III) leads to values of σ_a in reasonable agreement with those from earlier data.[1,2]

Recently there have appeared two papers which are related to our study, the one dealing with the alkaline hydrolysis of ethyl 2-thenoate and 2-furoate[3] and the other of ethyl 1- and 2-naphthoate,[4] both in 85% ethanol. Using these data[3,4] together with the rates of saponification and ρ in the same solvent,[5] we can calculate the Hammett σ-constants for the saponification rates of ethyl benzoate, 2-furoate, 2-thenoate, 1- and 2-naphthoate, as shown in Table VI.

Although the temperature-independent factors in these two separate experiments[3,4] are quite far apart, the over-all picture thus calculated is in fairly reasonable agreement with our data.

To test the hypothesis that the heterocyclic acids might have intra- rather than intermolecular hydrogen bonding, the degree of association of benzoic, 2-thenoic and 2-furoic acids were determined cryoscopically in benzene. These data, summarized in Table IV, indicate that all three acids have almost the same degree of association, and our data do not support the earlier claim that 2-furoic acid is largely monomeric in benzene.[6] For the solid acids, infrared spectra in potassium bromide disks, as shown in Table V, reveal no significant changes in position or relative intensity of the bands associated with the carboxyl group, in support of the conclusion that all the acids are associated in the crystalline state, as was already pointed out previously by X-ray study,[7] in the case of 2-furoic acid.

TABLE VI

HAMMETT σ-CONSTANTS FOR THE ACID DISSOCIATION CONSTANTS AND THE RATES OF ALKALINE SAPONIFICATION OF THE ESTERS IN 85% ETHANOL

Acid	pKa[e]	$k_2$sapn. × 10^4 at 25°	σa[e]	σs[f]	$\Delta\sigma$
Benzoic	6.70	6.07[a]	0.00	0.00	0.00
2-Thenoic	5.95	5.63[b]	.36	− .01	.37
2-Furoic	5.43	24.5[c]	.61	.24	.37
1-Naphthoic	6.25	4.79[d]	.22	− .04	.26
2-Naphthoic	6.30	10.0[d]	.03	.08	.05

[a] Taken from ref. 5. [b] Extrapolated from the value of ΔE (18.9 kcal./mole) and log PZ (10.6) in ref. 3. [c] Directly taken from ref. 3. [d] Extrapolated from the values of ΔE (14.5 kcal./mole for 1-naphthoate and 16.1 kcal./mole for 2-naphthoate) and log PZ (7.3 for 1-naphthoate and 8.8 for 2-naphthoate, respectively) in ref. 4. [e] Taken from our measurement—see Table III. [f] $\sigma_s = \log (k_{sap}/6.07 \times 10^4)/2.54$.

---

(3) E. Imoto, Y. Otsuji, T. Hirai and H. Inoue, *J. Chem. Soc. Japan* (Pure Chem. Section), **77**, 804, 809 (1956).

(4) P. Fitzgerald, J. Parker, J. Vaughan and A. F. Wilson, *J. Chem. Soc.*, 170 (1956).

(5) (a) D. P. Evans, J. J. Gordon and H. B. Watson, *ibid.*, 1430 (1937); (b) C. K. Ingold and W. S. Nathan, *ibid.*, 222 (1936); (c) H. H. Jaffe, *Chem. Revs.*, **53**, 191 (1953).

(6) L. M. Nazarova and Y. K. Syrkin, *Isvest. Akad. Nauk. S. S. R., Odtel. Khim. Nauk.*, **35** (1949) (*C. A.*, **43**, 4913 (1949)).

(7) T. Goodwin and C. M. Thomson, *Acta Cryst.*, **7**, 166 (1954) (*C. A.*, **48**, 7385 (1956)).

PHILADELPHIA 4, PENNA.

[CONTRIBUTION FROM THE ORGANIC RESEARCH DEPARTMENT, PENNSYLVANIA SALT MANUFACTURING CO.]

Thermal Syntheses of Telomers of Fluorinated Olefins. I. Perfluoropropene[1]

BY MURRAY HAUPTSCHEIN, MILTON BRAID AND FRANCIS E. LAWLOR

RECEIVED NOVEMBER 21, 1956

A novel method of producing addition-type polymers by a process which does not proceed by chain propagation is described. The formation of telomers of perfluoropropene of formula $R[CF_2CF(CF_3)]_nI$ where R = CF_3, C_3F_7, $C_4F_9CF(CF_3)$, $C_4F_9CF(CF_3)CF_2CF(CF_3)$ and $CF_2ClCFCl$ and $n = 1$ to 15 has been accomplished by purely thermal means. The unique advantages of this simple process as a method of producing telomers of certain types of relatively non-polymerizable olefins are expounded.

This is the first paper in a series dealing with the syntheses of telomers of fluorinated olefins by purely thermal means.

Considerable work from both academic and industrial laboratories has been described on photochemical and peroxide-induced telomerizations of fluoroölefins which are readily polymerized by free radical initiators. Little information has been reported, however, on (1) thermally induced telomerizations and (2) telomerizations of olefins which do not readily homopolymerize in the presence of free radical initiators.[2]

Although perfluoropropene has been copolymerized with fluorinated[3,4] and unfluorinated[3,5] olefins as well as with ethylene oxide,[6] there is no literature reference to the homopolymerization of perfluoropropene to $[-CF_2CF(CF_3)-]_n$, in spite of considerable study.[5] We have now found that polyperfluoropropenes of molecular weights to 2500 may be synthesized by reaction of perfluoropropene with perfluoroalkyl iodides at about 200°. Moreover, the reaction may be controlled to give products of any desired narrow molecular weight range from $n = 1$ to 15.

Replacement of the iodine atom by fluorine or

---

(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) See R. N. Haszeldine, *J. Chem. Soc.*, 4291 (1955), for an excellent review of many of the factors affecting telomerization.

(3) J. C. Sauer, U. S. Patent 2,549,935 (1951).

(4) W. T. Miller, U. S. Patent 2,598,283 (1952).

(5) R. M. Adams and F. A. Bovey, *J. Polymer Sci.*, **9**, 481 (1952).

(6) M. Hauptschein and J. M. Lesser, THIS JOURNAL, **78**, 676 (1956).

chlorine, or its removal by a coupling reaction converts the telomer

$$R_f[\text{-}CF_2CF(CF_3)\text{-}]_nI \text{ into } R_f[\text{-}CF_2CF(CF_3)\text{-}]_nF,$$
$$R_f[\text{-}CF_2CF(CF_3)\text{-}]_nCl$$

or R_f $[-CF_2CF(CF_3)-]_n[(CF_3)CFCF_2-]_nR_f$ where R_f is a perfluoroalkyl group.[7] These fluorocarbon materials are useful as heat transfer fluids, hydraulic fluids, oils, greases, waxes, insulators, dielectrics, plasticizers and modifiers of certain fluorocarbon plastics.

The photochemical reaction of perfluoropropene with trifluoroiodomethane was first described by Haszeldine.[8] Under conditions similar to those used in the rapid reaction of tetrafluoroethylene with trifluoroiodomethane[9] (*i.e.*, *vapor phase* irradiation in a silica tube), which gave mainly solid products, $CF_3(CF_2CF_2)_nI$ where $n = 4$ to >20, the slow perfluoropropene–trifluoroiodomethane reaction gave 2-iodoperfluorobutane. A small amount of $CF_3[CF_2CF(CF_3)]_nI$ where $n = 2$ also was formed but no material where the value of n exceeded 2 was reported. It was similarly shown that 2-iodoperfluorobutane reacted very slowly with perfluoropropene to give only $CF_3[CF_2CF(CF_3)]_2I$.

Heretofore, in addition to $CF_3CF{=}CF_2$, certain unsaturated compounds including C_2H_4, C_2H_2, $CH_2{=}CHCF_3$, $CH_2{=}C{=}CH_2$, $CH_3CH{=}CH_2$ and $CFCl{=}CFCl$ have been shown to "telomerize" with great difficulty by ultraviolet or peroxide initiation. The products obtained in these cases were almost entirely the 1:1 adducts. Previous efforts to force olefins such as ethylene, propene, 3,3,3-trifluoropropene or hexafluoropropene to give a polymer RCFX[olefin]$_n$Y with $n > 4$ or 5, by cutting down the proportion of chain-transfer agent RCFXY,[10] merely caused the intermediate radical to undergo reactions other than by addition with a second molecule of olefin, *e.g.*, disproportionation, dimerization or internal expulsion of halogen to give an olefin.[2]

The results of the present investigation (see Tables I and II) demonstrate that perfluoropropene can give telomers such as $C_2F_7[CF_2CF(CF_3)]_nI$ where $n = 10$ and higher.

This simple thermal method of producing telomers of perfluoropropene is applicable to other relatively non-polymerizable or poorly polymerizable olefins (*vide infra*). It is proposed that this method proceeds by "successive addition steps" (probably involving transient radical formation and a single transition state for each addition) with little contribution from a chain mechanism including a propagation step, *i.e.* $RCFX[\text{olefin}]\cdot + (n - 1)\ \text{olefin} \rightarrow RCFX[\text{olefin}]\cdot_n$, etc. For example, in the case of the perfluoropropene reaction with perfluoropropyl iodide, the formation of telomers may be regarded as occurring in discrete steps.[11]

$$C_3F_7I + CF_2{=}CFCF_3 \longrightarrow C_3F_7CF_2CF(CF_3)I$$

$$C_3F_7CF_2CF(CF_3)I + CF_2{=}CFCF_3 \longrightarrow C_3F_7[CF_2CF(CF_3)]_2I, \text{ etc.}$$

$$C_3F_7[CF_2CF(CF_3)]_nI + CF_2{=}CFCF_3 \longrightarrow C_3F_7[CF_2CF(CF_3)]_{n+1}I$$

Thermal syntheses of perfluoropropene with CF_3I, C_3F_7I, $C_4F_9CFICF_3$, $C_4F_9CF(CF_3)CF_2CF(CF_3)I$ and $CF_2ClCFClI$[12] have been successfully carried out. $R[CF_2CF(CF_3)]_nI$ where R = CF_3, C_3F_7, $C_4F_9CF(CF_3)$, $C_4F_9CF(CF_3)CF_2CF(CF_3)$ and $CF_2ClCFCl$ and $n = 1$ to >10 have been obtained. Thus any reactant containing the moieties: $-CF_2I$, $-CF(C_nF_{2n+1})I$ and $-CFXI$ (where X = polyhalogenoalkyl) can be used. In addition, modified reactions of perfluoropropene have been effected simply by heating the olefin in the presence of iodine monochloride.[7] A new reactant, CF_3CFICF_2Cl, is formed *in situ* to begin the formation of telomers. Likewise, iodine has been made to react with perfluoropropene to form modified telomers. At somewhat higher temperatures CF_2Br_2 and fluoroalkyl bromides containing the groups $-CF(C_nF_{2n+1})Br$ and $-CFClBr$ may be used as reactants.[7]

Although the full scope of this method of producing telomers has not been determined, certain conclusions with regard to the types of unreactive (relatively non-polymerizable) olefins to which it is applicable may be drawn. 1. An olefin which on addition of R_fI would form a $-CF_2I$, $-CF(C_nF_{2n+1})I$ or similar linkage, *e.g.*, $R_fI + CF_2{=}CHCF_3 \rightarrow R_fCH(CF_3)CF_2I$,[13] $R_fI + CH_2{=}CFCF_3 \rightarrow R_fCH_2CF(CF_3)I$, would be expected to produce a telomer.

2. Olefins such as ethylene and propene would form on addition of R_fI the linkages $-CH_2CH_2I$ and $-CH_2CHICH_3$. Such C–I bonds do not undergo facile homolytic fission[3] and the temperatures required for telomer formation would probably exceed those necessary for competing size reactions or decomposition. Thus, successful thermal synthesis of telomers of these olefins is improbable.

The maintenance of a sufficiently high energy level to overcome the energies of activation required to promote and sustain the reaction is undoubtedly one of the principal reasons why telomers of unreactive olefins can be produced at appreciable rates by thermal synthesis but not by photochemical or peroxide-induced initiation.

The data in Tables I and II present the important conditions, results and product characterizations of the reactions of perfluoropropene with n-C_3F_7I, CF_3I, $C_4F_9CFICF_3$ and $C_4F_9CF(CF_3)CF_2CFICF_3$.

---

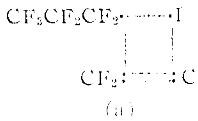
[7] M. Hauptschein, M. Braid and F. E. Lawlor, forthcoming publication.

[8] R. N. Haszeldine, *J. Chem. Soc.*, 3559 (1953).

[9] R. N. Haszeldine, *ibid.*, 3761 (1953).

[10] C–Y in RCFXY is weak, yet RCFX is sufficientiy reactive to attack the olefin, *e.g.*, when RCFXY = CF_3I, $CF_2ClCFClI$ or $CF_2ClCFClBr$.

[11] It is proposed that in these addition steps the $C_3F_7\cdot$ and the $I\cdot$ from the same molecule add simultaneously to the double bond, *i.e.*, chain transfer with the solvent (C_3F_7I) is a minor effect. It is likely that the thermally activated molecules undergo these rearrangements as shown schematically by the transition complex (a) without primary


(a)

dissociation. See A. D. Kirschenbaum, A. G. Streng and M. Hauptschein, THIS JOURNAL, **75**, 3141 (1953).

[12] P. Tarrant and M. R. Lilyquist, *ibid.*, **77**, 3640 (1955), attempted the reaction of perfluoropropene with 1,2-dichloro-2-iodo-1,1,2-trifluoroethane in the presence of benzoyl peroxide as the catalyst at 100°. No addition products or simple telomers were obtained.

[13] The direction of the photochemical addition of CF_3I to $CF_2{=}CHCF_3$ has been established by R. N. Haszeldine and B. R. Steele, *J. Chem. Soc.*, 3005 (1955).

TABLE I

NEW COMPOUNDS

$C_3F_7(CF_2\overset{\overset{CF_3}{\vert}}{C}F)_nI$ n	B.p. °C.	B.p. Mm.	n^t_D	t, °C.	Mol. wt. Calcd.	Mol. wt. Found	λmax,[a] mμ	ε[b]	Analyses, %[m] Carbon Calcd.	Carbon Found	Fluorine Calcd.	Fluorine Found
1	62	95	1.3284	24	446	..	282	210	16.2	..	55.4	55.4
	110	760										
2	62	10	1.3310	24	596	..	282	210	18.1	18.0	60.6	60.5[c]
	104	100										
3	101	10	1.3340	24	746	..	282	200	19.3	19.4	63.7	63.6
4	83	*ca.* 0.1	1.3395	19	896	..	282	190	20.1	20.3	65.7	66.0
			1.337	24								
3.7 (av.)[d,e]	73–94	*ca* 0.1	1.336	24	..	854[e]	282	..	..	..	..	..
7 (av.)[f,h]	125–135	<0.1			1346	1300[e]	282	..	21.4	21.4	69.2	69.4
10 (av.)[f,i]	135–160	<0.1			1786	1700[e]	282	..	22.1	22.2	70.9	70.7
$CF_3(CF_2\overset{\overset{CF_3}{\vert}}{C}F)_nI$ n												
1[g]	64	760	1.3282	25	346	..	280	205	13.9	13.8	49.4	49.6
2[g]	64	71	1.3322	26	496	..	282	210	17.0	17.1	57.5	57.3
3	73	10	1.3350	25.5	646	..	282	205	18.6	18.8	61.8	61.8
4	105	10	1.3368	25	796	..	282	210	19.6	19.8	64.4	64.4
9 (av.)[j]	130–150	*ca.* 0.1	1.3358	32	1546	..	282	245	21.8	21.7	70.0	70.0
11 (av.)[k,l]	150–170	*ca.* 0.1	1.3357	35	1846	1800[e]	282	..	22.1	22.2	71.0	..

[a] Ultraviolet spectrum maxima in isoöctane, 2,3,3-trichloroheptafluorobutane and 1,1,2-trichlorotrifluoroethane. [b] Molar extinction coefficient in isoöctane. [c] *Anal.* Calcd. for $C_9F_{19}I$: I, 21.29. Found: I, 21.1. [d] Kinematic viscosities in centistokes: 199.5 (78.4°F.), 11.7 (141.4°F.), 4.04 (197.8°F.). [e] Molecular weight calculated in the usual way from the absorbancy (at 282 mμ) of a known concentration in isoöctane, 2,3,3-trichloroheptafluorobutane or 1,1,2-trichlorotrifluoroethane. [f] Solids at room temperature. [g] R. N. Haszeldine, *J. Chem. Soc.*, 3559 (1953), reported for $n = 1$, b.p. 65.5°, n^{20}_D 1.340. The latter value is apparently in error. For $n = 2$, the reported boiling point is 136–138°. [h,i,j,k,l] Melting point ranges of these clear glass-like solids, respectivley, are: 55–58°, 74–80°, 35–42°, 47–56°, 68–76° (l is the m.p. range of $CF_3[CF_2CF(CF_3)]_{ca.15}I$). [m] Most of the microanalyses were done by the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y. In all cases percentage hydrogen was zero.

TABLE II

THERMAL TELOMERIZATIONS AT 200° IN SHAKING AUTOCLAVE

Mole ratio $C_3F_6:C_3F_7I$	Time, hr.	Pressure, p.s.i. Initial	Pressure, p.s.i. Terminal	Conversion,[a] %	Yield, % $n = 1$	$n = 2$	$n = 3$	$n = 4$	$n > 4$ [%, (av. n-value)]
1.32[b]	41(220°)	2100	800	37	72	22	5	1	
1.39[b]	88	2000	1000	37	84	14	2	..	
1.51	64	2800	1200	50	68	22	10	[c]	
2.63	22	3600	2300	41	75	18	7	[c]	
2.75	42	5000	2900	57	63	22	15	[c]	
4.07	63	4700	2300	73	56	24	16	4	
4.26	112	3000	1300	84	65	21	13	1	
4.83	98[f]	4600	2100	88	44	28	16	8	4 (5)
4.89	20	4600	3500	52	66	19	16	[c]	
10.4	336	4700	1900	94	7	11	41	30	3 (5), 7 (7), 2 (10)
$C_3F_6:C_4F_9CFICF_3$									
2.97	21.5	2400	1950	23	..	79	21	..	
9.2	137	9000	4800	*ca.* 70	..	*ca.* 10		*ca.* 50[g]	*ca.* 40 (7)[h]
$C_3F_6:C_3F_7(CF_2\overset{\overset{CF_3}{\vert}}{C}F)_2I$									
7.47	144	3400	1700	*ca.* 80					*ca.* 50% by wt. $n < 4$ *ca.* 50% by wt. $n \gtreqless 4$
12.8	137	10,700	5950	*ca.* 90	..	..		*ca.* 60[g]	*ca.* 40 (10)[i]
$C_3F_6:CF_3I$									
4.64	113	3500	1800	68	48	22	17	[d]	13 (5)
5.43	122(194°)	4150	2800	51(?)	47	23	19	8	4 (8)[e]

[a] Conversion of iodide to telomer $C_3F_7[CF_2CF(CF_3)]_nI$. [b] No shaking. [c] Small amounts of $n = 4$ included in $n = 3$. [d] Some $n = 4$ included in $n = 5$. [e] Some $n = 11$ and $n = ca.$ 15 in residue. [f] This run was repeated but was repressured with perfluoropropene to 4700 p.s.i. after one day. Comparable conversions were obtained in only 2 days. [g] n = 3–5. [h] n = 5–10 (a balsam-like solid.). [i] n = 6–15 (estd.). The residue ($n = ca.$ 13–15) was a transparent, friable solid boiling above 190° at <0.1 mm.

In agreement with the findings of Haszeldine[8] for the photochemical addition of trifluoroiodomethane to perfluoropropene, the direction of radical attack of $CF_3\cdot$, $C_3F_7\cdot$, $C_4F_9\underset{\cdot}{C}F(CF_3)$, $C_4F_9CF(CF_3)CF_2\underset{\cdot}{C}F(CF_3)$ and $CF_2ClCFCl\cdot$ under thermal conditions is exclusively on the CF_2 group of perfluoropropene. The ultraviolet spectra maxima shown in Table I are at 280–282 mμ in agreement with the value for the $-CF_2CFICF_2-$ chromophore which is *ca.* 10 mμ further to the red than that for the $-CF_2$-

CF_2I chromophore (271 mμ).[8] Thus, in the addition of 1-iodoperfluoropropane to perfluoropropene, the adduct is I and not II. Fluorination of this adduct with cobalt trifluoride gave only perfluoro-*n*-hexane as the product, which confirms the structure I.

$$\underset{\text{I}}{CF_3CF_2CF_2CF_2CFICF_3} \qquad \underset{\text{II}}{CF_3CF_2CF_2CF(CF_3)CF_2I}$$

Thermal reactions (telomerizations) in autoclaves of reactive olefins such as chlorotrifluoroethylene and tetrafluoroethylene in contrast to the unreactive perfluoropropene are much more difficult to control to give well defined products of narrow molecular weight ranges. Using reaction times of 1–5 hr. in contrast to several days for the photochemical liquid phase reaction[2] and under otherwise comparable conditions, the $CF_2ClCFClI + CF_2{=}CFCl$ thermal reaction gave products of much wider molecular weight ranges. Under certain thermal conditions $CF_2ClCFClI$ and $CF_2ClCFCl(CF_2CFCl)_nI$ can react with comparable facility with additional olefin. Thus it is difficult even in the presence of an excess of this very efficient chain transfer agent and very short reaction times in autoclaves, to conveniently limit the spread of molecular weights.

The best control of a thermal reaction of chlorotrifluoroethylene was carried out in the liquid phase using a short contact time in a spiral tube reactor at a 5.8:1 mole ratio of $CF_2ClCFClI$ to $CF_2{=}CFCl$. The product composition was *ca.* 22% each of n = 1, 2 and 3 and *ca.* 33% of n = 4 to >10.

In an autoclave reaction, $CF_2ClCFClI + CF_2{=}CF_2$ gave predominantly very high molecular weight telomers of formula $CF_2ClCFCl(CF_2CF_2)_nI$. A liquid-phase reaction in the tube reactor, however, should provide more effective control of the reaction (especially since the C–I bond in a $-CF_2I$ group is stronger than in a $-CFClI$ group) but is potentially extremely hazardous.

In contrast, control of the thermal reaction of perfluoropropene with 1-iodoperfluoropropane is simple. High or even equal ratios of iodide to olefin are not necessary to realize high yields of $n = 1$ and $n = 2$, since a chain transfer step is not necessary. The reaction time is the important variable in controlling the process, and high yields of $n = 1$ may be achieved with iodide-to-olefin ratios varying from 1:1 to <1:5 by terminating the reaction after a suitable time interval and pressure drop. Thus, since perfluoropropene does not telomerize significantly by chain propagation, it is always advantageous to use reasonably high proportions of olefin regardless of the ultimate chain length desired and obtain particular ranges of n by limiting the reaction time. A high initial pressure (olefin concentration) and good agitation enhance olefin–iodide contact and increase the reaction rate.

The rate of reaction of C_3F_7I with perfluoropropene to give $n = 1$ is somewhat more rapid than the reaction of the products $C_3F_7[CF_2CF(CF_3)]_nI$ with the same olefin. This may be attributed to the greater reactivity of the primary $CF_3CF_2CF_2\cdot$ radical relative to the secondary $-\underset{\cdot}{C}F(CF_3)$ radical.

An examination of Table II will reveal that when the mole ratio of C_3F_6:C_3F_7I was 4.8:1 and the initial pressure was 4600 p.s.i. an increase in time of approximately fivefold raised the conversion from 52 to 88%. The product distribution (% yields) for 20 and 98 hr., respectively, were for n = 1, 66, 44; n = 2, 19, 28; n = 3, 16, 16; n = 4, —, 8; n = 5, 0, 4.

When the mole ratio of C_3F_6:C_3F_7I was 10.4 and the time was 336 hr., the total yield of product for n = 3–10 was 83%; n = 3, 41%; n = 4, 30%.

At an initial pressure of 10,700 p.s.i. and at a mole ratio of C_3F_6:$C_3F_7[CF_2CF(CF_3)]_2I$ = 12.8 the yield of product after 137 hr. reaction time was *ca.* 60% for n = 3–5 and *ca.* 40% for n = 6–15.

It has been demonstrated that reaction times (for a given conversion) can be shortened greatly by the periodic addition of olefin to maintain a high pressure or concentration.

Experimental

General Procedure.—A 300-ml. Monel autoclave was charged with the fluoroalkyl iodide. The autoclave was cooled in Dry Ice or liquid nitrogen and the olefin was introduced by vacuum transfer. The autoclave was closed and heated to about 200°, usually in a shaker. After the reaction period, the olefin was recovered by condensation in appropriately refrigerated traps. Rectification of the remaining reaction products in a Vigreux unit effected the separation of the individual telomer fractions. Table I lists the physical constants and the analytical data for the new compounds. The conditions and results of the various runs are summarized in Table II. In most cases two-thirds of the autoclave volume was occupied by liquid phase.

In a typical run, 98.0 g. (0.331 mole) of 1-iodoperfluoropropane and 240 g. (1.60 moles) of perfluoropropene (4.83 mole ratio of olefin:iodide) were used. The pressure dropped from 4600 to 2100 p.s.i. in 4 days, most of the drop occurring during the first day. [If after one day the autoclave was repressured with sufficient perfluoropropene (20–40 g.) to raise the pressure to 4500–5500 p.s.i., the rate of reaction as indicated by the pressure drop was increased markedly. Thus, the maintenance of a high olefin concentration by periodic addition of more olefin, would have greatly shortened the times given in Table II.] There were recovered 157 g. of perfluoropropene and 6.7 g. of 1-iodoperfluoropropane. A total of 176 g. of product was collected and characterized as summarized in the tables.

In all of these experiments no more than a few tenths of a gram of free iodine was collected from the autoclave, indicating the absence of significant side reactions at the temperatures used. The perfluoropropene telomers are considerably more stable during distillation than the $CF_2ClCFCl(CF_2CFCl)_nI$ telomers.

During these procedures precautions were taken to exclude oxygen to prevent reactions with the iodides. The $C_3F_7[CF_2CF(CF_3)]_nI$ telomers where n = 1 to 5 are clear fluids varying in viscosity range from a light to a barely flowing liquid. The solids of $n > 5$ are transparent waxes and glasses.

Fluorination of 2-Iodoperfluorohexane.—Cobalt trifluoride (60 g.) supported on copper shot was placed in vertical copper tube, which was surrounded by a tube furnace. 2-Iodoperfluorohexane (20 g., 0.0448 mole) was added drop by drop on top of the cobalt trifluoride under a dry nitrogen atmosphere at 260–290°. The exit gases were condensed in a Dry Ice-cooled trap, washed with 5% sodium hydroxide (some handling losses occurred), dried with Drierite and distilled to give only *n*-perfluorohexane (75%), b.p. 54°, as shown by its infrared spectrum.[14]

The Thermal Reaction of 1,2-Dichloro-2-iodo-1,1,2-trifluoroethane with Perfluoropropene.—A 300-ml. Monel autoclave filled with Monel balls to reduce the effective volume to 150 ml. was charged with 50 g. of $CF_2ClCFClI$ and 75 g. of perfluoropropene and heated for 112 hr. at 172–197° in a molten salt-bath and then for 15.5 hr. in a shaker at 201°. During this period the pressure dropped from 950 p.s.i. at 172° to 750 p.s.i. at 201°. At this time

---

[14] A. D. Kirschenbaum, A. G. Streng and M. Hauptschein, THIS JOURNAL, **75**, 3141 (1953).

an additional 20 g. of perfluoropropene was charged into the autoclave which was heated for 40 hours more at 201°. Seventy grams of olefin and 15 g. of $CF_2ClCFClI$ were recovered. Rectification of the remaining product *in vacuo* gave $CF_2ClCFCl[CF_2CF(CF_3)]_nI$ where $n = 1$ (25 g.), b.p. mostly 58.5–60.5° at 20 mm., $n^{25}D$ 1.3908, λ_{max} 282 mμ, ε 203. *Anal.* Calcd. for $C_5Cl_2F_9I$: C, 14.0. Found: C, 14.4, 14.5. Where $n = 2$ (15 g.), b.p. mostly 97.5–104° at 20 mm., $n^{25}D$ 1.3760, λ_{max} 282 mμ, ε 205. *Anal.* Calcd. for $C_8Cl_2F_{15}I$: C, 16.6. Found: C, 16.6, 16.9. Where $n = 3_{av.}$ (7 g.), b.p. mostly 77–87° at *ca.* 0.1 mm., $n^{27}D$ 1.3706, (not analyzed). Where $n = 4_{av.}$ (4 g.), b.p. 87–138° at *ca.* 0.1 mm., $n^{27}D$ 1.3691, λ_{max} 282 mμ. *Anal.* Calcd. for $C_{14}Cl_2F_{27}I$: C, 19.1; mol. wt., 879. Found: C, 19.0; mol. wt. (from absorbancy at 282 mμ of a known concentration in 2,3,3-trichloroheptafluorobutane using an ε value of 205), 850.

The Thermal Reaction of 1,2-Dichloro-2-iodo-1,1,2-trifluoroethane with Chlorotrifluoroethylene. (a) In Autoclaves.—A 1-l. stainless steel autoclave was charged with 650 g. (2.33 moles) of 1,2-dichloro-2-iodo-1,1,2-trifluoroethane and 248 g. (2.13 moles) of chlorotrifluoroethylene (1.1:1 mole ratio of iodide to olefin) and heated for 5 hr. at 180° in a molten salt-bath. During this time a pressure drop from 500 to 300 p.s.i. was observed with the major portion of the reaction occurring in the first hour ($\Delta P = 125$ p.s.i.).

Forty-five grams of olefin was recovered from the autoclave by gaseous transfer to a Dry Ice-cooled trap, and the remaining products were distilled through a short Vigreux column. A total of 581 g. of $CF_2ClCFClI$ was recovered, b.p. 99–102°, and telomer fractions, $CF_2ClCFCl(CF_2CFCl)_nI$, were taken as follows: $n = 1–2$, b.p. 45–93° at 1 mm. (36 g.); $n = 3–4$, b.p. to 150° at <0.1 mm. (80 g.). When the vapor temperature of 150° was reached, the temperature of the still-pot was sufficiently elevated due to the presence of very high molecular weight telomers to cause extensive liberation of iodine and the distillation had to be stopped. The distilled fractions were identified and the composition of the hard waxy residue (127 g.) was estimated to be $n = 4$ to >20 (mostly $n > 10$) by reference to published physical data[2] and ultraviolet molar extinction determinations.

Another experiment was carried out using a molar ratio of $CF_2ClCFClI:CF_2{=}CFCl$ of 15:1 at 160–170° for 5.7 hr. The yield of $n = 1$ and 2 was <20%, whereas under liquid phase photochemical conditions (5 days) a 75% yield of $n = 1$ was obtained by Haszeldine.[2]

(b) In Hot Tubes.—An attempt to prepare $n = 1$ by passing $CF_2{=}CFCl$ through a large excess of refluxing $CF_2ClCFClI$ in a vertical column heated to 180° failed to give any significant reaction. Therefore, an alternative reaction system allowing higher pressures and temperatures as well as short contact time was designed.

At an average rate of 9.6 g./min., a mixture of 2230 g. (8.0 moles) of 1,2-dichloro-2-iodo-1,1,2-trifluoroethane and 160 g. (1.37 moles) of chlorotrifluoroethylene was pumped by means of a Lapp Pulsafeeder micropump from a charge cylinder through a stainless steel coil immersed in a molten salt-bath at 200°. Practically all of the coil volume was occupied by liquid phase, and the contact time in this hot zone was calculated as <10 min. During the reaction, the pressure was maintained at 750 p.s.i. by adjusting the rate at which products were vented from the coil to a Dry Ice-cooled receiving gas cylinder. Twelve grams of chlorotrifluoroethylene and 2150 g. of $CF_2ClCFClI$ were recovered. The product distribution of the remaining 211 g. of crude telomer was $n = 1$ (22%), $n = 2$ (22%), $n = 3$ (22%) and $n = 4$ to >10 (33%).

In the above apparatus at a rate of 17 g./min. at 195–200° and at pressures of 600–650 p.s.i. only slight reaction occurred.

The Thermal Reaction of 1,2-Dichloro-2-iodo-1,1,2-trifluoroethane with Tetrafluoroethylene.—1,2-Dichloro-2-iodo-1,1,2-trifluoroethane (200 g., 0.716 mole) and 30 g. (0.316 mole) of tetrafluoroethylene (2.4 mole ratio of iodide to olefin) were charged into a 300-ml. nickel autoclave and heated in a molten salt-bath for 2.75 hr. at 171°. After the reaction period, during which the pressure fell from 600 to 450 p.s.i., 15 g. of tetrafluoroethylene was recovered. From the remaining products 170 g. of $CF_2ClCFClI$ was recovered (some handling losses), and 16 g. of a white crumbly solid was the only other product. This solid contained only very small amounts of iodine and its ultraviolet spectrum showed a very faint maximum at *ca.* 270 mμ. Its infrared spectrum closely resembled that of polytetrafluoroethylene.

Ultraviolet Spectra.—A Beckman ratio recording spectrophotometer, model DK-2, was used.

Acknowledgment.—We wish to thank Mr. John J. Mullaney for technical assistance, Miss Ruth Kossatz, Miss Eva Raieta and Mr. Harry Rein for spectroscopic measurements, and Mr. John Y. Steel for certain carbon analyses.

PHILADELPHIA 18, PENNA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF WAYNE STATE UNIVERSITY]

Studies in Organic Sulfur Compounds. IX.[1] Preparation and Desulfurization of Optically Active 1,1-Diphenyl-3-mercaptopropan-2-ol[2]

BY CARL DJERASSI AND J. GROSSMAN

RECEIVED DECEMBER 12, 1956

Acid cleavage of spiro-(5-diphenylmethyl-1,3-oxathiolane-2,3′-cholestane) (I) followed by lithium aluminum hydride reduction of the resulting disulfide VII led to optically pure 1,1-diphenyl-3-mercaptopropan-2-ol (IV). Raney nickel desulfurization of this β-mercaptoethanol or of its O,S-dibenzoate (VI) furnished 1,1-diphenylpropan-2-ol or its benzoate, respectively. The rotations of this alcohol (IIIa) and its derivatives were identical with those of the earlier prepared desulfurization product of the hemithioketal I. These results show that no racemization occurs in the formation of alcohols by Raney nickel desulfurization of hemithioketals (*e.g.*, I) or of β-mercaptoethanols (*e.g.*, IV).

The observation[1] that Raney nickel desulfurization of hemithioketals (1,3-oxathiolanes) results in introduction of oxygen has led to an investigation of the scope of this reaction, and the appropriate experiments will be reported at a future time. We have also been concerned with the mechanism of this reaction and certain observations bearing on this aspect form the subject of the present paper.

The desulfurization of spiro-(5-diphenylmethyl-1,3-oxathiolane-2,3′-cholestane) (I) led[1] to over 50% each of cholestan-3-one (II) and 1,1-diphenylpropan-2-ol (III). This alcohol (III) was optically active ($[\alpha]D$ +5.8°, 3,5-dinitrobenzoate $[\alpha]D$ −46.8°), and since an antipode with the same optical properties (but opposite in sign) was isolated by desulfurization of a diastereoisomer of the hemithioketal I, it was assumed that complete re-

---

[1] Paper VIII, C. Djerassi, M. Gorman and J. A. Henry, THIS JOURNAL, **77**, 4647 (1955).

[2] This work was carried out under contract No. DA-20-018-ORD-13474 with the Office of Ordnance Research, U. S. Army.