point was reached by first cleaving the starting ester and then adding the reactant. Although the yields of the acid-soluble esters were limited by the equilibrium degree of conversion of the intermediates to product and varied from 5–73%, in some cases the equilibrium was upset by the precipitation of the product from solution. Esters such as 2,4,6-trichlorophenyl 3′,5′-dinitrobenzoate and terephthalate were insoluble to the extent that very little remained dissolved in the reaction solution. Introducing an excess of one reactant forced the reaction toward higher conversion to product in the normal manner of an equilibrium process.

In considering a mechanism for the transesterification reaction, experimental results do not indicate the actual reacting species in sulfuric acid solutions since there are a number of possible ionic reactants from the starting ester equilibrium and from the equilibria resulting from the introduced reactants. A possible mode of reaction involves an initial cleavage of the starting ester followed by formation of a new equilibrium system which favors the product ester, summarized in equations 1–4 for the alcoholysis reaction.

$$\mathrm{RCOOCH_3 + H_2SO_4 \rightleftarrows [RCOOCH_3]H^+ + HSO_4^-} \quad (1)$$

$$\mathrm{[RCOOCH_3]H^+ + H_2SO_4 \rightleftarrows [RCOOH]H^+ + CH_3OSO_3H} \quad (2)$$

$$\mathrm{[RCOOH]H^+ + R'OH \rightleftarrows [RCOOR']H^+ + H_2O} \quad (3)$$

$$\mathrm{[RCOOR']H^+ + HSO_4^- \rightleftarrows RCOOR' + H_2SO_4} \quad (4)$$

These equations are in agreement with the formation of product ester by either alcohol–ester, acid–ester or ester–ester interchange in which the common reactants are some form of the negatively substituted acid and alcohol. A principal factor which influences the extent of reaction is the weak basicity of the product ester relative to sulfuric acid, with the forward reaction represented in equation 3 favored. The protonation equilibrium of the product with sulfuric acid, equation 4, accounts for the formation of the un-ionized form which may or may not precipitate from solution. Otherwise the reaction would not proceed beyond ester cleavage represented by equations 1 and 2. This interpretation is consistent with the effect of electron-withdrawing substituents in the reactants, namely a decrease in basicity of the ester grouping with concomitant increase in stability toward sulfuric acid.

Acknowledgment.—We wish to acknowledge our indebtedness to Dr. J. I. Conley, whose work in a related reaction inspired this project, and to Dr. D. V. Sickman for many helpful suggestions.

Experimental

The preparation of 2,4,6-trichlorophenyl 4′-nitrobenzoate by alcoholysis of methyl 4-nitrobenzoate exemplifies the general method used for the ester interchange reactions in sulfuric acid solution:

Method A.—A solution of 1.81 g. (0.010 mole) of methyl 4-nitrobenzoate and 1.97 g. (0.010 mole) of 2,4,6-trichlorophenol in 16 g. of fuming sulfuric acid containing 0.008 mole of sulfur trioxide was heated 6 hours at 70°. (Alternatively, 2,4,6-trichlorophenyl acetate was heated for 30 minutes with 4-nitrobenzoic acid or for 6 hours with methyl 4-nitrobenzoate.) After cooling, the solution was poured onto ice and filtered. The crude wet product mixture was slurried with sodium carbonate solution for several hours, filtered, dried, and recrystallized from aqueous methanol. There was obtained 1.45 g., 42%, of 2,4,6-trichlorophenyl 4′-nitrobenzoate, m.p. 105–106°. This product proved to be identical to the ester obtained by metal halide catalysis of the reaction of 4-nitrobenzoyl chloride with 2,4,6-trichlorophenol[5] by lack of reduction in melting point when mixed and by identical infrared traces.

The same experiment was run using 32 g. of 4% fuming sulfuric acid instead of 16 g. The yield was reduced to 24%.

Method B.—A solution of 1.81 g. (0.010 mole) of methyl 4-nitrobenzoate in 16 g. of fuming sulfuric acid containing 0.008 mole of sulfur trioxide was heated at 70° for 6 hours, the required period for complete cleavage of the methyl 4-nitrobenzoate. To this solution was added 1.97 g. (0.010 mole) of 2,4,6-trichlorophenol and the resulting reaction solution was heated an additional 30 minutes. (Alternatively 2,4,6-trichlorophenyl acetate was heated 5 minutes, an acid added and the solution heated for 1 hour.) After cooling, the product was isolated as in method A. A yield of 1.38 g., 40%, of 2,4,6-trichlorophenyl 4′-nitrobenzoate, m.p. 105–106°, was obtained.

The results of other reactions are summarized in Table I which also contains elemental analyses of new compounds.

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[5] M. E. Hill, THIS JOURNAL, **76**, 2329 (1954).

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

Novel Elimination Reactions of Telomer Iodides of 1,1-Difluoroethylene[1]

BY MURRAY HAUPTSCHEIN AND ROBERT E. OESTERLING

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Telomer iodides having $-\mathrm{CF_2CH_2CF_2I}$ end groups have been found to undergo dehydroiodination preferentially when treated with a wide variety of strong and weak bases and nucleophiles. Only the relatively non-basic halide ion nucleophiles have been shown to produce the dehydroiodination product $\mathrm{—CF_2CH{=}CF_2}$ exclusively. Lithium chloride in dimethylformamide, in particular, gave high conversions in a rapid and selective elimination reaction, and the synthesis of a series of the olefins $\mathrm{R}_f(\mathrm{CH_2CF_2})_n\mathrm{CH{=}CF_2}$ is described. The preparations of some of the related chlorides and fluorides $\mathrm{R}_f(\mathrm{CH_2CF_2})_n\mathrm{X}$ where X = Cl or F are reported.

During the course of investigations on ultraviolet-catalyzed chlorinations of telomer iodides of 1,1-difluoroethylene[2]; *i.e.*, $\mathrm{R}_f(\mathrm{CH_2CF_2})_n\mathrm{I}$ where R_f = perfluoroalkyl and $n = 1–10$, the reaction products were found to be contaminated with olefinic by-products. Thus, when $\mathrm{C_3F_7CH_2CF_2I}$ was chlorinated at room temperature in the presence of ultraviolet irradiation, the organic products were

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[1] Presented at the 136th Meeting of the American Chemical Society, Atlantic City, N. J., September, 1959.

[2] M. Hauptschein, M. Braid and F. E. Lawlor, THIS JOURNAL, **80**, 846 (1958). It should be noted that substitution chlorination of hydrogen atoms does not occur under the present conditions; iodine replacement by chlorine is much more energetically favored.

shown to consist of 15 mole % of the olefin $C_3F_7CH{=}CF_2$, in addition to 85 mole % of the expected chlorination product $C_3F_7CH_2CF_2Cl$. On the other hand, if these chlorinations were carried out thermally at 160–180° so that the iodine chlorides produced were removed in the vapor phase from the reaction zone after only very short contact with the telomer iodides, olefinic impurities were reduced to negligible amounts.[3] Evidence that iodine monochloride actually caused dehydrohalogenation was obtained independently in a reaction with $R_f(CH_2CF_2)_nI$ by the appearance of absorption bands in the infrared spectra of the products at 5.7 μ (corresponding to the $—CH{=}CF_2$ group). The suspected influence of chloride ions in effecting dehydrohalogenation reactions was dramatically confirmed when nearly quantitative conversions to $CF_3CH{=}CF_2$ with none of the chlorination product $CF_3CH_2CF_2Cl$ resulted from the reaction of $CF_3CH_2CF_2I$ with excess lithium chloride in dimethylformamide (DMF) or dimethyl sulfoxide at 100 to 150°. Similar results were obtained with other members of the $R_f(CH_2CF_2)_nI$ telomer series.

As a result of these findings, probing experiments were designed to study the action of various nucleophilic reagents on these iodides. In a series of comparative tests carried out at 100° for ten minutes using DMF[4] as the solvent, $CF_3CF_2CF_2CH_2CF_2I$ was demonstrated to react with lithium chloride, potassium fluoride, sodium bromide, iodine monochloride, potassium hydroxide, ammonia, sodium 2,2,2-trifluoroethoxide, sodium cyanide, sodium nitrite and sodium thiophenoxide to produce the elimination product $CF_3CF_2CF_2CH{=}CF_2$. Of particular interest was the fact that only the halides, lithium chloride, potassium fluoride, sodium bromide and iodine monochloride gave clean-cut dehydroiodinations to produce $C_3F_7CH{=}CF_2$ as the sole product. All of the other reactions resulted in some loss of fluoride ion, representing either direct dehydrofluorination or substitution reactions followed by hydrolysis and loss of hydrogen fluoride. For example, the sodium nitrite reaction resulted mostly in dehydroiodination, but some carboxylic acid $C_3F_7CH_2COOH$ was formed *via* a $C_3F_7CH_2CF_2ONO + H_2O$ reaction (*vide infra*). It is interesting to note that in contrast to the sodium nitrite reaction a silver nitrite reaction in DMF gave little elimination, if any; instead evidence was obtained that the reaction

$$\begin{aligned} &C_3F_7CH_2CF_2I + AgONO \longrightarrow \\ &\qquad C_3F_7CH_2CF_2ONO + H_2O \longrightarrow \\ &\qquad\qquad [C_3F_7CH_2CF_2OH] \longrightarrow C_3F_7CH_2COOH \end{aligned}$$

predominates.

Various preliminary experiments indicated that sodium and potassium chloride in dimethyl sulfoxide, DMF, and in other solvents will cause dehydroiodination of these telomer iodides. The recommended route to olefins of the type $—CF_2CH{=}CF_2$ from telomer iodides of the type $—CF_2CH_2CF_2I$ is by reaction with lithium chloride[5] in DMF.

$$CF_3CH_2CF_2I + LiCl \xrightarrow{DMF} CF_3CH{=}CF_2 + HCl + LiI$$

This reaction is rapid and selective producing only the dehydroiodination product in essentially quantitative conversion.

The conventional dehydrohalogenation procedures for fluorinated alkyl halides involved the use of strong bases such as aqueous or alcoholic alkali. For example, Henne and Waalkes[6] reported that $CF_3CH_2CF_2Cl$ reacts with alcoholic potassium hydroxide to give a 65% yield of $CF_3CH{=}CF_2$ and also reacts intermolecularly to produce condensation products. A comparable reaction with $CF_3CH_2CF_2I$ and alcoholic potassium hydroxide at reflux for two hours gave only a 50% conversion to the olefin. The infrared spectrum of the product of the reaction of $C_3F_7CH_2CF_2I$ with potassium hydroxide in DMF showed a strong absorption band at 5.82 μ[7] in addition to the band at 5.7 μ assigned to the $—CH{=}CF_2$ structure in $C_3F_7CH{=}CF_2$.

The novel olefins prepared by the action of lithium chloride in DMF on the telomer iodides $R_f(CH_2CF_2)_nI$ include $C_3F_7(CH_2CF_2)_nCH{=}CF_2$ where $n = 0,1$ and $CF_3(CH_2CF_2)_nCH{=}CF_2$ where $n = 1,2$. The characteristic infrared absorption maxima of the series of olefins are presented in Table I.

After the discovery of this efficient elimination reaction of the telomer iodides involving chloride ion as the attacking reagent, examination of the literature revealed reports on dehydrohalogenations of certain cyclic halides such as 4-halo-3-ketosteroids[8] and chloro-methylcyclohexanones[9] with lithium chloride in DMF. As a possible mechanism Holysz[8] proposed a transition state involving the halo-ketosteroid, lithium chloride and DMF in a six-membered ring orientation and simultaneous bond cleavage and bond formation to give the olefinic product. Winstein, *et al.*,[10] suggested a merged bimolecular substitution and elimination mechanism for the reaction of 4-*t*-butylcyclohexyl toluenesulfonate with lithium bromide in acetone to give both substitution and elimination products. These investigators proposed a transition state similar to that for the usual nucleophilic displacement which leads either to the normal S_N2 substitution product or to an olefin by a process which disengages a β-proton and both the incoming and outgoing nucleophiles.

The rapid and selective β-elimination of HI from a $—CF_2CH_2CF_2I$ system to form the $—CF_2-$

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(3) M. Hauptschein and M. Braid, forthcoming publication.

(4) Under these experimental conditions no appreciable interaction occurred between DMF and $C_3F_7CH_2CF_2I$. At 153° for several hours, however, elimination reactions occurred in very low conversions, the product of which showed weak peaks at 5.7 and 5.82 μ in the infrared. N. Kornblum and R. K. Blackwood, THIS JOURNAL, **78**, 4037 (1956), reported the slow dehydrohalogenation of alkyl bromides with DMF at room temperature and suggested the possibility that *cis* elimination occurs, involving a cyclic transition state. In addition, these investigators stated that DMF also induces nucleophilic displacements in alkyl halides presumably resulting in salt formation.

(5) The potassium fluoride–DMF reaction also gives excellent yields of the desired olefins but hydrogen fluoride, rather than hydrogen chloride, is the other product of the reaction.

(6) A. L. Henne and T. P. Waalkes, THIS JOURNAL, **68**, 496 (1946).

(7) As noted previously, fluoride ion was formed in this reaction. It is possible that this peak belongs to that of the dehydrofluorination product $C_3F_7CH{=}CFI$.

(8) R. R. Holysz, THIS JOURNAL, **75**, 4432 (1953).

(9) E. M. Warnhoff, D. G. Martin and W. S. Johnson, *Org. Syntheses*, **37**, 8 (1957).

(10) S. Winstein, D. Darwish and N. J. Holness, THIS JOURNAL, **78**, 2915 (1956).

TABLE I

INFRARED ABSORPTION SPECTRA, WAVE LENGTHS IN MICRONS

vw, very weak; w, weak; m, medium; s, strong; vs, very strong

$C_3F_7CH_2CF_2I$				7.02w	7.24m	7.36s	7.82s	8.06vs	8.25s	8.41s	
$C_3F_7CF_2CH_2I$				7.03w		7.38m	7.71m	8.00vs		8.43m	
$C_3F_7CH_2CF_2Cl$	3.30vw			6.98m	7.18s	7.35s	7.79s	8.02vs	8.24s	8.37s	8.59m
$C_3F_7CH_2CF_3$	3.37vw			7.12s		7.35s	7.69s	7.99vs			8.50s
$C_3F_7CH_2CF_2CH_2CF_3$	3.32vw	3.37vw		7.16s		7.37s		7.91s	8.09vs	8.45vs	
$CF_3(CH_2CF_2)_2CH_2CF_2Cl$	3.34vw			7.18s				7.93s	8.20s	8.43vs	
$CF_3CH{=}CF_2$	3.25vw		5.68vs		7.23s		7.75m	7.96s			8.66vs
$CF_3CH_2CF_2CH{=}CF_2$	3.25vw		5.70vs	7.02m	7.22vs		7.82s	7.93s	8.08s		8.63vs
$CF_3(CH_2CF_2)_2CH{=}CF_2$	3.20vw		5.68vs	6.98s	7.12vs	7.30s	7.64s	7.82s	8.15vs		8.53vs
$C_3F_7CH{=}CF_2$	3.18vw		5.70vs		7.23s	7.40m		7.99s	8.13s	8.39s	
$C_3F_7CH_2CF_2CH{=}CF_2$	3.26vw		5.70vs	7.01w	7.24s	7.38s	7.63m	7.71s	8.11vs	8.29s	8.47s

$CH{=}CF_2$ olefin is, of course, facilitated by the acidic hydrogens present (due to the adjacent electron-withdrawing fluorinated clusters). It is thus conceivable that the mechanism of the reaction involves a straightforward E2 elimination even by a relatively non-basic halide ion nucleophile. The development of a transitory deep color during the reaction (see Experimental), however, lends support to an initial transition state (complex) ascribed to SN2 displacements as proposed by Winstein and co-workers,[10] but which due to the strong electronic effects of the fluorine atoms results essentially entirely in facile elimination as the final step.

Since attempted displacements of the iodine in $R_fCH_2CF_2I$ by fluorine using potassium fluoride in DMF or dimethyl sulfoxide resulted instead in elimination, fluorination with antimony dichlorotrifluoride was tried and afforded good yields of the desired fluoride $R_fCH_2CF_3$ without accompanying elimination. The characteristic infrared absorption bands of some new fluorides and chlorides are included in Table I.

Experimental

2H,2H-1-Iodononafluoropentane and 1H,1H-1-Iodononafluoropentane.—Thermal telomerization of 1,1-difluoroethylene with 1-iodoperfluoropropane according to the method of Hauptschein, *et al.*,[2] gave the following telomer iodides: $C_3F_7CH_2CF_2I$, b.p. 63° (146 mm.), and $C_3F_7(CH_2CF_2)_2I$, b.p. 79° (45 mm.).

Analysis of the former by vapor-liquid partition chromatography (VLPC) using a 2-meter Perkin-Elmer "B" column at 76° and 30 p.s.i.g. helium pressure showed 95 mole per cent. of $C_3F_7CH_2CF_2I$, elution time 13.1 min., and 5 mole per cent. of $C_3F_7CF_2CH_2I$ at 14.8 min; air elution time was 0.6 min. The ultraviolet λ_{max} in isoöctane for $C_3F_7CH_2CF_2I$ was 272 mμ, and for $C_3F_7CF_2CH_2I$ 265 mμ, in agreement with the λ_{max} for CF_3CH_2I at 262 mμ.

The same column at 132° showed only one component for the $C_3F_7(CH_2CF_2)_2I$; elution time, 14.5 min; air, 0.5 min; λ_{max} in isoöctane, 270 mμ.

2H,2H-Decafluoropentane.—Ten grams (0.028 mole) of $C_3F_7CH_2CF_2I$ was added dropwise with stirring to 7 g. (0.028 mole) of antimony dichlorotrifluoride at room temperature in a flask fitted with a short, packed column and distillation head. Heat of reaction caused a temperature rise to 50–60°. The mixture was stirred for 30 minutes and heated to distil the fluorinated product. The latter was washed with dilute sodium bisulfite solution, dried over anhydrous magnesium sulfate and redistilled to give 5 g. (71%) of 2H,2H-decafluoropentane $CF_3CF_2CF_2CH_2CF_3$, a colorless liquid, b.p. 47°; VLPC analysis of the distillate showed 99.5 mole per cent. purity.

Anal. Calcd. for $C_5H_2F_{10}$: C, 23.8; H, 0.79. Found: C, 23.9; H, 1.20.

2H,2H-1-Chlorononafluoropentane.—Chlorine gas was passed through 23 g. (0.064 mole) of $C_3F_7CH_2CF_2I$ at room temperature in a quartz tube illuminated with a Hanovia SH ultraviolet lamp. A dense, dark layer of liquid iodine monochloride was formed and, after two hours, the mixture was poured over ice and water. The organic layer was separated, washed with aqueous sodium bisulfite solution, then with water, and dried over anhydrous magnesium sulfate. The crude product, 13.5 g., was distilled to give a main fraction, 10.8 g. (63%), b.p. 68–70°; VLPC analysis of this product using a 2-meter Perkin-Elmer "B" column at 30° and a helium pressure of 30 p.s.i.g. showed two components: 15 mole per cent. of $C_3F_7CH{=}CF_2$, the infrared spectrum of which was identical to that of the authentic sample prepared below, and 85 mole per cent. of $C_3F_7CH_2CF_2Cl$. Respective elution times for air, $C_3F_7CH{=}CF_2$ and $C_3F_7CH_2CF_2Cl$ were 0.5 min., 1.2 min. and 8.6 min. Fractional distillation gave the pure colorless liquid, $C_3F_7CH_2CF_2Cl$, b.p. 70°.

Anal. Calcd. for $C_5H_2ClF_9$: C, 22.4; H, 0.75. Found: C, 22.5; H, 1.34.

2H,2H,4H,4H-Dodecafluoroheptane.—By the above procedure 21.2 g. (0.05 mole) of $C_3F_7(CH_2CF_2)_2I$ was fluorinated with 12.5 g. (0.05 mole) of SbF_3Cl_2 and distilled to give 14.3 g. (90% yield) of $C_3F_7(CH_2CF_2)_2F$, b.p. 102°; VLPC showed 99.2 mole per cent. purity for the product.

Anal. Calcd. for $C_7H_4F_{12}$: C, 26.6; H, 1.26. Found: C, 26.8; H, 1.38.

General Procedure for Synthesis of Olefins from Vinylidene Fluoride Telomer Iodides.—A mixture of 0.1 mole of the telomer iodide, *e.g.*, 36 g. of 2H,2H-1-iodononafluoropentane with 6.3 g. (0.15 mole) of lithium chloride in 50 ml. of DMF[11] was placed in a 250-ml. flask fitted with a stirrer, thermometer well and short distilling column leading directly to a trap cooled to −78°. The reaction temperature was gradually raised to 155° over a period of 2 hours, then held at this temperature for 30 minutes to 1 hour longer. Shortly after heating was started (50–60°) the reaction mixture became a dark reddish-brown color, and at 100° distillation of olefin from the mixture was evident. When the distillation of the olefin from the reaction mixture was complete the deep color had reverted to pale yellow. The product collected in the cold trap was washed with sodium carbonate solution, dried over anhydrous magnesium sulfate and distilled. 2H-Nonafluoro-1-pentene, $C_3F_7CH{=}CF_2$, was obtained in 91% yield (21 g.) as a colorless liquid, b.p. 37°., shown to be 99 mole per cent. pure by VLPC.

Anal. Calcd. for C_5HF_9: C, 25.9; H, 0.44. Found: C, 25.5; H, 0.54.

A similar procedure using dimethyl sulfoxide as the solvent gave approximately 90% yield of the same olefin; however, VLPC analysis showed this product to be contaminated with 2% of dimethyl sulfide, b.p. 26°.

2H,4H,4H-Undecafluoro-1-heptene.—By the same procedure using $C_3F_7(CH_2CF_2)_2I$ the olefin $C_3F_7CH_2CF_2CH{=}CF_2$ was prepared in 90% yield as a colorless liquid, b.p. 93°.

Anal. Calcd. for $C_7H_3F_{11}$: C, 28.4; H, 1.02. Found: C, 28.8; H, 1.10.

2H-Pentafluoropropene.[6]—The procedure using lithium chloride in DMF gave $CF_3CH{=}CF_2$ from $CF_3CH_2CF_2I$ in 94% yield. When this iodide was refluxed for 2 hours with alcoholic potassium hydroxide dehydrohalogenation solution, only 50% conversion to the olefin was effected.

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[11] In all cases it was considered desirable to use sufficient DMF to dissolve the lithium chloride completely at the reaction temperatures used. Although the solubility was not precisely determined, it was found that a concentration greater than 10% by weight of lithium chloride dissolved readily at 100°, and the solubility appeared to be much higher than this at the boiling point of DMF, 153°.

8.86w	9.05m		9.33m		10.0w	10.2m	10.3m	10.6s	11.2w	12.1w	13.2w	13.5m		14.9w
8.80s			9.45m	9.75m				10.7w	11.3m	11.6m		13.8m		
8.82s		9.27m		9.89m			10.3m		11.2w	12.3w		13.5m	14.3w	14.7m
	9.12m						10.3m	10.5w	11.0w	11.9w	12.4m	13.4m		15+w
8.89s	9.05s			9.75w			10.4m	10.6m		11.6m	12.2w	13.4w	13.6w	14.6w
8.85s	9.09s						10.4m	10.5m	11.0m	11.2m	12.0w	13.3w	13.6w	14.6m
8.90vs		9.32m		9.70w			10.3m	10.5m	11.4vw	12.8vw	12.9vw	13.4w	14.1w	14.2w
		9.20m	9.65w				10.4m	11.1w	11.5w	12.8vw		13.7vw	14.4w	14.8w
	9.07s						10.5s	11.2w	11.6w	11.8w	12.8vw	13.3vw	13.9vw	14.6w
8.91s	9.21m				10.0s		10.8s	11.2m			12.3m	12.9w	13.7m	14.9w
8.85s	9.22m		9.55m				10.3s	11.2m		11.8w	12.5m	12.7m	13.5s	14.8w

2H,4H,4H-Heptafluoro-1-pentene.—Using the lithium chloride–DMF procedure, $CF_3(CH_2CF_2)_2I$ gave 74% yield of the pure colorless liquid, $CF_3CH_2CF_2CH{=}CF_2$, b.p. 58°.

Anal. Calcd. for $C_5H_3F_7$: C, 30.6; H, 1.54. Found: C, 30.9; H, 1.68.

2H,4H,4H,6H,6H-Nonafluoro-1-heptene.—Similarly, the $CF_3(CH_2CF_2)_3I$ reaction with lithium chloride in dimethylformamide at 140–150° for 2.5 hr. gave only 30% conversion to the olefin, $CF_3(CH_2CF_2)_2CH{=}CF_2$, b.p. 120°.

Anal. Calcd. for $C_7H_5F_9$: C, 32.3; H, 1.94; F, 65.7. Found: C, 32.3; H, 2.13; F, 65.6.

Also obtained in 50% conversion from this reaction was the chloride, apparently formed by addition of the product hydrogen chloride to the olefin. Vacuum distillation gave the colorless liquid, $CF_3(CH_2CF_2)_3Cl$, b.p. 80° (47 mm.).

Anal. Calcd. for $C_7H_6ClF_9$: C, 28.3; H, 2.04; Cl, 11.96. Found: C, 28.5; H, 2.05; Cl, 11.81.

This experiment was repeated using a reflux condenser so that none of the product distilled from the reaction mixture. After heating at 140–150° for 8 hr. the mixture was diluted with water, separated, dried, and distilled. None of the olefin (above) was obtained and only the chloride $CF_3(CH_2CF_2)_3Cl$ was found in 60% yield.

It is therefore probable that conversions to the elimination product could be increased by shorter reaction times in higher boiling solvents under reduced pressures in order to remove the olefin from the reaction zone.

Elimination Reactions of $C_3F_7CH_2CF_2I$ with Various Reagents.—The iodide $C_3F_7CH_2CF_2I$ was treated with a variety of nucleophilic, alkaline and metal halide reagents. In general, the iodide was mixed with each reagent in DMF and heated to 100° for 10 minutes. The mixture was diluted with water and the organic layer was separated and dried over anhydrous magnesium sulfate. Estimation of the extent of elimination reaction was made by infrared analysis of the products. The aqueous layer was acidified with acetic acid and tested for fluoride ion with cerous nitrate solution. The infrared spectra all contained the carbon-carbon double bond absorption at 5.7 μ assigned to $C_3F_7CH{=}CF_2$, and only the inorganic halide reactions, LiCl, NaBr and ICl, showed no fluoride ion present in the aqueous layer. All of the other reagents gave positive fluoride ion tests.

The results are summarized below to show in order the reagent, the relative intensity of the 5.7 μ double bond absorption band and the fluoride ion test result: lithium chloride, very strong, negative; potassium fluoride, very strong; sodium bromide, moderate, negative; iodine monochloride, moderate, negative; potassium hydroxide, strong, positive: ammonia,[12] weak, positive; sodium trifluoroethoxide,[13] strong, positive; sodium cyanide, moderate, positive; sodium nitrite, moderate, positive; sodium thiophenoxide, weak, positive.

Reaction of $C_3F_7(CH_2CF_2)_nI$ with Silver Nitrite.—Silver nitrite in ether under reflux for 6 hours failed to react with $C_3F_7(CH_2CF_2)_2I$.

A mixture of 23 g. (0.054 mole) of the iodide in 50 ml. of DMF with 12.3 g. (0.08 mole) of silver nitrite was stirred at 100° for 2 hours. The reaction mixture was then diluted with water and steam distilled to give 8.5 g. of pale yellow oil. Vacuum distillation gave 6.0 g. of a colorless acidic liquid, b.p. 80° (3 mm.), for which the infrared spectrum was consistent with the structure $C_3F_7CH_2CF_2CH_2COOH$ showing a strong carbonyl absorption at 5.79 μ and bonded-OH absorption between 3 and 3.8 μ, in addition to the intense absorption 8–9 μ characteristic of C–F stretching vibrations. No products containing nitro groups were found.

A similar reaction of $C_3F_7CH_2CF_2I$ with silver nitrite in DMF gave only a small amount of the corresponding acid with considerable unreacted iodide.

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[12] This reaction was carried out at 35° for 2 hours in the absence of DMF.

[13] This reaction was carried out at 35° for 2 hours with trifluoroethanol as the solvent.