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TELOMERIZATION REACTIONS IN THE SYNTHESIS OF MODELS FOR SOME FLUOROCARBON POLYMERS[1]

R. D. CHAMBERS, J. HUTCHINSON, R. H. MOBBS and W. K. R. MUSGRAVE
The Chemistry Department, The University, Durham

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Abstract—Heptafluoro-2-iodopropane, i-C_3F_7I, is a very efficient chain-transfer agent in telomerization reactions with 1,1-difluoroethylene and tetrafluoroethylene; other telomerization reactions of CF_3I, C_2F_5I and n-C_3F_7I with 1,1-difluoroethylene and of n-C_3F_7I with tetrafluoroethylene are reported and the relative efficiencies of the iodides as chain-transfer agents are discussed. The telomer iodides have been converted to useful models for some fluorocarbon polymer systems. A novel stereospecific synthesis of *cis*-$(CF_3)_2CF\cdot CH{=}CHF$ is reported.

IN THE course of a programme of work concerning the properties and chemical reactivity of various fluorocarbon polymer systems and since part of this work involves the synthesis and study of model compounds we have carried out a number of telomerization reactions using 1,1-difluoroethylene and tetrafluoroethylene with various fluorocarbon iodides. Some of these telomerization reactions are new and others have been repeated for purposes of comparison. Telomer iodides have been converted to model compounds containing the pertinent structural elements for investigation.

The use of heptafluoro-2-iodopropane[2] as a chain-transfer agent has not been reported previously and it is a convenient source of "tertiary" fluorine (in the sense that only fluorocarbon groups are attached to the C—F carbon and not other fluorine atoms or hydrogen). This particular structural feature is relevant because of its occurrence in some fluorocarbon polymer systems of known utility e.g. "Viton A",[3] which is a co-polymer of hexafluoropropane and 1,1-difluoroethylene and where the predominating arrangement is known to be $—CF_2\cdot CF(CF_3)\cdot CH_2\cdot CF_2\cdot CH_2\cdot CF_2—$[4] and in "Teflon 100X",[3] a co-polymer of tetrafluoroethylene and hexafluoropropene, $—CF_2\cdot CF(CF_3)\cdot CF_2\cdot CF_2—$.

Heating together, in a stainless steel autoclave, equimolecular amounts of heptafluoro-2-iodopropane and 1,1-difluoroethylene to 185°, for 36 hr gave the simple adduct (I) as the main product. That the

$$\underset{\text{I}}{(CF_3)_2CF\cdot CH_2\cdot CF_2I} \qquad\qquad \underset{\text{II}}{(CF_3)_2CF\cdot CF_2\cdot CH_2I}$$

structure of the adduct was I and not the isomer II, or a mixture, was deduced from

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[1] Preliminary communication, R. D. Chambers, J. Hutchinson and W. K. R. Musgrave, *Tetrahedron Letters* No. 10, 619 (1963).

[2] R. D. Chambers, W. K. R. Musgrave and J. Savory, *J. Chem. Soc.* 3779 (1961).

[3] Registered trade mark of E. I. du Pont de Nemours & Co. Inc.

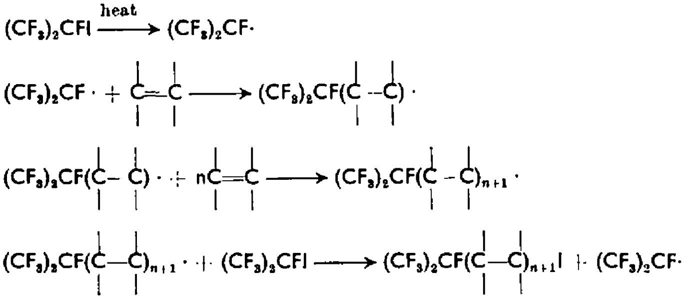
[4] R. C. Ferguson, *J. Amer. Chem. Soc.* **82**, 2416 (1960).

the following observations. A sharp, single main peak was observed with a very small (<5 %) peak following on analytical scale vapour-phase chromatography (VPC), and the main peak showed no tendency to be resolved on any of several stationary phases; the UV spectrum of a sample of the main component (separated by preparative-scale VPC) had λ_{max} 274 mμ which is characteristic of a terminal —CF_2I and is easily distinguishable from —CH_2I which usually gives λ_{max} near 262 mμ.[5] Dehydroiodination (see later) of the adduct gave an olefin whose NMR spectrum is consistent with the structure $(CF_3)_2CF{\cdot}CH{=}CF_2$. This dehydroiodination gave high yields of olefin (85 %) which indicates that isomer II could only be present in very small amounts. Hauptschein and Oesterling[6] have observed that the 1:1 adduct from the thermal addition of heptafluoro-1-iodopropane to 1,1-difluoroethylene consisted of 95 % n-$C_3F_7{\cdot}CH_2{\cdot}CF_2I$ and 5 % n-$C_3F_7{\cdot}CF_2{\cdot}CH_2I$. Preferential free-radical attack at the $=CH_2$ group in this type of olefin appears to be general.[6,7–9] Telomers were produced by increasing the ratio of 1,1-difluoroethylene to i-C_3F_7I.

$$\text{i-}C_3F_7I + nCF_2{=}CH_2 \rightarrow \text{i-}C_3F_7(CH_2{-}CF_2)_nI$$

The results of these and other telomerization reactions using 1,1-difluoroethylene, which we have investigated are summarized in Table 1. Our results with CF_3I and $CF_2{=}CH_2$ are at variance with those reported by Hauptschein *et al.*[9] who report an 80 % conversion of the iodide into telomers when equimolecular amounts of reactants were heated together at 188° for 22 hr. The composition of the mixture of telomers $CF_3(CH_2CF_2)_nI$ ($n = 1, 2, 3, 4$), obtained by these workers, was 80, 10, 5 and 5 mole % respectively. At 188° we observed very little conversion and at the temperature which we used to promote reaction, a larger proportion of the higher telomers was obtained. Haszeldine and Steele[8] found that at 220° equimolar quantities of C_2F_5I and $CF_2{=}CH_2$ reacted to give mainly (95 %) the 1:1 adduct $C_2F_5{\cdot}CH_2{\cdot}CF_2I$; we have also observed a high proportion of the adduct.

Telomerization reactions are usually assumed to proceed by a radical-chain mechanism, as represented by equations (i–iv), although Hauptschein has suggested a mechanism which involves a stepwise series of additions of iodide to olefin, for the thermal telomerization of hexafluoropropene with n-C_3F_7I.[10]



$$(CF_3)_2CFI \xrightarrow{\text{heat}} (CF_3)_2CF\cdot$$

Initiation (i)

$$(CF_3)_2CF\cdot + \gt C{=}C\lt \longrightarrow (CF_3)_2CF(\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}})\cdot$$

(ii)

$$(CF_3)_2CF(\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}})\cdot + n\overset{|}{\underset{|}{C}}{=}\overset{|}{\underset{|}{C}} \longrightarrow (CF_3)_2CF(\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}})_{n+1}\cdot$$

Propagation (iii)

$$(CF_3)_2CF(\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}})_{n+1}\cdot + (CF_3)_2CFI \longrightarrow (CF_3)_2CF(\overset{|}{\underset{|}{C}}{-}\overset{|}{\underset{|}{C}})_{n+1}I + (CF_3)_2CF\cdot$$

Chain Transfer (iv)

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[5] R. N. Haszeldine and B. R. Steele, *J. Chem. Soc.* 923 (1954).

[6] M. Hauptschein and R. E. Oesterling *J. Amer. Chem. Soc.* **82**, 2868 (1960).

[7] R. N. Haszeldine, *J. Chem. Soc.* 356 (1953).

[8] R. N. Haszeldine and B. R. Steele, *J. Chem. Soc.* 3005 (1955).

[9] M. Hauptschein, M. Braid and F. E. Lawlor, *J. Amer. Chem. Soc.* **80**, 846 (1958).

[10] M. Hauptschein, M. Braid, and F. E. Lawlor, *J. Amer. Chem. Soc.* **79**, 2549 (1957).

TABLE 1. TELOMERIZATION REACTIONS WITH 1,1-DIFLUOROETHYLENE

Molar ratio	Temp. °C	Time (hr)	Conversion of iodide (%)	Composition of $R_f(CH_2CF_2)_nI$, (mole%)					
				n = 1	n = 2	n = 3	n = 4	n = 5	n = 6
CF_3I/CH_2CF_2									
1/1	200–210	17 + 24	35	46	33	14·5	5·5	1	
C_2F_5I/CH_2CF_2									
1/1	190	45	55	92	6	2			
n-C_3F_7I/CH_2CF_2									
1/1	200	36	88	70	25	5			
$(CF_3)_2CFI/CH_2CF_2$									
1/1	185	36	88	90	10	trace			
1/1	220	36	90	87	13	trace			
1/3	220	36	100	14	38	34	11	3	
1/4	220	36	100	2	21	29	26	18	4

It is interesting to note that a lower range of telomers was produced using i-C_3F_7I than n-C_3F_7I, with 1,1-difluoroethylene which indicates that i-C_3F_7I is the more efficient chain-transfer agent (iv). Also, reaction of i-C_3F_7I with tetrafluoroethylene gave telomers i-$C_3F_7(CF_2CF_2)_nI$ where the range of values for n was much more difficult to control (see Table 2) than with $CF_2:CH_2$ and required a greater proportion of iodide to obtain a reasonable telomer range, indicating that the propagation step (iii) is much more efficient with tetrafluoroethylene than 1,1-difluoroethylene. Trifluoromethyl iodide or C_2F_5I with tetrafluoroethylene gives a broad range of telomers unless a considerable excess of iodide is employed[11] and so, i-C_3F_7I is a very useful reactant for the preparation of low molecular-weight compounds from tetrafluoroethylene. That the rates of (a) initiation and (b) the chain-transfer steps relative to propagation may be increased by raising the temperature is illustrated by the fact that at 190° only low conversion to a mixture of high telomers occurred with n-C_3F_7I and tetrafluoroethylene but at 240°, a high conversion to low telomers was obtained. These observations parallel those of Krespan *et al.*[12] who found that raising the temperature increased the rate of chain transfer in the reaction of carbon tetrachloride with tetrafluoroethylene.

TABLE 2. TELOMERIZATION OF TETRAFLUOROETHYLENE WITH HEPTAFLUOROPROPYL IODIDES

Mole ratio	T°(C)	Time (hr)	Conversion of olefin (%)	Composition of $C_3F_7(CF_2CF_2)_nI$, mole%			
				n = 1	n = 2	n = 3	n = 4
i-C_3F_7I/C_2F_4							
4·61	175	24	89	69	18	10	3[a]
10·02	175	58	69	78	10	12	0
4·70	173 190	41 23	76	78	13	6	3[b]
n-C_3F_7I/C_2F_4							
3·86	190	24	20[c]				
4·1	240	24	94	76	22	2	—

[a] 8·3% (by wt) of the total product contained telomers > n = 4.

[b] 12·4% (by wt) of the total product contained telomers > n = 4.

[c] The product was a viscous pasty mass containing only a small proportion (<5 mole%) of n = 1, n = 2 telomers and larger amounts of higher telomers.

The results of an investigation of the exchange of labelled iodine and a number of fluorocarbon iodides[13] show that the strength of the carbon-iodine bond decreases sharply in the series $CF_3I > C_2F_5I >$ n-$C_3F_7I >$ i-C_3F_7I. That i-C_3F_7I is the most efficient chain-transfer agent in the series is in accordance with these results. The gradual increase in percentage conversion of iodide to telomers as members of the series from CF_3I to i-C_3F_7I are reacted with 1,1-difluoroethylene can be attributed to the increasing ease of bond fission and hence initiation of the chain. But, an anomaly in this simple picture is the reaction of C_2F_5I with 1,1-difluoroethylene where, although

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[11] R. N. Haszeldine, *J. Chem. Soc.* 3761 (1953).

[12] C. G. Krespan, R. J. Harder and J. J. Drysdale, *J. Amer. Chem. Soc.* **83**, 3424 (1961).

[13] R. D. Chambers, J. Hutchinson and W. K. R. Musgrave, unpublished results.

the conversion (55%) is less than for n-C_3F_7I (88%) the range of telomers produced with the former iodide is considerably less, giving mainly the 1:1 adduct. We must regard C_2F_5I as a more efficient chain-transfer agent than n-C_3F_7I and this is not consistent with the relative C—I bond strengths of the two iodides. Another point which is difficult to rationalise is the much greater reactivity of i-C_3F_7I than n-C_3F_7I with tetrafluoroethylene at 190°, a temperature at which iodides react readily with 1,1-difluoroethylene giving high conversion to telomers. If a radical-chain mechanism is assumed, then the latter reaction indicates that enough radicals are produced at this temperature from *both* iodides and the more stable radical $(CF_3)_2CF\cdot$ would be expected to be *less* reactive than $CF_3CF_2CF_2\cdot$. This situation can be rationalised in terms of the greater electrophilic character of the latter radical than $(CF_3)_2CF\cdot$ and the more electrophilic character of tetrafluoroethylene than 1,1-difluoroethylene. This would make tetrafluoroethylene more discriminating than 1,1-difluoroethylene in reactions with the relatively electrophilic fluorocarbon radicals. However, we conclude that there are important factors which influence the course of these telomerization reactions in addition to those implied in the simple radical-chain process referred to above, and elsewhere.[14] There is possibly a duality of mechanism in the series which we are reporting, between a radical-chain and a four-centre process but we cannot distinguish these on the evidence so far available.

Reactions of the telomer iodides

Coupling. Heptafluoropropyl iodides and higher fluorocarbon iodides may be coupled by irradiating with UV light, in the presence of mercury.[9] This technique has been applied successfully to the 1:1 adducts of i-C_3F_7I to tetrafluoroethylene and 1,1-difluoroethylene to give products which are suitable models for the systems referred to earlier.

$$(CF_3)_2CF{\cdot}CF_2{\cdot}CF_2{\cdot}I \xrightarrow{Hg/UV} [(CF_3)_2CF{\cdot}CF_2{\cdot}CF_2]_2$$

$$(CF_3)_2CF{\cdot}CH_2{\cdot}CF_2I \xrightarrow{Hg/UV} [(CF_3)_2CF{\cdot}CH_2{\cdot}CF_2]_2$$

Replacement of iodine

(a) *By hydrogen.* When no β-hydrogen is present, substitution of iodine in a fluorocarbon iodide by hydrogen can be achieved easily using alkali in aqueous acetone;[15] however, under these conditions, elimination of hydrogen iodide occurred from telomers derived from 1,1-difluoroethylene. Attempts to replace the iodine by hydrogen, using zinc and sulphuric acid resulted mainly in coupling.[8] Lithium aluminium hydride with $(CF_3)_2CF{\cdot}CH_2{\cdot}CF_2I$ gave a low yield of $(CF_3)_2CF{\cdot}CH_2{\cdot}CF_2H$ and a small amount of this material was also obtained by hydrolysis of the corresponding fluoroalkyl-zinc iodide in dioxane. During the preparation of the zinc compound, by the method used by Miller *et al.*[16] for heptafluoro-n-propylzinc iodide, two olefins distilled from the reaction mixture. The NMR spectra of the olefins indicates that they are *cis-* and *trans-*isomers of 1H,2H-octafluoro-(3-methylbut-1-ene). This rearrangement, which most probably proceeds by a carbene intermediate, is

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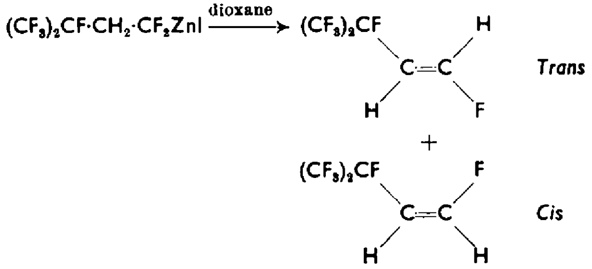
[14] R. N. Haszeldine, *J. Chem. Soc.* 4291 (1955).

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

[16] W. T. Miller, E. Bergman and A. H. Fainberg, *J. Amer. Chem. Soc.* 79, 4159 (1957).

stereospecific in that the *cis*-isomer is formed in much greater proportion than the *trans*-isomer.



(b) *By fluorine.* Iodine can be replaced readily using antimony trifluoride dichloride.

$$(CF_3)_2CF{\cdot}CH_2{\cdot}CF_2I \xrightarrow{SbF_3Cl_2} (CF_3{\cdot})_2CF{\cdot}CH_2{\cdot}CF_3$$

Dehydroiodination. Telomers of 1,1-difluoroethylene i.e. $R_f{\cdot}(CH_2{\cdot}CF_2)_nI$ are very susceptible to dehydroiodination using solid potassium hydroxide[5] and tertiary amines. We have prepared a number of olefins of the type $R_f{\cdot}CH{=}CF_2$ by this route, for use in co-polymerization studies.

$$R_f(CH_2{-}CF_2)_nI \longrightarrow R_f(CH_2{\cdot}CF_2)_{n-1}CH{=}CF_2$$

EXPERIMENTAL

IR and UV spectra were recorded using Grubb Parsons, type G.S.2A and Optica C.F.4 spectrometers, respectively.

Telomerization Reactions

Typical reactions of 1,1-*difluoroethylene*

(a) *With heptafluoro-2-iodopropane.* An autoclave (150 ml) was charged with heptafluoro-2-iodopropane (68 g, 0·23 mole) and 1,1-difluoroethylene (18 g, 0·28 mole) by vacuum transfer. The autoclave was rocked at 185° for 36 hr and then allowed to cool. Recovered olefin (1 g) was collected by venting through a trap cooled in liquid air and then a violet liquid (84 g) was obtained from the autoclave. Distillation of this liquid (red. press.) gave 3 fractions: b.p. 40–45°/750 mm (6·5 g); b.p. 102–105°/750 mm (70 g); and b.p. 63–67°/25 mm (7 g). The main component in each fraction was isolated by preparative scale vapour-phase chromatography (VPC) and shown to be, respectively, heptafluoro-2-iodopropane; 2H,2H-1-iodononafluoro-(3-methylbutane), $(CF_3)_2CF{\cdot}CH_2{\cdot}CF_2I$, (Found: F, 48·1; I, 34·8%; M, 354. $C_5H_2F_9I$ requires; F, 47·5; I, 35·3%; M, 360), n_D^{20} 1·3555, λ_{max} 274 mμ (332); and $(CF_3)_2CF(CH_2CF_2)_2I$, (Found: F, 49·7; I, 29·6%; M, 416. $C_7H_4F_{11}I$ requires: F, 49·3; I, 29·9%; M, 424), n_D^{20} 1·3646, λ_{max} 272 mμ (313). The composition of the crude product, as shown in Table 1, was determined by analytical scale VPC.

(b) *With trifluoroiodomethane.* An autoclave (150 ml) was charged with trifluoroiodomethane (93 g, 0·48 mole) and 1,1-difluoroethylene (30·5 g, 0·48 mole) by vacuum transfer and then heated at 200–210° for 41 hr. Volatile material (54·2 g) was vented and collected in a trap cooled in liquid air and a reddish liquid (50·5 g) was recovered from the autoclave. The composition of the telomer-iodide mixture was estimated by analytical VPC and the bulked liquid products from several similar reactions were fractionated through a 20 cm Vigreux column to give 2H,2H-1-iodopentafluoropropane, b.p. 71–72°[17] (46 mole%). In an identical reaction in which the autoclave was heated to 188° there was no pressure drop, indicating that little or no reaction had occurred.

(c) *With pentafluoroiodoethane.* An autoclave (150 ml) was charged with pentafluoroiodoethane (120 g, 0·49 mole) and 1,1-difluoroethylene (31·6 g, 0·49 mole) and then rocked at 190° for 45 hr. After venting, the contents of the autoclave (77 g) were distilled (red. press.), giving 3 fractions: b.p. 89–93°/756 mm (65 g); b.p. 75–80°/80 mm (5 g); and b.p. 68–73°/7 mm (1·7 g) containing, respectively, 2H,2H-1-iodoheptafluorobutane, $C_2F_5{\cdot}CH_2CF_2I$ (Found: F, 43·1, I, 40·9%; M, 306.

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[17] R. N. Haszeldine, *J. Chem. Soc.* 923 (1954).

Calc. for $C_4H_2F_7I$: F, 42·9; I, 40·9%; M, 310) b.p. 91°/756 mm, n_D^{20} 1·3578, λ_{max} 272 mμ (318);[7] $C_2F_5(CH_2CF_2)_2I$ (Found: F, 45·5; I, 33·4%; M, 360. $C_6H_4F_9I$ requires: F, 45·7; I 33·9%; M, 374), n_D^{20} 1·3673, λ_{max} 272 (345); and $C_2F_5(CH_2CF_2)_3I$, which was dehydroiodinated (see later).

(d) *With heptafluoro-*1*-iodopropane.* An autoclave (150 ml) charged with heptafluoro-1-iodopropane (90 g, 0·31 mole) and 1,1-difluoroethylene (23 g, 0·36 mole) was rocked at 200° for 36 hr. Distillation of the reaction product gave: b.p. 40–43°/760 mm (9 g); and b.p. 108–112°/760 mm (50 g). The first fraction consisted mainly of n-C_3F_7I while the second fraction consisted mainly of 2H,2H-1-iodononafluoropentane, n-$C_3F_7{\cdot}CH_2{\cdot}CF_2I$, (Found: F, 47·8; I, 35·0%; M, 355. Calc. for $C_5H_2F_9I$; F, 47·5; I, 35·3%; M, 360), n_D^{20} 1·3513, b.p. 108°/770 mm.[8]

Reaction of tetrafluoroethylene

(a) *With heptafluoro-*2*-iodopropane.* In a typical reaction an autoclave (150 ml) was charged with heptafluoro-2-iodopropane (164 g, 0·55 mole) and tetrafluoroethylene (11·7 g, 0·12 mole) by vacuum transfer, and ca. 6 drops dipentene was added as inhibitor. The autoclave was rocked at 190° for 40 hr and then cooled and vented. Recovered olefin (0·5 g) was collected in a trap cooled in liquid air and then a violet liquid (159·6 g) was recovered from the autoclave. Excess heptafluoro-2-iodopropane was distilled off and the residual liquid (35 g) was distilled through a 10 cm Vigreux column to give 2 fractions: b.p. 40°–45 (8·3 g); b.p. 80°–95° (14·1 g) and a residue b.p. > 95° (9·8 g). Analytical scale VPC showed that the second fraction was mainly a single component (95%). Several reactions were worked up similarly and the bulked main fractions, b.p. 80–95°, when distilled through a 15 cm Vigreux column gave a fraction identified as 1*-iodoundecafluoro-*(3*-methylbutane*), (Found: F, 52·1; I, 31·3%; M, 382. $C_5F_{11}I$ requires: F, 52·8; I, 32·05%; M, 396) b.p. 89°–90°/747 mm n_D^{20}, 1·3347. The bulked residues were fractionated (red. press.) and the main components from 2 fractions b.p. 50–70°/17 mm, and b.p. 100–110°/15 mm were separated by preparative VPC and identified, respectively, as: $(CF_3)_2CF{\cdot}(CF_2CF_2)_2I$, (Found: F, 57·0; I, 25·43%; M, 517. $C_7F_{15}I$ requires: F, 57·5; I, 25·6%; M, 496), b.p. 139°/770 mm and $(CF_3)_2CF(CF_2CF_2)_3I$, (Found: F, 58·5; I, 21·7%; M, 635. $C_9F_{19}I$ requires: F, 59·0, I, 21·3%; M, 596), b.p. 189·5/756·5 mm. Composition of the original telomer mixture was estimated by analytical VPC after an initial distillation to separate the more volatile components.

(b) *With heptafluoro-*1*-iodopropane.* In a typical reaction an autoclave (150 ml) was charged with heptafluoro-1-iodopropane (147 g, 0·49 mole) and tetrafluoroethylene (11·9 g, 0·12 mole) by vacuum transfer, and 6 drops dipentene was added as inhibitor. The autoclave was rocked at 240° for 24 hr, cooled, and then recovered olefin (0·7 g) was collected by venting through a trap cooled in liquid air. A violet liquid (146·7 g) was recovered from the autoclave. Excess heptafluoro-1-iodopropane was distilled off and the residual liquid (36·9 g) distilled through a 15 cm Vigreux column to give 2 fractions b.p. 40–93°(14·3 g); b.p. 93°–95°/755 (8·0 g) and a residue (11·6 g). Analytical VPC showed that the second fraction was mainly a single component (97%); this was isolated by preparative scale VPC and shown to be 1*-iodoundecafluoropentane*, b.p. 94·5 /743 mm (Found: F, 52·5%; I, 33·1%. $C_5F_{11}I$ requires: F, 52·8; I, 32·05%). The composition of the original telomer mixture was estimated by analytical scale VPC.

Reactions of Telomers of 1,1*-Difluoroethylene*

1. *Dehydroiodination of* $(CF_3)_2CF{\cdot}CH_2{\cdot}CF_2I$

(a) *Using solid potassium hydroxide.* A three-necked flask, fitted with mercury-seal stirrer, dropping funnel and condenser connected to a trap at −78°, was charged with powdered KOH (56 g; 1·0 mole). The temp. of the flask was raised to 90° and the iodide (30 g, 0·084 mole) was slowly added; after 2 hr, volatile material remaining in the flask was swept into the cold trap with a stream of nitrogen. Distillation of the contents of the trap gave 2H*-nonafluoro-*(3*-methylbut-*1*-ene*), $(CF_3)_2CF{\cdot}CH{=}CF_2$, (18 g, 85%), b.p. 30°/752 mm, (Found: F, 73·5%; M, 226. C_5HF_9 requires: F, 73·7%; M, 232), $n_D^{20} < 1{\cdot}3$.

(b) *Using triethylamine.* Using the apparatus described in (a), the flask was charged with the iodide (80 g, 0·22 mole) and triethylamine (27 g, 0·268 mole) was added, dropwise, over 10 min. An exothermic reaction occurred immediately on the addition of amine and crystals of the amine hydroiodide were precipitated. The mixture was stirred 1 hr and then volatile material was swept into the cold trap with nitrogen giving $(CF_3)_2CF{\cdot}CH{=}CF_2$ (38 g, 75%) whose IR spectrum was identical with that of the sample characterized in (a).

(2) *Dehydroiodination of* $(CF_3)_2CF{\cdot}(CH_2CF_2)_nI$

(a) $(CF_3)_2CF{\cdot}(CH_2CF_2)_2I$. Using the techniques described above yields of 70% (using KOH) and 80% (using Et_3N) of $(CF_3)_2CF{\cdot}CH_2{\cdot}CF_2{\cdot}CH{=}CF_2$ were recorded (Found: F, 70·0%; M, 291. $C_7H_3F_{11}$ requires: F, 70·6%; M, 296), b.p. 93°/756 mm, $n_D^{20} < 1{\cdot}3$.

(b) $(CF_3)_2CF(CH_2CF_2)_3I$. A yield of 83% of $(CF_3)_2CF(CH_2CF_2)_2CH{=}CF_2$ was obtained using KOH (Found: F, 68·0%; M, 354. $C_9H_5F_{13}$ requires: F, 68·6%; M, 360), b.p. 146°/760 mm, n_D^{20} 1·3173.

(3) *Dehydroiodination of* $C_2F_5(CH_2CF_2)_nI$

(a) $C_2F_5CH_2CF_2I$. Reaction with solid KOH gave (85%) 1H-*heptafluorobut*-1-*ene* (Found: F, 72·9%; M, 177. C_4HF_7 requires: F, 73·1%; M, 182), b.p. 10–11°/760 mm.

(b) $C_2F_5(CH_2{\cdot}CF_2)_2I$. Reaction with triethylamine gave (75%) $C_2F_5{\cdot}CH_2{\cdot}CF_2{\cdot}CH{=}CF_2$ (Found: F, 69·0%; M, 238. $C_6H_3F_9$ requires: F, 69·5%; M, 246), b.p. 75°/760 mm, $n_D^{20} < 1{\cdot}3$.

(c) $C_2F_5(CH_2CF_2)_3I$. Triethylamine gave (55%) $C_2F_5(CH_2CF_2)_2CH{=}CF_2$ (Found: F, 66·8%; M, 296. $C_8H_5F_{11}$ requires: F, 67·4%; M, 310), b.p. 134°/760 mm, n_D^{20} 1·3167.

All of the olefins characterized above, i.e. containing the element of structure —$CH{=}CF_2$, showed a strong absorption in their IR spectra in the region 1748–1764 cm^{-1} (C=C stretch) and this is consistent with the findings of Hauptschein and Oesterling[6] who also found that olefins having this structural element showed strong absorption in the same region.

(4) *Coupling of* $(CF_3)_2CF{\cdot}CH_2{\cdot}CF_2I$

(a) *With mercury and ultraviolet light.* The iodide (75 g 0·208 moles) was sealed under vacuum in a thin-walled tube (200 ml) with enough Hg to form a continuous pool when horizontal. The tube was then shaken in a horizontal position at 14 cm from a 1 kW UV lamp until the contents turned black (4 days). The temp. in the region of the tube was 80°. A colourless liquid (33 g) was distilled under vacuum from the tube and analytical scale VPC showed that it consisted of one major and two very minor components. Distillation of this product gave fractions b.p. 20–60° and b.p. 139–140° (28 g, 75%), the latter fraction being $[(CF_3)_2CF{\cdot}CH_2CF_2]_2$ (Found: F, 73·3%; M, 458. $C_{10}H_4F_{18}$ requires: F, 73·5%; M, 466), $n_D^{20} < 1{\cdot}3$. The more volatile fraction was separated by preparative-scale VPC into two components, identified by comparison of their IR spectra with those of authentic specimens, as $(CF_3)_2CF{\cdot}CH{=}CF_2$ and $(CF_3)_2CF{\cdot}CH_2{\cdot}CHF_2$.

(b) *With zinc and acetic anhydride.*[18] The iodide (10 g, 0·27 mole) in methylene chloride (15 ml) was contained in a flask (100 ml) fitted with reflux condenser and stirrer. Granulated Zn (5·7 g) and acetic anhydride (6 g) were added and the methylene chloride began to reflux: after 15 min heat was applied to maintain reflux and this was continued for 3½ hr. The mixture was then filtered and the methylene chloride solution was heated under reflux with dil. H_2SO_4 to hydrolyse the acetic anhydride; the organic layer was separated, washed ($NaHCO_3$) and dried (P_2O_5), then distillation through a short packed column left a residue from which $[(CF_3)_2CF{\cdot}CH_2CF_2]_2$ (2·9 g, 44·6%) was obtained by preparative scale VPC; the sample gave an IR spectrum identical with that of samples prepared as described above.

(5) *Coupling of* $R_fCH_2CF_2I$ *with mercury and ultraviolet light*

(a) $C_2F_5CH_2CF_2I$. Using the technique described above $C_2F_5CH_2CF_2I$ (46 g, 0·15 mole), irradiated for 5 days at 10 cm from a 500 watt lamp (temp. 60°), gave a colourless liquid (24 g) from which was obtained $[C_2F_5CH_2CF_2]_2$ (19 g, 70%) (Found: F, 72·5%; M, 359. $C_8H_4F_{14}$ requires: F, 72·7%, M, 366), $n_D^{20} < 1{\cdot}3$.

(b) $CF_3{\cdot}CF_2{\cdot}CF_2{\cdot}CH_2CF_2I$. Reaction of $CF_3CF_2CF_2CH_2CF_2I$ (54 g, 0·15 moles) with Hg, as described in (a) gave $[CF_3CF_3CF_2CH_2CF_2]_2$ (24 g, 70%) (Found: F, 73·0%; M, 457. $C_{10}H_4F_{18}$ requires: F, 73·5%, M, 466), b.p. 157°/770 mm, m.p. 42°.

(6) *Reaction of* $(CF_3)_2CF{\cdot}CH_2CF_2I$ *with lithium aluminium hydride*

A three-necked flask (250 ml) fitted with a mercury-seal stirrer, dropping funnel, and condenser leading to a trap at −78°, was charged with $LiAlH_4$ (1·5 g, 0·04 mole) and dry ether (50 ml). The mixture was cooled to −70° and a solution of the iodide (10 g, 0·028 mole) in ether (25 ml) was

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[18] A. L. Henne and W. Postelneck, *J. Amer. Chem. Soc.* 77, 2334 (1955).

slowly added. The mixture was then allowed to reach room temp. after which, dil. H_2SO_4 was added, dropwise, until hydrolysis was complete and then the mixture was heated at reflux for 6 hr. A colourless liquid (15 ml) had collected in the trap and a further quantity of liquid (25 ml) was distilled from the flask. This liquid contained mainly ether and 2 minor components, one of which was separated by preparative scale VPC and identified as 1H,2H,2H-*nonafluoro-(3-methylbutane)* (Found: F, 72·2%; M, 238. $C_5H_3F_9$ requires: F, 73·1%; M, 234), b.p. 50°/752 mm, $n_D^{20} < 1{\cdot}3$.

(7) *Preparation and hydrolysis of* $(CF_3)_2CF{\cdot}CH_2CF_2ZnI$

Dioxane were purified according to the procedure of Miller *et al.*[16] and the reaction was carried out according to the method described by these workers for the preparation of n-C_3F_7ZnI. A three-necked flask (250 ml) fitted with mercury-seal stirrer, dropping funnel, and condenser leading to a trap at −78°, was charged with Zn (20 g, 0·3 g atoms) and dioxane (40 ml). The temp. was raised to 70° and the iodide (30 g, 0·083 mole) was added, dropwise. When this addition was complete the solution was heated at reflux 3 hr, during which time a colourless liquid (0·5 g) collected in the cold trap. The reflux condenser was removed and a further quantity of liquid (15 g) distilled. Preparative scale VPC (over tritolylphosphate) showed that the liquid contained 3 components; the component having the shortest retention time was present in only small proportion but sufficient was isolated for the NMR and IR spectra to be recorded (see later) which indicate the compound to be 1H,2H-octafluoro-(3-methylbut-*trans*-1-ene), $(CF_3)_2CF{\cdot}CH{=}CHF$. The next component was identified as $(CF_3)_2CF{\cdot}CH_2{\cdot}CHF_2$ by comparing the IR spectrum with that of an authentic specimen. Finally the component with longest retention time was identified as 1H,2H-*octa-fluoro-(3-methylbut-*cis*-1-ene)* $(CF_3)_2CF{\cdot}CH{=}CHF$ (Found: F, 70·8%; M, 208. $C_5H_2F_8$ requires: F, 71·0%; M, 214), $n_D^{20} < 1{\cdot}3$, b.p. 51°/752 mm (see below). The composition of the liquid mixture was determined by analytical scale VPC as 10:20:70% weight, in order of increasing retention time. Hydrolysis (NaOH) and distillation of the remaining reaction mixture gave $[(CF_3)_2CF{\cdot}CH_2CF_2]_2$ (3·5 g), $(CF_3)_2CF{\cdot}CH_2CHF_2$ (2 g) and the component thought to be *cis*-$(CF_3)_2CF{\cdot}CH{=}CHF$ (0·5 g).

Proof of structure of 1H,2H-*octafluoro-(3-methylbut-*cis*-1-ene)*

The ^{19}F resonance spectrum of the isomer having the longer retention time showed 3 groups of chemically shifted peaks, in intensity ratio 6:1:1, having chemical shifts: CF_3, +1·82; =CF, +32·6; and CF, +108·9 ppm respectively. Chemical shifts were measured from trifluoroacetic acid as external reference and positive values represent shifts to high field of the reference signal. These observed shifts are consistent with the structure $(CF_3)_2CF{\cdot}CH{=}CHF$. Also the ^{1}H spectrum contained a J_{HH} splitting of 5·9 c/s, a frequency which is of an order characteristic of *cis* H–H coupling in olefinic systems[19] e.g. in vinyl fluoride, the value J_{HH} *cis* is 4·7 c/s.[20]

The isomer with the shorter retention time gave an IR spectrum which was strikingly similar to the *cis* isomer and the ^{19}F resonance spectrum showed 3 groups of chemically shifted fluorine in the ratio 6:1:1 having shifts: CF_3, +2·47; =CF, 40·17; and CF, 108·67 ppm. A J_{HH} coupling of 11·3 c/s in the ^{1}H spectrum indicated that this component was the *trans* isomer of the olefin characterized above.

(8) *Fluorination of* $(CF_3)_2CF{\cdot}CH_2{\cdot}CF_2I$

Antimony trifluoride dichloride (35 g) was contained under dry nitrogen in a dry three-necked flask (250 ml) fitted with dropping funnel, mercury-seal stirrer and condenser leading directly to a cold trap (−78°). The iodide (15 g, 0·0415 mole) was added slowly and reaction occurred immediately, liberating iodine. After the reactants had been heated at reflux 1 hr, volatile material (9 g) remaining in the flask was swept into the cold trap in a stream of dry nitrogen. Analytical scale VPC showed that the product contained two components, one in excess. The principal component was separated by preparative scale VPC and identified as 2H,2H-*decafluoro-(3-methylbutane)*, $(CF_3)_2CF{\cdot}CH_2{\cdot}CF_3$ (Found: F, 75·1%; M, 247. $C_5H_2F_{10}$ requires: F, 75·4%; M, 252), b.p. 45°/770 mm, $n_D^{20} < 1{\cdot}3$.

Reactions of $(CF_3)_2CF{\cdot}CF_2CF_2I$

(1) *Coupling, using mercury and ultraviolet light.* The iodide (20 g, 0·051 mole) was sealed under vacuum in a thin-walled Pyrex tube (30 ml) with enough Hg to form a continuous pool when horizontal (60 g). The tube was rotated for 216 hr at a distance of 10 cm from a 500 watt UV lamp, the

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[19] T. Schaefer, *Canad. J. Chem.* **40,** 1 (1962).

[20] C. N. Banwell and N. Sheppard, *Proc. Roy. Soc.* **A263,** 136 (1962).

temp. in the region of the tube being about 80°. A colourless liquid (11·15 g) was distilled from the tube under vacuum and analytical scale VPC showed that it consisted of one major component (96·5%) and starting material (3·5%). Preparative scale VPC was used to isolate the main component which was shown to be $[(CF_3)_2CF{\cdot}CF_2{\cdot}CF_2]_2$ (Found F, 77·7%; M, 567. $C_{10}F_{22}$ requires: F, 77·7%; M, 538), b.p. 144·5°/771 mm, $n_D^{20} < 1{\cdot}3$.

(2) *Reduction using zinc and dilute sulphuric acid.* A three-necked flask (250 ml) fitted with mercury-seal stirrer, dropping funnel and 10 cm Vigreux column leading to a trap at −78° was charged with powdered Zn (50 g) and 5N H_2SO_4 (50 ml). The temp. of the flask was raised to 80° and the iodide (20 g, 0·05 mole) added over 15 min; immediate reaction occurred. After 30 min at 90–100° volatile material remaining in the flask was swept into the cold trap in a stream of nitrogen giving a crude product (10·25 g). Distillation through a 10 cm Vigreux column yielded a fraction (5·6 g) b.p. 30–40° and a residue (4·5 g). Analytical VPC showed that the volatile material consisted of mainly one component (96% purity) and this was isolated by preparative scale VPC and shown to be 1H-*undecafluoro*-(3-*methylbutane*) (Found: F, 76·4%; M, 271, $C_5F_{11}H$ requires: F, 77·5%; M, 270) (39% yield), $n_D^{20} < 1{\cdot}3$, b.p. 45·5 /777 mm.

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