimethyldecane, exclusively; the physical constants and infrared spectrum were identical to an authentic sample prepared by the ultraviolet light–mercury method.

The Thermal Reaction of 1,2-Dichloro-2-iodo-1,2-trifluoroethane and Mercuric Oxide.—Two reactions were carried out in sealed Carius tubes. The first reaction was carried out at 232° for 2 days using 5.6 g. of $CF_2ClCFClI$ and 6.51 g. of yellow mercuric oxide. The second reaction was conducted at 220° for 18 hours using 28 g. of $CF_2ClCFClI$ and 43.2 g. of yellow mercuric oxide.[20] The coupling compound $CF_2ClCFClCFClCF_2Cl$ was clearly shown by infrared spectroscopic analysis to be among the products formed. The conversion to $CF_2ClCFClCFClCF_2Cl$ was approximately 10% in both reactions.

The Reaction of 2-Iodoperfluorohexane with Zinc and Acetic Anhydride–Methylene Chloride.—Forty ml. of acetic anhydride, 40 ml. of methylene chloride, 5 g. of 30 mesh granular zinc (which was activated by successive washings with dilute hydrochloric acid, water, acetone, ethanol and ether) and 22.3 g. (0.05 mole) of 2-iodoperfluorohexane were allowed to react for several hours and then worked up by the procedure of Henne and Postelneck[15] for the coupling of $CF_2ClCFClI$. About 10 g. of a white powder (0.047 mole of ZnFI) representing elimination of essentially one mole of IF per mole of 2-iodoperfluorohexane was isolated. Furthermore, all of the liquid product boiled below 60°, thus confirming the absence of formation of any coupling product, *i.e.*, perfluoro-5,6-dimethyldecane.

The main product surprisingly was found in the several ml. of material condensed in the Dry Ice-cooled trap backing up the system. Although much product was lost during the separation of the codistilled methylene chloride, sufficient material remained to partially characterize this fraction by infrared spectroscopic examination. The spectrum was quite characteristic of perfluorinated olefins, and the presence of two bands of equal intensity at 5.60 and 5.82 μ strongly supported the presence of the two isomeric perfluorohexenes containing terminal and internal double bonds, *i.e.*, $C_4F_9CF{=}CF_2$ and $C_3F_7CF{=}CFCF_3$, respectively.[21]

The Reaction of $CF_2ClCFClCF_2CFClI$ with Zinc and Acetic Anhydride–Methylene Chloride.—Eighty ml. of acetic anhydride, 80 ml. of methylene chloride, 6.5 g. (0.10 g. atom) of 30 mesh granular activated zinc and 39.5 g. (0.1 mole) of $CF_2ClCFClCF_2CFClI$ were allowed to react for about 5 hours at 10–32° according to the previously described procedure.[15] There was isolated 22.3 g. (83%) of $(CF_2ClCFClCF_2CFCl)_2$, b.p. 140–147° (20 mm.), identical to that reported previously.[14]

Miscellaneous Methods for Coupling $C_3F_7[CF_2CF(CF_3)]_nI$. (a) By Heating in the Presence of Mercury.—$C_3F_7[CF_2CF(CF_3)]I$ (4.5 g.) and mercury (10 ml.) were heated in a sealed tube with shaking at 150° for 1 day. $C_3F_7[CF_2CF(CF_3)]_2I$ (21.5 g.) and mercury (10 ml.) were heated in a flask with stirring at 120° for 1 day. Identification of $C_3F_7[CF_2CF(CF_3)]_n[(CF_3)CFCF_2]_nC_3F_7$ where $n = 1$ and 2, respectively (in low yield), in the crude reaction product which consisted largely of unidentified mercurials was made by infrared analysis of certain distilled fractions.

(b) **By Heating with Concentrated Sulfuric Acid.**—2-Iodoperfluorohexane (4.7 g.) and concentrated sulfuric acid (22 g.) were sealed in a Pyrex tube and heated at 235° for 3 weeks. Perfluoro-5,6-dimethyldecane was formed in *ca.* 7% conversion (yield based on reacted 2-iodoperfluorohexane was >95%).

(c) **By Thermal Reaction.**—Thirty grams of $C_3F_7[CF_2CF(CF_3)]_nI$ where $n = 3$ were sealed under a dry nitrogen atmosphere in a 65-ml. Monel autoclave and heated at 258–262° for 16 hours. The autoclave was cooled and vented *in vacuo* to a Dry Ice-cooled trap in which 10 g. (33% of the total product) of perfluoropropene were condensed. The autoclave was opened and the remaining 18.9 g. of oil was fractionated under reduced pressure. The composition of the products obtained from this distillation was evaluated on the basis of boiling ranges, refractive indices and infrared spectra to be approximately 40% of 2-iodoperfluorohexane, 25% of coupling products, symmetrical and mixed, and 30% of recovered reactant iodide.

(d) **By Thermal Reaction in the Presence of Excess Perfluoropropene.**—A 2.7-l. 316 stainless steel autoclave was charged with 875 g. of iodoperfluoropropane and 2050 g. of perfluoropropene and then heated at 200° for 60 hours with continuous shaking. The temperature was then allowed to rise to about 300–305° for several hours. From this reaction were recovered 1355 g. of perfluoropropene, *ca.* 65 g. of iodine and 1360 g. of higher boiling products. The latter were shown to be composed of iodine-free stabilized fluorocarbon materials in addition to the usual telomer iodides. Fractionation of this material by means of a 1-inch diameter by 1-foot glass helices-packed column was used to separate 667 g. of 2-iodoperfluorohexane. The remaining 693 g. of product (ranging from oils to solids) boiling from 100° at 100 mm. to >110° at *ca.* 0.1 mm. consisted of approximately 20% by weight of perfluoro-5,6-dimethyldecane, 25% of higher coupling products and 55% of higher telomer iodides.

This mixture of products was subjected to ultraviolet irradiation in the presence of mercury to convert the remaining perfluoroalkyl iodides to coupled products. The resulting product was shown by infrared spectra to be composed primarily of symmetrical and unsymmetrical coupling products. However, the presence of other fluorocarbon materials arising from the thermal degradation or rearrangement of the fluorocarbon iodides or their coupling products was not precluded.

Finally, an 89-g. fraction boiling at *ca.* 30–50° at atmospheric pressure exhibited a refractive index too low (*ca.* 1.29) to be solely recovered C_3F_7I. This fraction was therefore treated with alcoholic potassium hydroxide to remove the iodide as the gas C_3F_7H.[22] Elimination as the hydride accounted for approximately 60% of the original mixture. Most of the residual product, b.p. 34–47°, consisted largely of *perfluoro*-(dimethylcyclobutane)[23] as shown by comparison of the infrared spectrum with that of an authentic specimen. From the remaining product there was isolated a small fraction, b.p. 57–58°, which analyzed as C_6F_{14} but was shown by its infrared spectrum not to be n-C_6F_{14}.

Anal. Calcd. for C_6F_{14}: C, 21.3; F, 78.7. Found: C, 21.1; F, 78.8.

The Reaction of 2-Iodoperfluorohexane with Sulfur.—Forty-eight grams (0.108 mole) of 2-iodoperfluorohexane and 33.5 g. of sublimed sulfur were charged into a 300-ml. Monel autoclave under a dry nitrogen atmosphere. The sealed autoclave was heated in a shaker at 172–176° for 112 hours. The autoclave was cooled to room temperature and vented *in vacuo* to a Dry Ice-cooled trap. No volatile material was collected in this trap. From the autoclave was drained an oil shown to be $[C_4F_9CF(CF_3)]_2S_n$, red in color due to a small amount of dissolved iodine, b.p. 87° (8 mm.)–*ca.* 103° (0.1 mm.). Only 0.9 g. (0.003 mole) of 2-iodoperfluorohexane was recovered, and 41 g. of a hard "stick" of a mixture of sulfur and iodine was collected.

Careful rectification of the 30 g. of crude oil collected gave the pure compounds shown in Table IV. Based on the determined average value of 3 for n in $[C_4F_9CF(CF_3)]S_n$, the conversion was 76% and the yield was 78%.

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[20] The second reaction was performed by H. Iserson of this Laboratory.

[21] R. N. Haszeldine, *J. Chem. Soc.*, 4423 (1952), reported an absorption band for the C=C stretching vibration at 5.56 μ for $CF_3CF{=}CF_2$ and at 5.77 μ for $CF_3CF{=}CFCF_3$. R. N. Haszeldine and B. R. Steele (ref. 7) reported a band at 5.84 μ for $C_2F_5CF{=}CFC_2F_5$. T. J. Brice, L. D. LaZerte, L. J. Hals and W. H. Pearlson, THIS JOURNAL, **75**, 2698 (1953), reported a band at 5.58 μ for $CF_3CF_2CF{=}CF_2$ and at 5.77 μ for $CF_3CF{=}CFCF_3$.

[22] J. Banus, H. J. Emeleus and R. N. Haszeldine, *J. Chem. Soc.*, 60 (1951).

[23] See M. Hauptschein, A. H. Fainberg and M. Braid, THIS JOURNAL, in press, for a description of the thermal dimerization of perfluoropropene.

TABLE IV

PERFLUORO-2-HEXYL POLYSULFIDES

$[C_4F_9CF(CF_3)]_2S_n$ n value	B.p., °C.	B.p., Mm.	n^tD	t, °C.	Analyses, %[a] Carbon Calcd.	Carbon Found	Sulfur Calcd.	Sulfur Found
2	94	8	1.3300	23	20.5	20.4	9.1	9.6[b]
3	66	<0.1	1.3469	28.8	19.6	19.5	13.1	12.8
4	*ca.* 80	<0.1	1.3791	20	18.8	19.2	16.7	16.7
5	Residue (viscous oil)		1.3975	19.5	18.1	18.0	20.1	19.6

[a] Microanalyses by Schwarzkopf Microanalytical Laboratory. In all cases % H was zero. [b] *Anal.* Calcd. for $C_{12}F_{26}S_2$: F, 70.34. Found: F, 70.7.

Another experiment conducted in a sealed Pyrex tube at 180° for 75 hours gave similar results.

Thermal Reaction of Perfluoro-2-hexyl Polysulfide with Chlorine.—A 70-cc. heavy-wall Pyrex ampule containing 4.2 g. (0.059 mole) of chlorine and 8 g. (0.011 mole) of perfluoro-2-hexyl polysulfide, $[C_4F_9CF(CF_3)]_2S_n$, where $n = 2.5_{av}$, was sealed and heated at a temperature of 105° for 125 hours. The tube was cooled in Dry Ice and opened, and unreacted chlorine was removed by warming. The remaining liquid products were carefully fractionated in a small Vigreux still, and there was collected a total of 6.6 g. (0.017 mole) of perfluoro-2-hexylsulfenyl chloride, a pale yellow liquid, middle cut, b.p. 63–63.8° (97 mm.), n^{26}D 1.3237. *Anal.* Calcd. for $C_6ClF_{13}S$: C, 18.6; Cl, 9.2. Found: C, 18.8; Cl, 8.9.

The compound had ultraviolet absorption maxima (in isoöctane) at 213.5 mμ (strong) and at 340 mμ (weak).

Finally, there was recovered by further distillation 1.1 g. of perfluoro-2-hexyl disulfide. The conversion to the sulfenyl chloride was 77%, and the yield 89% of theoretical.

The Reaction of 1,2-Dichloro-2-iodo-1,1,2-trifluoroethane with Sulfur.—Into a 300-ml. nickel autoclave were charged 1,2-dichloro-2-iodo-1,1,2-trifluoroethane (279 g., 1 mole) and sublimed sulfur (64 g.). The sealed autoclave was heated in a shaker at 187° for 12.2 hours. Upon rectification of the 161 g. of crude liquid product, there were obtained 56 g. of recovered 1,2-dichloro-2-iodo-1,1,2-trifluoroethane, 15 g. of an intermediate cut, b.p. 68–85° (5 mm.), and *ca.* 90 g. of material boiling from 60° (1 mm.)->118° (0.5 mm.). From the latter fraction which was shown to be primarily $(CF_2ClCFCl)_2S_n$ where $n = 2–5$, the following three cuts were separated by rectification at 0.5 mm.: (1) b.p. 67–69° (0.5 mm.), n^{30}D 1.4638. *Anal.* Calcd. for $(CF_2ClCFCl)_2S_2$: C, 13.0; S, 17.4; Cl, 38.5. Calcd. for $(CF_2ClCFCl)_2S_3$: C, 12.0; S, 24.1; Cl, 35.5. Found: C, 12.3; S, 21.1; Cl, 36.5.

(2) B.p. 83–84°, n^{29}D 1.4888. *Anal.* Calcd. for $(CF_2ClCFCl)_2S_3$: C, 12.0; S, 24.1; Cl, 35.5. Found: C, 11.8; S, 25.2; Cl, 35.6.

(3) B.p. 112–118°, n^{29}D 1.5217. *Anal.* Calcd. for $(CF_2ClCFCl)_2S_4$: C, 11.1; S, 29.7; Cl, 32.8. Found: C, 10.8; S, 30.7; Cl, 32.8.

The ultraviolet spectra of these fractions showed λ_{max} in 95% ethanol at 242–245 mμ, which is characteristic of S–S bonds in compounds of this type.[24]

The residue, b.p. >118° (0.5 mm.), had an n^{29}D of 1.5595 and probably contained some of the pentasulfide.

Infrared and Ultraviolet Spectra.—The infrared spectra were determined by use of a Perkin–Elmer model 21 instrument with sodium chloride optics. The ultraviolet spectra were determined with a Beckman ratio recording spectrophotometer, model DK-2.

Acknowledgment.—We wish to thank Mr. Fred Curtis and Mr. John J. Mullaney for technical assistance, Miss Ruth Kossatz for infrared spectra determinations and Mr. John Y. Steel for viscosity measurements.

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[24] G. R. A. Brandt, H. J. Emeléus and R. N. Haszeldine, *J. Chem. Soc.*, 2549 (1952).

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[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF PURDUE UNIVERSITY]

Meerwein Reactions on Isolated Olefinic Bonds. Free Radical Addition Reactions on Vinylsilanes

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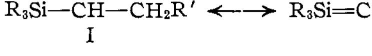
Aromatic diazonium salts add to vinyl groups attached to a silicon atom under conditions typical for the Meerwein reaction. Since the latter is usually successful only with conjugated olefins, the reaction is diagnostic of the "conjugative nature" of a vinyl group joined to silicon. Vinylsilanes also add chloroform, carbon tetrachloride and ethyl bromoacetate with great ease under free radical conditions.

Evidence has been presented in recent years which indicates that the valence joining a silicon atom to an aromatic ring may possess some double bond character, particularly when the silicon atom is conjugated with strong electron-supplying groups[1-3] such as $-NH_2$, $-OH$, or $-N(CH_3)_2$. In a similar fashion the enhancement of acidity of various silylbenzoic acids has been attributed to d-pπ bonding between the π-orbital system of the aromatic ring and the vacant 3-d orbitals of the silicon atom.[4]

It would seem reasonable that this conjugative ability of silicon might well be reflected in the chemistry of an attached vinyl group, since one can envision (at least in a transition state) contributions from electronic forms such as



$$R_3Si—\overset{\ominus}{C}H—CH_2R' \longleftrightarrow R_3\overset{\ominus}{Si}=CH—CH_2R'$$

I

If such forms have any validity one might expect the chemistry of such a vinyl group to resemble that of a conjugated olefin. Thus such a group might be expected to undergo Michael-type addition reactions. In keeping with this prediction, vinylsilanes reportedly do undergo nucleophilic additions, in a manner such that the anion portion of the attacking group becomes attached to the β-

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[1] H. Soffer and T. DeVries, THIS JOURNAL, **73**, 5817 (1951).

[2] R. A. Benkeser and H. R. Krysiak, *ibid.*, **75**, 2421 (1953).

[3] R. A. Benkeser, C. E. DeBoer, R. E. Robinson and D. M. Sauve, *ibid.*, **78**, 682 (1956).

[4] J. Chatt and A. A. Williams, *J. Chem. Soc.*, 4403 (1954); 688 (1956).