re-dried. The β-acetylacrylic acid,[20] γ,γ,γ-trichlorocrotonic acid,[21] β-chloroacrylic acid[22] and γ,γ-dichlorocrotonic acid[23] were prepared by methods described in the literature. The other materials used were of the best commercially available grade, purified until their m.p.'s agreed with those in the literature.

Stereochemistry of the Acrylic Acids.—The *trans* nature of fumaric acid is too well known to require comment. The crotonic acid isomer that we used (m.p. 72°) has also been fairly convincingly shown to be *trans*,[24] by an argument that also supports the *trans* structural assignment for the γ,γ-dichlorocrotonic acid and the γ,γ,γ-trichlorocrotonic acids that we used. Backer and Beute[22] have given the evidence for the structure of *trans*-β-chloropropionic acid which includes its higher melting point, lower acidity and lower solubility. According to Shaw, the ultraviolet spectrum of solutions of β-acetylacrylic acid is like that of an α,β-unsaturated lactone, showing that the compound must exist almost entirely as the pseudo acid.[11] The nitroacrylic acid used was kindly supplied for us by Dr. Lloyd A. Kaplan of the Naval Ordnance Laboratory.

Technique of Rate Determination.—The technique used in carrying out the rate determination is most easily described in terms of a representative sample.[25]

To about 40 ml. of absolute ethanol in a 50-ml. volumetric flask was added 0.9855 g. of γ,γ,γ-trichlorocrotonic acid. This solution was placed in a 30° thermostated bath with an ethanolic solution about 0.035 M in diphenyldiazomethane and a number of 25-ml. low-actinic volumetric flasks. When thermal equilibrium had been reached the acid solution was brought up to 50 ml. with ethanol at 30°. Then 2.00 ml. of the diphenyldiazomethane solution, 5.00 ml. of ethanol and 3.00 ml. of trichlorocrotonic acid solution was pipetted into a 25-ml. flask, where the solutions were mixed and transferred immediately to a thermostated cell in the Beckman DU spectrophotometer. From 15 to 30 seconds elapsed between the start of acid addition and the initial optical density reading (at 525 μ). The time of this reading was defined as "zero" time and subsequent readings were taken during at least two half-lives of the reaction. A plot of time *vs.* the logarithms of the optical density readings (including any necessary cell correction) is shown in Fig. 4. The second-order rate was calculated from the slope of this line and the trichlorocrotonic acid concentration.

Acknowledgments.—We wish to acknowledge with gratitute our indebtedness to the Department of the Navy, Bureau of Ordnance, for support of this work; to Dr. Lloyd A. Kaplan for preparing and supplying us with many of the compounds used in this study and for useful discussions of the problems involved in their use. We also wish to thank Dr. D. V. Sickman, Dr. M. J. Kamlet and other members of the staff of the Chemistry Research Department of the U. S. Naval Ordnance Laboratory for intellectual and material assistance during the course of this investigation.

ATLANTA, GA.

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[20] W. G. Overend, L. M. Turton and L. F. Wiggins, *J. Chem. Soc.*, 3500 (1950).

[21] K. von Auwers, *Ber.*, **56B**, 715, 731 (1923).

[22] H. J. Backer and A. E. Beute, *Rec. trav. chim.*, **54**, 167 (1935).

[23] G. Braun, THIS JOURNAL, **52**, 3167 (1930).

[24] *Cf.* E. H. Rodd, "Chemistry of Carbon Compounds," Elsevier Publishing Co., Houston, Tex., Vol. IA, p. 632.

[25] *Cf.* J. D. Roberts and W. T. Moreland, THIS JOURNAL, **75**, 2167 (1953).

[CONTRIBUTION FROM BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

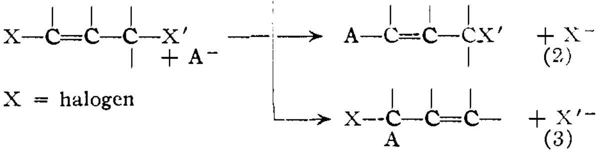
Substitution and Addition Reactions of the Fluoroölefins. III.[1] SN2′ Substitution Reactions of Chlorofluoroallyl Chlorides with Halide Ions[2]

BY JOHN H. FRIED AND WILLIAM T. MILLER, JR.

RECEIVED AUGUST 22, 1958

The synthesis of 3,3-dichloro-1,1,3-trifluoropropene and 3,3-dichlorotetrafluoropropene is reported. Both compounds were shown to undergo substitution reactions readily with fluoride, chloride and iodide ions. In all cases only rearranged products were obtained corresponding to the SN2′ type mechanism. The order of nucleophilic reactivity for the halide ions with the above fluoropropenes was shown to be $F^- > Cl^- > I^-$ the reverse of the order for SN2 reactions. The observed order is discussed in terms of the extended SN2′ transition state. Attention is drawn to the great importance to carbon-fluorine chemistry of the high order of nucleophilic reactivity shown by fluoride ion with the fluoroölefins.

Three typical products may be formed by reaction of a nucleophilic anion, A^-, with a fluorinated olefin in solution. These correspond to: (1) addition of HA in the presence of HA or other source of protons, (2) substitution of vinyl halogen, and (3) substitution of allyl halogen.[3] All three type reactions have now been shown to take place with halide ions. For example, 1,1-difluorohaloethylenes and -propenes add HX under mild conditions in the presence of a proton donor.[4] Substitution of vinyl halogen has been shown to take place with olefins of the type $CFX{=}\overset{|}{C}CF_3$.[7] Olefins of the



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[1] This paper is a continuation of the series previously entitled, "Preferential Replacement Reactions of Highly Fluorinated Alkyl Halides"; preceding paper, A. H. Fainberg and W. T. Miller, Jr., THIS JOURNAL, **79**, 4170 (1957).

[2] Presented at the 130th Meeting of the American Chemical Society, Atlantic City, N. J., September, 1956, Abstracts of Papers, p. 18M. Based on the thesis submitted by John H. Fried to the Graduate School of Cornell University in partial fulfillment of the requirements for the Ph.D. degree, June, 1955.

[3] M. D. Hurwitz and W. T. Miller, Jr., Abstracts of Papers, 114th Meeting, Amer. Chem. Soc., Washington, D. C., August, 1948, p. 4L.

[4] The addition of HF to fluoroölefins is brought about by reaction with potassium fluoride in formamide.[5] The addition of HCl, HBr and HI occurs readily in acetic acid solution. The addition of HF occurs with difficulty in acetic acid solution due presumably to the formation of relatively unreactive the HF_2^- ion.[6]

[5] W. T. Miller, Jr., and John Fried, Abstracts of Papers, 132nd Meeting, Amer. Chem. Soc., New York, N. Y., September, 1957, p. 29M.

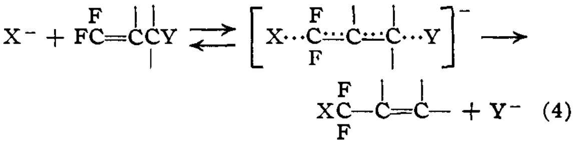
[6] W. T. Miller, Jr., and H. F. Koch, unpublished work.

[7] For example, substitution of the chlorine in $CClF{=}CFCF_3$ takes place on reaction with potassium fluoride in formamide.[5]

type $CF_2{=}\overset{|}{C}CX_3$ in which at least one X is a halogen other than fluorine undergo preferential substitution of such allylic halogen with great ease.[8,9]

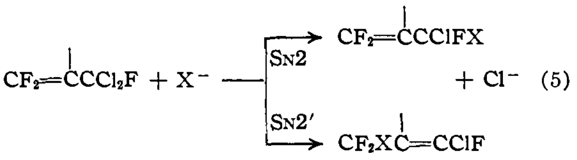
The present paper presents the results of an experimental test of the mechanism of substitution of allylic halogen in fluorochloroölefins (reaction 3). Reactions of this type have been considered to take place with rearrangement by the SN2′ mechanism principally on the basis of the observed clean-cut effects of structure upon reactivity. For example, $CF_2{=}CFCClF_2$ and $CF_2{=}CClCClF_2$ react readily with sodium iodide in acetone to yield the substitution products, $CF_2{=}CFCF_2I$ and $CF_2{=}CClCF_2I$. On the other hand, $CCl_2{=}CClCClF_2$ and $CClF{=}CFCClF_2$ are inert under the same conditions. Since these olefins have substantially the same environment around the α-carbon atoms as $CF_2{=}CFCClF_2$ and $CF_2{=}CClCClF_2$, their lack of reaction furnished evidence against the SN1 and SN2 substitution mechanisms with reaction initiated at the α-carbon atoms.[8,9]

The decisive structural difference of these fluoroolefins resides in the terminal vinyl carbon atom. Olefins possessing a terminal difluoromethylene group react easily, whereas those with a chlorofluoromethylene or dichloromethylene group do not. The same structural requirement applies to the base-catalyzed addition reactions of the fluoroperhaloethylenes.[10] These considerations pointed to the conclusion that the substitution reactions of the fluoroallyl halides occur by an SN2′ type mechanism involving attack by a nucleophile at the difluoromethylene group rather than at the saturated carbon atom holding the group displaced.[3,8,9] Additional support for this general picture[12] was furnished by the lack of reactivity found for phenylchlorodifluoromethane toward iodide ion in acetone[8] and by kinetic results showing the dependence of rate upon reagent concentration.[13]



$$X^- + F\overset{F}{C}{=}\overset{|}{C}\underset{|}{\overset{|}{C}}Y \rightleftarrows \left[X\cdots\underset{F}{\overset{F}{C}}\cdots\overset{|}{C}\cdots\underset{|}{\overset{|}{C}}\cdots Y\right]^- \longrightarrow X\underset{F}{\overset{F}{C}}-\overset{|}{C}{=}\overset{|}{C}- + Y^- \tag{4}$$

The purpose of the present work was to test further the operation of the SN2′ mechanism by examining the structure of substitution products for rearrangement. This could not be done for the cases cited above since the allylic halides utilized would yield the same products by the SN1, SN2 or SN2′ substitution mechanisms. Other reactive allylic halides which would yield distinguishable products were not available. Accordingly, two new fluoroallyl chlorides, 3,3-dichloro-1,1,3-trifluoropropene and 3,3-dichlorotetrafluoropropene, were synthesized and their reactions studied with fluoride, chloride and iodide ions. Both these olefins possess the difluoromethylene terminal group and their rearranged substitution products corresponding to an SN2′ type reaction are structurally different from those which would be formed by substitution without rearrangement by an SN2 type mechanism.



$$CF_2{=}\overset{|}{C}CCl_2F + X^- \begin{cases} \xrightarrow{\mathrm{S_N2}} CF_2{=}\overset{|}{C}CClFX \\ \xrightarrow{\mathrm{S_N2'}} CF_2X\overset{|}{C}{=}CClF \end{cases} + Cl^- \tag{5}$$

The desired olefins were prepared by the free-radical addition of dichlorofluoroiodomethane to 1,1-difluoroethylene and to trifluoroethylene followed by dehydrohalogenation of the addition products. The addition of free radicals to terminal olefins usually leads to one of the two possible isomers exclusively.[14] This type of behavior was found for 1,1-difluoroethylene, which gave an addition product with a freezing range of less than 0.2°. The reactions of other halogenated free radicals with difluoroethylene also have yielded only products corresponding to initial attack at the $CH_2{=}$ carbon.[15] On the other hand, trifluoroethylene represented an unusual type olefin and yielded a mixture of two isomeric addition products. The major isomer was the expected 1,1-dichloro-1,2,3,3-tetrafluoro-3-iodopropane, corresponding to the preferential addition of the dichlorofluoromethyl radical to the least hindered carbon of the trifluoroethylene, as shown by dehalogenation with potassium hydroxide. The other isomer, CCl_2FCF_2CHFI, did not dehalogenate under the conditions utilized.[16] The addition products $CCl_2FCH_2CF_2I$ and $CCl_2FCHFCF_2I$ both yielded a mixture of propenes corresponding to the loss of HI and HCl in the ratio of about five to one.

$$CCl_2FI + CH_2{=}CF_2 \xrightarrow[\text{peroxide}]{\text{benzoyl}} CCl_2FCH_2CF_2I \tag{6}$$

$$CCl_2FCH_2CF_2I \xrightarrow{\text{KOH}} CCl_2FCH{=}CF_2 + CClF{=}CHCF_2I \tag{7}$$

$$CCl_2FI + CHF{=}CF_2 \xrightarrow[\text{peroxide}]{\text{benzoyl}} CCl_2FCHFCF_2I + CCl_2FCF_2CHFI \tag{8}$$

$$CCl_2FCHFCF_2I \xrightarrow{\text{KOH}} CCl_2FCF{=}CF_2 + CClF{=}CFCF_2I \tag{9}$$

The structures of the propenes $CCl_2FCH{=}CF_2$ and $CCl_2FCF{=}CF_2$ were based on the methods of

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[8] W. T. Miller, Jr., and A. H. Fainberg, THIS JOURNAL, **79**, 4164 (1957).

[9] A. H. Fainberg and W. T. Miller, Jr., *ibid.*, **79**, 4170 (1957).

[10] See ref. 8 for a summary. The mechanism of addition involves the formation of an intermediate carbanion.[11]

[11] W. T. Miller, Jr., E. W. Fager and P. H. Griswold, THIS JOURNAL, **70**, 431 (1948).

[12] While the possible formation of an intermediate anion must be considered, available experimental evidence is consistent with the conclusion that in all cases reaction 3 proceeds preferentially through a lower energy SN2′ transition state. Substitution of α-halogen, other than fluorine, appears to occur exclusively before the addition of HA (1) in protogenic solvents. Similar evidence indicates that the substitution of vinyl halogen (2) also proceeds through a single transition state.

[13] M. Gazith and W. T. Miller, Jr., Abstracts of Papers, 130th Meeting Amer. Chem. Soc., Atlantic City, N. J., Sept., 1956, p. 17M.

[14] F. R. Mayo and C. Walling, *Chem. Revs.*, **27**, 351 (1940).

[15] R. N. Haszeldine and B. R. Steel, *J. Chem. Soc.*, 923 (1954); P. Tarrant, A. M. Lovelace and M. R. Lilyquist, THIS JOURNAL, **77**, 769, 2783 (1955).

[16] Since this work was first presented,[1] Haszeldine and Steele have reported similar results for the photochemical addition of CF_3I to $CHF{=}CF_2$. A 4 to 1 ratio of products corresponding to attack by $CF_3\cdot$ on $CHF{=}$ and $CF_2{=}$ was found.[17]

[17] R. N. Haszeldine and B. R. Steele, *J. Chem. Soc.*, 2800 (1957).

synthesis and the following considerations. A sharp freezing point was obtained for $CCl_2FCH{=}CF_2$, indicating purity, and oxidation yielded CCl_2FCOOH. Its infrared spectrum showed a peak at 5.70 μ which could be assigned to the chromophore $R_xCH{=}CF_2$. There was no absorption at 5.95 μ which would be expected for $R_xCH{=}CClF$. Similarly, infrared absorption at 5.60 μ and lack of absorption at 5.80 μ was used to confirm the structure $CCl_2FCF{=}CF_2$ and exclude the isomeric $CClF_2CF{=}CClF$. Olefins of the type $R_xCF{=}CClF$ absorb at 5.80 μ while olefins of the type $R_xCF{=}CF_2$ absorb at 5.60 μ.

Utilizing the above olefins the following reactions were carried out with fluoride, chloride and iodide ions. Rates of reaction were observed

$$CF_2{=}CHCCl_2F + F^- \longrightarrow CF_3CH{=}CClF + Cl^- \quad (10)$$

$$CF_2{=}CHCCl_2F + Cl^- \longrightarrow CClF_2CH{=}CClF + Cl^- \quad (11)$$

$$CF_2{=}CHCCl_2F + I^- \longrightarrow CF_2ICH{=}CClF + Cl^- \quad (12)$$

$$CF_2{=}CFCCl_2F + F^- \longrightarrow CF_3CF{=}CClF + Cl^- \quad (13)$$

to depend upon type and concentration of nucleophile. With solvent alone no reaction occurred under the conditions employed. In all cases only rearranged products were obtained thus confirming the operation of the S_N2' mechanism. In fact, work in this Laboratory points to the conclusion that the fluoroallyl halides provide a considerable range of compounds which can react easily and exclusively by the S_N2' mechanism. For isomeric compounds $CF_2X\overset{|}{C}{=}CFX$ is more clearly stable than $CFX_2\overset{|}{C}{=}CF_2$ (11). The structures of the products were established by infrared and chemical evidence. As indicated above, the starting olefins $CCl_2FCH{=}CF_2$ and $CCl_2FCF{=}CF_2$ exhibited C=C stretching absorptions at 5.70 and 5.60 μ. All the substitution products of $CCl_2FCH{=}CF_2$ showed a shift in C=C stretching absorption to 5.95 μ due to the $R_xCH{=}CClF$ structure. No detectable absorption was observed at 5.70 μ due to $R_xCH{=}CF_2$, although this type of group shows especially strong absorption. The reaction product of $CCl_2FCF{=}CF_2$ and fluoride ion absorbed at 5.82 μ due to $R_xCF{=}CClF$. Further the complete infrared spectrum of this material was superimposable with a curve previously obtained for $CF_3CF{=}CClF$ prepared by an unambiguous procedure.[18] The infrared curves for $CF_2ICH{=}CClF$ isolated from the reaction of $CCl_2FCH{=}CF_2$ with iodide ion and obtained as a by-product from the dehydrohalogenation of $CCl_2FCH_2CF_2I$ were also found to coincide.

The relative reactivities of the halide ions toward $CCl_2FCH{=}CF_2$ could be deduced qualitatively from the reaction conditions employed. They were in the order $F^- > Cl^- > I^-$. This result is especially interesting since the relative nucleophilicities of the halogen ions have been assigned in the opposite order, $I^- > Br^- > Cl^- > F^-$, for carbon bond formation in S_N2 reactions.[19,20] Swain and Scott attribute the high nucleophilic reactivity of iodide and bromide ions to the easy electronic polarizability and large size of these ions which make the transition state less difficult to obtain. For an S_N2 attack by iodide ion on an organic halide the repulsion of the two partial negative charges in the transition state is decreased relative to reactions involving attack by the other halide ions because the negative charge can be more effectively distributed to reduce charge repulsion. For the S_N2' reaction (4) the entering and leaving groups are more widely separated in the transition state than for the S_N2 case[21] and the charge can be spread out through the three-carbon system. This picture is consistent with a decrease in the importance of the polarizability of the attacking anion and suggests that the strength of the new bond being formed is the factor of greatest significance. Steric effects may also be expected to be important in determining reactivity for the perhalo-systems. For these effects the predicted order for halide ion reactivity would be the observed order, $F^- > Cl^- > (Br^-) > I^-$.

The high order of reactivity of fluoride ion observed with fluoroölefins is of especial importance to carbon–fluorine chemistry. For unsaturated fluorocarbons fluoride ion occupies a unique position as a nucleophile, analogous to that of a proton as an electrophile for unsaturated hydrocarbons. Addition of fluoride ion to a fluoroölefin produces a highly reactive fluorocarbanion intermediate; reaction by the S_N2' path provides a rearrangement mechanism,[5] and, as shown above, for fluorination by substitution of other halogen. Additional work on the reactions of fluoride ion with fluoroölefins will be presented in subsequent communications.

Experimental Results

Bromodichlorofluoromethane.—Dichlorofluoromethane, Freon 21, was brominated in the vapor phase at 475° using the procedure of Howald and Miller[18] to yield 78% bromodichlorofluoromethane with a 41% conversion; b.p. 50.4° (727 mm.), f.p. −106° (range 0.5°), $n^{20}D$ 1.4308, d^{20}_4 1.9343; reported: b.p. 51–52°,[24] 50.2° (734 mm.), f.p. −106° (range 0.2°), $n^{20}D$ 1.4304, d^{20}_4 1.9317.[18]

Dichlorofluoroiodomethane.—This compound was obtained by treating bromodichlorofluoromethane with sodium iodide in acetone following the procedure of Howald and Miller.[18] A total of 311 g., 1.71 moles, of $CBrCl_2F$ and 240 g., 1.61 moles, of NaI dissolved in 560 ml. of acetone and sealed in seven heavy walled glass ampules were heated at 120° for two hours in a rocker furnace. The combined product was drowned in ice-water, the iodine present reduced with sodium thiosulfate and the organic layer separated and dried over calcium chloride. Distillation through a 450 × 18 mm. glass helices packed column under nitrogen yielded: (1) 92 g., b.p. 33–52°, largely b.p. 48–49° (recov. $CBrCl_2F$); (2) 16 g., b.p. 58–85°; (3) 189 g., b.p. 85–90° (739 mm.); (4) 28 g. residue. Fraction 3 was washed with ice-water to remove traces of acetone, dried and redistilled twice to yield a center cut with b.p. 88.8–88.9° (724 mm.), f.p. −107° (range 0.3°), $n^{20}D$ 1.5100, d^{20}_4 2.3153; reported: b.p. 44–46° (210 mm.[24]); b.p. 90.0 (760 mm.), f.p. −107° (range 0.2°), $n^{20}D$ 1.5100, d^{20}_4 2.3080.[18] The iodomethane was a straw-yellow color when freshly distilled but darkened on standing with liberation of iodine.

For a series of reactions the average conversion of $CBrCl_2F$ and yield of CCl_2FI were 65 and 73%, respectively.

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(18) J. M. Howald, Ph.D. Thesis, Cornell University, 1953.

(19) C. G. Swain and C. B. Scott, THIS JOURNAL, **75**, 141 (1953).

(20) J. O. Edwards, *ibid.*, **76**, 1540 (1954); **78**, 1819 (1956).

(21) Note that a *cis* configuration for the S_N2' transition state[22,23] will limit this separation.

(22) W. G. Young, I. D. Webb and H. L. Goering, THIS JOURNAL, **73**, 1076 (1951).

(23) G. Stork and W. N. White, *ibid.*, **75**, 4119 (1953); **78**, 4699 (1956).

(24) R. N. Haszeldine, *J. Chem. Soc.*, 4265 (1952).

1,1-Dichloro-1,3,3-trifluoro-3-iodopropane.[25]—A steel lecture cylinder was charged with 129 g. (0.56 mole) of CCl_2FI, freshly washed free of iodine with aqueous sodium thiosulfate and dried with calcium chloride; 2.8 g. (0.012 mole) of benzoyl peroxide; and 36 g. (0.56 mole) of vinylidene fluoride,[26] added last under pressure with Dry Ice cooling. The lecture cylinder was shaken by hand and heated at 85 ± 3° for 15 hours. After heating, unreacted $CH_2=CF_2$ was vented into a cold trap and the residue washed free of iodine and dried. Distillation yielded: (1) 15.8 g. of Dry Ice trap condensate; (2) 44.5 g., b.p. 20–37°, largely b.p. 35–37° (100 mm.); (3) 68.2 g., b.p. 40–45°, largely b.p. 44–45° (15–20 mm.); (4) 8.0 g. of residue which solidified on cooling. Fractions 1 and 2 were very largely unreacted CCl_2FI. The conversion of CCl_2FI and yield of $CCl_2FCH_2CF_2I$ based upon unrecovered CCl_2FI were 54 and 78%, respectively.

Several fractions prepared in the same way as 3 were combined and redistilled to yield a center cut, b.p. 41.5° (14 mm.), estimated b.p. 148° (760 mm.), f.p. −63.0° (range <0.2°), n^{20}_{D} 1.4658, d^{20}_4 2.0956; calcd. for $CCl_2FCH_2CF_2I$ MR_{D} 38.6,[27] chlorine plus iodine 67.6%; found MR_{D} 38.7, chlorine plus iodine 67.3% (total silver halide precipitate). This compound slowly turned dark red on standing in a refrigerator.

3,3-Dichloro-1,1,3-trifluoropropene[25] **and 1-Chloro-1,3,3-trifluoro-3-iodopropene.**—To 136 g., 2.23 moles, of powdered KOH in a Claisen flask heated by means of an oil-bath to a temperature of 120 ±10° was added 117 g., 0.40 mole, of $CCl_2FCH_2CF_2I$ over a period of five hours. Distillate boiling from 40 to 60° was collected. After all the halopropane had been added, unreacted starting material was removed from the reaction flask at 2 mm. pressure. The crude material was separated from water and dried over $MgSO_4$. Distillation of the combined products from three typical runs which utilized 362 g. of $CCl_2FCH_2CF_2I$ yielded: (1) 97 g., b.p. 45–52°, largely b.p. 51.5–52.0° (734 mm.); (2) 20 g., b.p. to 85° (100 mm.); (3) 54 g., residue, principally $CCl_2FCH_2CF_2I$. The conversion of $CCl_2FCH_2CF_2I$ and yield of $CCl_2FCH=CF_2$ were 85 and 56%, respectively. Redistillation of fraction 1 yielded a center cut, b.p. 52.0–52.2° (741 mm.), f.p. −103.2° (range 0.8°), n^{20}_{D} 1.3702, d^{20}_4 1.4504; calcd. for $CCl_2FCH=CF_2$ MR_{D} 25.7, mol. wt. 165; found: MR_{D} 25.7, mol. wt. 164 (Dumas).

1-Chloro-1,3,3-trifluoro-3-iodopropene was obtained by redistilling fractions corresponding to (2) under dry nitrogen with exclusion of light. Free iodine was removed by shaking with mercury. The center cut from the third redistillation through a 350 × 12 mm. glass helice packed column had the properties: b.p. 41° (70 mm.), formed a glass at approximately −120°, n^{20}_{D} 1.4670, d^{20}_4 2.0884; calcd. for $CF_2ICH=CClF$: MR_{D} 33.6, chlorine plus iodine 63.3%; found: MR_{D} 34.1, chlorine plus iodine 62.1% (total silver halide precipitate). After two further redistillations a fraction was obtained, b.p. 41° (70 mm.), n^{20}_{D} 1.4680; found: chlorine plus iodine 62.5%.

Ethyl Dichlorofluoroacetate.—The olefin $CCl_2FCH=CF_2$ was oxidized by potassium permanganate in the presence of excess sodium bicarbonate.[29] The resulting acid was converted to the ethyl ester by refluxing with absolute ethanol. Oxidation of 32.0 g., 0.20 mole, of olefin yielded after esterification 11.3 g., 33%, of $CCl_2FCOOEt$, b.p. 130.0–130.5° (742 mm.), n^{17}_{D} 1.4061, d 1.324 (Densitometer, CCl_4, at 22°); reported[30] for $CCl_2FCOOEt$: b.p. 130°, n^{17}_{D} 1.4073; $d^{14.6}$ 1.3312. Treatment of an alcoholic solution of $CCl_2FCOOEt$ with ammonia gas gave the amide, CCl_2FCONH_2, in 90% yield. After removal of the alcohol and crystallization from benzene–petroleum ether, the amide melted at 129.7–130.2°, micro b.p. 217°; calcd. for CCl_2FCONH_2: chlorine, 48.6%; found: chlorine, 48.8%; reported[30] for CCl_2FCONH_2: m.p. 126.5°, b.p. 215°.

Trifluoroethylene was prepared from $CBrF_2CHClF$[26] and zinc in 86% yield by dehalogenation with zinc.[31] Dioxane was utilized as the solvent.

1,1-Dichloro-1,2,3,3-tetrafluoro-3-iodopropane.—A steel lecture cylinder was charged with 114 g., 0.50 mole, of CCl_2FI, 5.0 g., 0.021 mole, of benzoyl peroxide and 56 g., 0.68 mole, of $CHF=CF_2$. The cylinder was heated in a rocker shaker for 18 hours at 93 ± 5°. After removing unreacted $CHF=CF_2$, 141 g. of residue remained. Distillation yielded: (1) 38.0 g., material condensed in a Dry Ice trap at 20 mm., n^{20}_{D} 1.4837; (2) 34.5 g., b.p. 40–43° (20 mm.), n^{20}_{D} 1.4533; (3) 39.5 g., b.p. 43–46° (20 mm.), n^{20}_{D} 1.4500; (4) 15.0 g., b.p. 46° (20 mm.), n^{20}_{D} 1.450; (5) 9.0 g. of residue. Fraction 1 was mainly unreacted CCl_2FI, 30%; fractions 2–4 consisted of 89.0 g. of $CCl_2FCHFCF_2I$, 49%.

The products from several runs carried out as described above were combined, treated with mercury to remove free iodine, and redistilled to yield a center cut, b.p. 63.5–64.0° (50 mm.), formed a glass in liquid nitrogen, n^{20}_{D} 1.4493, d^{20}_4 2.1550; calcd. for $C_3HCl_2F_2I$: MR_{D} 38.8; found: MR_{D} 38.7.

3,3-Dichlorotetrafluoropropene.—The halopropane $CCl_2FCHFCF_2I$ was dropped onto 130 g., 2.28 moles, of powdered anhydrous KOH in a Claisen flask maintained at 150 ± 10° by means of an oil-bath. A total of 128 g., 0.41 mole, was added over a period of three hours. Distillate boiling from 40 to 60° was collected. At the end of the reaction unconverted starting material was distilled from the reaction flask under reduced pressure. After separating codistilled water and drying over $MgSO_4$, 72 g. of crude material was obtained. Distillation yielded: (1) 32 g., b.p. 43–46° (728 mm.); and (2) 39 g., residue.

Fraction 1 was the expected product $CCl_2FCF=CF_2$. The residue was distilled and found to contain approximately 8% $CCl_2FCF=CF_2$, 63% $CCl_2FCHFCF_2I$ and 29% of an intermediate fraction, presumably the dehydrochlorinated product, $CF_2ICF=CClF$. On this basis a total of 46% $CCl_2FCF=CF_2$, 18% $CCl_2FCHFCF_2I$ and 9% $CF_2ICF=CClF$ were obtained in the reaction.

Products from two runs carried out as indicated above were distilled to yield a center cut of $CCl_2FCF=CF_2$, b.p. 46.0° (735 mm.), formed a glass in liquid nitrogen, n^{20}_{D} 1.3556, d^{20}_4 1.5378; calcd. for $CCl_2FCF=CF_2$: MR_{D} 25.9, mol. wt. 183, chlorine 38.8%; found: MR_{D} 26.0, mol. wt. 187 (Dumas), chlorine 39.7%.

Reaction of Fluoride Ion with 3,3-Dichlorotetrafluoropropene.—A sample of $CCl_2FCF=CF_2$, 6.2 g., 0.034 mole, was sealed into a glass ampoule with 5.2 g., 0.09 mole, of potassium fluoride dissolved in 90 ml. of 99% commercial formamide (du Pont). The ampoule was shaken for 17 hours at 47 ± 3°. The formamide layer turned brown, but on opening the ampoule 3.5 g., 62%, of pure $CF_3CF=CClF$ was collected in a Dry Ice trap. The infrared spectrum of this material was identical with the spectrum of an authentic sample of $CF_3CF=CClF$[18]; calcd. for C_3ClF_5: mol. wt. 166; found: mol. wt. 168 (Dumas).

In all the experiments described with formamide the fluoroölefins were only partially soluble.

Photochemical chlorination of 2 g., 0.012 mole, of the $CF_3CF=CClF$ obtained above yielded 2.8 g., 94%, of $CCl_2FCClFCF_3$, micro b.p. 75° (740 mm.), f.p. *ca.* −60°, n^{20}_{D} 1.3540; reported[8] for $CCl_2FCClFCF_3$: b.p. 73.4° (760 mm.), f.p. −55.1°, n^{20}_{D} 1.3530.

Reaction of Fluoride Ion with 3,3-Dichloro-1,1,3-trifluoropropene.—To a solution of 12 g., 0.20 mole, of potassium fluoride in 100 ml. of formamide was added 22 g., 0.13 mole, of $CCl_2FCH=CF_2$. The mixture was sealed in a glass ampoule and rocked at 32° for 14 hours. The ampoule was opened and 17.5 g., 83%, of crude $CF_3CH=CClF$ distilled out. Redistillation from P_2O_5 yielded 14.0 g., 71%, of $CClF=CHCF_3$, b.p. 23.7–24.5° (731 mm.); calcd. for C_3HClF_4: mol. wt. 149; found: mol. wt. 152 (Dumas).

Stability of $CF_2=CHCCl_2F$ in Formamide Solution.[32]—A mixture of 1.7 g. of olefin and 6 g. of formamide was sealed in a glass ampoule and shaken at 36° for 44.5 hours. The olefin was recovered nearly quantitatively by distillation; its refractive index and infrared spectra were unchanged.

1,1,2,2-Tetrachlorotetrafluoropropane.—For proof of structure, $CClF=CHCF_3$ was chlorinated to the known

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[26] Supplied by the M. W. Kellogg Co.

[27] Molecular refraction was calculated with the following increments: C. 2.584; C=C exaltation, 1.4; H, 1.0; Cl in alkane CX_3, 5.85; Cl in allylic CX_3, 6.03; Cl in vinylic CX_3, 5.9; F, 1.165; I in alkane CX_3, 13.7; I in allylic CX_3, 14.0.[28]

[28] A. H. Fainberg and W. T. Miller, Jr., unpublished work.

[29] R. T. Carroll, Ph.D. Thesis, Cornell University, 1952.

[30] F. Swarts, *Bull. classe sci.. acad. roy. Belg.*, **28**, 15 (1894); *Bull. soc. chim. France*, [3] **13**, 992 (1895).

[31] J. D. Park, W. R. Lycan and J. R. Lacher, THIS JOURNAL, **73**, 711 (1951).

[32] This experiment was performed by H. Goldwhite.

$CCl_2FCCl_2CF_3$. An ampoule was charged with 12.0 g., 0.08 mole, of $CF_3CH{=}CClF$, 18.0 g., 0.25 mole, of Cl_2, and 10 ml. of water which was added to dissolve HCl formed during the reaction. The ampoule was irradiated with two 15 watt fluorescent lamps (General Electric 360 BL) for 19 days at 35°. On opening the ampoule excess chlorine was the only low boiling material found. The organic product was taken up in ether and the ether solution washed with sodium thiosulfate solution, dried over $MgSO_4$ and distilled. A solid distillate, 16.5 g., b.p. 109–112°, 79% yield calculated as $C_3Cl_4F_4$, was obtained. This material was redistilled to yield: (1) 2.0 g., b.p. to 110.5° (729 mm.); (2) 3.7 g., b.p. 110.5–111.5° (729 mm.); (3) 8.0 g., b.p. 111.5° (728 mm.); (4) 2.0 g. of residue.

The properties of fraction 3, $CCl_2FCCl_2CF_3$, were b.p. 111.5° (729 mm.), m.p. 41–43°, mixed melting point with a 1:1 ratio of an authentic sample of $CCl_2FCCl_2CF_3$ 42-44°. The infrared curves in the region 2–15 μ for the two samples were superimposable; reported[33] for $CCl_2FCCl_2CF_3$: m.p. 41.74°, b.p. 112.4° (760 mm.).

Reaction of Chloride Ion with 3,3-Dichloro-1,1,3-trifluoropropene.—An ampoule was charged with 11.5 g., 0.07 mole, of $CCl_2FCH{=}CF_2$, 50 g. of acetone and 4.0 g., 0.10 mole, of lithium chloride. The solution was shaken for one day at 27°. The ampoule was opened and the contents poured into 1 liter of ice-water. The resulting water-insoluble material was dried over $MgSO_4$ and distilled. The distillate, b.p. 53–55° (736 mm.), showed infrared peaks at 5.71 and 5.94 μ which indicated a mixture of starting material and rearranged product $CClF_2CH{=}CClF$.

It was believed that insufficient time had been allowed for the reaction. Accordingly, 8.0 g. of additional $CCl_2FCH{=}CF_2$ and 4.0 g. of the mixed product obtained above, a total of 0.073 mole, was treated as before but the reaction time was increased to 48 hours at 42 ± 2°. Simple distillation of the crude material yielded 7.1 g., 59%, of $CClF_2CF{=}CClF$. Redistillation yielded: (1) 5.4 g., b.p. 56–58° (734 mm.); (2) 1.0 g. of residue. The properties of fraction 1, $CClF_2CH{=}CClF$, were: b.p. 56–58° (734 mm.), $n^{20}D$ 1.3701, d 1.459 (Densitometer at 27.5°); calcd. for $C_3Cl_2F_4$ mol. wt. 165, found mol. wt. 167 (Dumas). An infrared absorption peak was observed only at 5.94 μ in the C=C region.

Stability of $CF_2{=}CHCCl_2F$ in Acetone Solution.[32]—Two tubes were filled with 2.5 g. of olefin and 10 ml. of dry acetone and sealed under vacuum. Each tube was held at 65° for 45 hours. The contents of each tube was then separately drowned in ice-water to yield 2.3 g., 92%, and 2.2 g., 88%, of water-insoluble material. This was shown to be unchanged olefin by refractive index and infrared spectra.

Reaction of Iodide Ion with 3,3-Dichloro-1,1,3-trifluoropropene.—A solution containing 11.5 g., 0.07 mole, of $CCl_2FCH{=}CF_2$, 30.0 g., 0.20 mole, of NaI and 105 g. of acetone was sealed in a glass ampoule and shaken at 60 ± 2° for 45 hours. The ampoule was opened and the contents were drowned in 1.5 liters of ice-water. The resulting insoluble material was washed with 50 ml. of ice-water, separated, and dried over $MgSO_4$, to yield 13.0 g. of product, $n^{20}D$ 1.4639. Distillation yielded: (1) 3.0 g. of Dry Ice trap condensate, water soluble and presumed to be acetone; (2) 0.5 g., b.p. 40–43° (70 mm.), $n^{20}D$ 1.4673; (3) 8.3 g., b.p. 43° (70 mm.), $n^{20}D$ 1.4682; (4) 1.0 g. of residue. Fractions 2–4 represented a 55% yield of $CClF{=}CHCF_2I$.

Fraction 3 was combined with material from another run decolorized with mercury and redistilled. The physical properties of this fraction, $CF_2ICH{=}CClF$, were b.p. 51° (100 mm.), formed a glass in liquid nitrogen, $n^{20}D$ 1.4681, d^{24}_4 2.0894; calcd. for $CF_2ICH{=}CClF$: *MR*D 33.5, chlorine plus iodine 63.3%; found: *MR*D 34.1, chlorine plus iodine, 62.9% (total silver halide precipitate). Redistillation yielded a center cut, b.p. 51° (100 mm.), $n^{20}D$ 1.4688.

The infrared absorption spectra of $CF_2ICH{=}CClF$ prepared by the dehydrochlorination of $CCl_2FCH_2CF_2I$ and of fraction 3 obtained by reacting NaI with $CCl_2FCH{=}CF_2$ were compared in the region 2–15 μ and found to be superimposable.

A further reaction of $CCl_2FCH{=}CF_2$ with NaI in acetone was carried out at 61 ± 1° for 24 hours. This was not sufficient time to obtain equilibrium. After distillation and removal of acetone by washing with ice-water there was obtained a fraction, 19%, whose infrared absorption spectrum in the region 2–15 μ was identical with that of the starting $CCl_2FCH{=}CF_2$. The only other product isolated in 52% yield, based on unrecovered $CCl_2FCH{=}CF_2$, was $CF_2ICH{=}CClF$. This result showed that under the conditions utilized reaction with chloride ion produced in the reaction to form $CClF_2CH{=}CClF$ did not take place to an appreciable extent.

Difluoroiodoacetamide.—The olefin, 12.5 g., 0.05 mole, $CF_2ICH{=}CClF$, prepared by treating $CCl_2FCH{=}CF_2$ with NaI in acetone, was oxidized with $KMnO_4$, in solution buffered by $NaHCO_3$.[29] The resulting acid was converted to its ethyl ester. The ester was not isolated, but a solution of the ester in ethanol was treated with anhydrous ammonia. Ethanol was removed under vacuum and the residue, which failed to crystallize, was passed through a 10 × 0.8 cm. column containing Magnesol–Celite 1:1. The eluent was diethyl ether–petroleum ether (b.p. 30–60°). Evaporation of the solvent yielded 2.9 g. of a solid m.p. 91–96°, 27% yield of CF_2ICONH_2. Two recrystallizations from benzene–petroleum ether, gave needles, m.p. 100.6-101.1° (cor.); calcd. for CF_2ICONH_2: iodine 57.4%; found: iodine 57.7%.

ITHACA, N. Y.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

Solvent and Chain Length Effects in the Non-catalyzed Hydrolysis of Some Alkyl and Aryl Trifluoroacetates

BY ARLO MOFFAT AND HERSCHEL HUNT

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The chain length effects on the rates of hydrolysis of the *n*-alkyl and *sec*-alkyl trifluoroacetates parallel those which are observed in base-catalyzed hydrolysis of esters of non-catalyzed hydrolyses also parallel the solvent effects which are observed for the base-catalyzed hydrolyses. An explanation is presented to account for the very large differences which are observed between acid-catalyzed and base-catalyzed acyl–oxygen cleavage as far as chain length effects and solvent effects are concerned. Chain length effects and reactivity are related through a function of the reciprocal of the mass of the intermediate involved. It is suggested that a possible explanation for this mass relationship might lie in the effect of chain length upon bond amplitudes or bond vibrations.

Introduction

We have shown that the non-catalyzed hydrolysis of the *n*-alkyl trifluoroacetates is very closely related to the base-catalyzed hydrolysis of the *n*-alkyl benzoates[1,2] as far as chain length *versus* structure is concerned. It was found that re-

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