[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

Substitution and Addition Reactions of the Fluoroölefins. IV.[1] Reactions of Fluoride Ion with Fluoroölefins[2,3]

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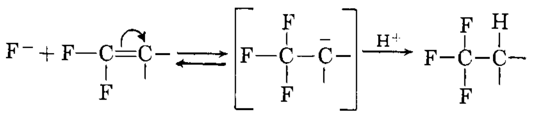
Experimental evidence is presented to show that a potentially broad area of carbon-fluorine chemistry consists of reactions of the fluoroölefins which are brought about by fluoride ion with initial attack on unsaturated carbon. The importance and generality of such reactions is due to the high order of nucleophilic reactivity shown by fluoride ion toward fluoroölefins and to the unique structural relationships which are involved. Reaction of fluoride ion with a fluoroölefin may result in: (1) substitution of vinyl halogen, (2) substitution of allyl halogen with rearrangement (SN2′), or (3) addition to form a fluorocarbanion. Substitution of allylic fluorine in a fluoroölefin provides a rearrangement mechanism. For all the cases investigated, where substitution (1) and (2) or addition (3) represented distinguishable reaction paths, substitution was shown to take place preferentially. Fluorocarbanions, formed reversibly by the addition of fluoride ion to a fluoroölefin, may add a proton to yield a hydrogen fluoride addition product or undergo other reactions as nucleophiles.

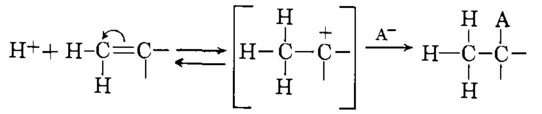
In contrast to hydrocarbon olefins, highly fluorinated olefins characteristically react with anionic and other nucleophiles and resist attack by cations. Reactivity has been shown to vary widely with structure, those olefins which contain a terminal difluoromethylene grouping being the most reactive.[4] Effective reagents include such relatively mild nucleophiles as the halide ions. These have been shown to exhibit nucleophilic reactivity toward fluoroölefins in SN2′ reactions in the order $F^- >> Cl^- > Br^-, I^-$,[1] the reverse of the order found for carbon bond formation in SN2 reactions. Three typical reactions, each initiated by attack at unsaturated carbon, have been shown to take place: (1) substitution of vinyl halogen, (2) substitution of allylic halogen with rearrangement (SN2′), and (3) addition of hydrogen halide.[1,5] The course of reaction is determined primarily by the structure of the fluoroölefin. No evidence for direct attack by a nucleophile on saturated carbon (SN2) has been obtained.

The reactions of fluoride ion with the fluoroölefins are of especial importance to carbon–fluorine chemistry because of the high order of nucleophilic reactivity shown by fluoride ion with such systems and because of the unique structural relationships which are involved. For unsaturated fluorocarbons, fluoride ion occupies a position as a nucleophile which is analogous to that of a proton as an electrophile for unsaturated hydrocarbons.

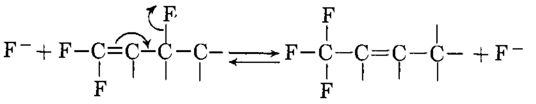
The reversible addition of a fluoride ion to a fluoroölefin produces a fluorocarbanion which may add a proton to yield a hydrogen fluoride addition product (1) or undergo other secondary reactions depending upon the experimental conditions and the reactants present.[7] Reaction of a fluoride ion with a fluoroölefin by the SN2′ path provides a rearrangement mechanism and, as shown previously, for fluorination by substitution of halogen other than fluorine. Direct substitution of vinyl halogen by fluorine may also take place.

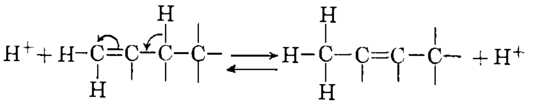
Addition:


$$\mathrm{F^- + F{-}\underset{F}{C}{=}C{-} \rightleftharpoons \left[F{-}\overset{F}{\underset{F}{C}}{-}\overset{-}{C}{-}\right] \xrightarrow{H^+} F{-}\overset{F}{\underset{F}{C}}{-}\overset{H}{C}{-}} \qquad (1)$$


$$\mathrm{H^+ + H{-}\underset{H}{C}{=}C{-} \rightleftharpoons \left[H{-}\overset{H}{\underset{H}{C}}{-}\overset{+}{C}{-}\right] \xrightarrow{A^-} H{-}\overset{H}{\underset{H}{C}}{-}\overset{A}{C}{-}} \qquad (2)$$

Substitution with rearrangement:


$$\mathrm{F^- + F{-}\underset{F}{C}{=}C{-}\overset{F}{C}{-}C{-} \rightleftharpoons F{-}\overset{F}{\underset{F}{C}}{-}C{=}C{-}C{-} + F^-} \qquad (3)$$


$$\mathrm{H^+ + H{-}\underset{H}{C}{=}C{-}\overset{H}{C}{-}C{-} \rightleftharpoons H{-}\overset{H}{\underset{H}{C}}{-}C{=}C{-}C{-} + H^+} \qquad (4)$$

The choice of reaction conditions suitable for studying the behavior of fluoride ion with fluoroölefins presents some difficulty. Stable inorganic fluorides tend to be insoluble in inert aprotic organic solvents while in protogenic solvents hydrogen ion transfer to fluorocarbanions limits the usefulness of such systems. Hydrogen ion transfer takes place with the formation of solvent anions which in turn may attack olefin to yield undesired by-products.

In the present paper initial work with two fluoride ion reagents is reported. These consist of potassium fluoride in formamide solution[1,9] and tetra-

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[1] Preceding paper, J. H. Fried and W. T. Miller, Jr., THIS JOURNAL, **81**, 2078 (1959).

[2] Presented in part at the 132nd Meeting of the American Chemical Society, New York, N. Y., September, 1957; Abstracts of Papers, p. 29 M.

[3] Presented in part at the International Symposium on Fluorine Chemistry, Birmingham, England, July, 1959.

[4] For a summary of observed reactions and references, see: W. T. Miller, Jr., and A. H. Fainberg, THIS JOURNAL, **79**, 4164 (1957).

[5] W. T. Miller, Jr., A. H. Fainberg and J. Fried, "Congress Handbook," XIVth International Congress of Pure and Applied Chemistry, Zurich, Switzerland, July, 1955, p. 55. These typical reactions of the fluoroölefins with nucleophilic anions were originally proposed on the basis of experimental results obtained with alkoxide ions.[6]

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

[7] Carbanions are the important polar reaction intermediates in fluorocarbon chemistry and it is a striking fact that they can be readily produced at low temperatures by the addition of nucleophilic anions. The rate-controlling production of intermediate fluorocarbanions in this way was first proposed by Miller, Fager and Griswold, to explain the base-catalyzed addition of alcohols to fluoroölefins.[8]

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

[9] Bergmann and Blank have reported reactions between ethyl chloroacetate and potassium fluoride in acetamide, N-methylacetamide, and methoxyacetamide.[10] Other nucleophilic substitution reactions have recently been carried out with potassium fluoride in dimethylformamide and in dimethyl sulfoxide.[11,12] Fluoride ion reactions with fluoroölefins in dimethylformamide and in other solvents will be described in a subsequent communication.

ethylammonium fluoride in lower molecular weight halogenated solvents such as chloroform or methylene chloride and in acetone. Both type reagents have serious limitations, but their use has nevertheless made it possible to realize with fluoride ion a number of examples of the typical reactions of fluoroölefins given above. The results obtained substantiate the existence of a broad area of carbon–fluorine chemistry consisting of the reactions of fluoroölefins which are brought about with initial attack by fluoride ion at unsaturated carbon.

Formamide has the valuable property of dissolving relatively large amounts of potassium fluoride. However, it is a poor solvent for fluoroölefins and immiscible mixtures are ordinarily obtained. It readily yields a proton to a fluorocarbanion with the resultant formation of reactive solvent anion. Another difficulty is that fluoroölefins may show appreciable reaction with the solvent alone at elevated temperatures. For example, 3,3-dichloro-1,1,3-trifluoropropene is completely converted into water-soluble products with the formation of a dark colored reaction mixture when heated with formamide at 105° for ninety hours.

As a consequence of the above considerations, the formamide–potassium fluoride reagent has proved to be most useful for reactions with fluoroolefins at comparatively low temperatures in which unreactive olefins are produced by substitution reactions without the formation of intermediate carbanions or in which it is desired to accomplish the addition of hydrogen fluoride. Other protogenic solvents containing fluoride ion may be expected to behave similarly.

Tetraethylammonium fluoride in common with the other halides is appreciably soluble in chlorinated solvents such as ethylene chloride, methylene chloride and particularly chloroform. It is less soluble in oxygenated solvents such as acetone.[13] As with potassium fluoride in formamide, this reagent has certain disadvantages. It is extremely hygroscopic, thermally unstable and difficult to prepare pure. Its solutions in chlorinated solvents underwent partial decomposition at room temperature. The material utilized usually contained some water of hydration and varying amounts of decomposition products. As might be expected, fluorocarbanions abstracted protons from the reagent. However, the use of solutions of tetraethylammonium fluoride in methylene chloride or chloroform has made possible the examination of some reactions of fluoroölefins with relatively high concentrations of fluoride ion in homogeneous solution.

Substitution and Rearrangement Reactions.—Evidence that substitution of allylic halogen in fluorohaloölefins of the type $CF_2{=}CYCX_3$, where X = halogen and Y = halogen or hydrogen, by reaction with halide ions takes place by the SN2′ mechanism has been presented previously.[1,4,15] Two examples of reactions with fluoride ion were included among those reported. Substitution of allylic chlorine by fluorine in 3,3-dichloro-1,1,3-trifluoropropene and in 3,3-dichloro-1,1,2,3-tetrafluoropropene was found to take place readily by reaction with potassium fluoride in formamide solution.[1] In each case the product was a relatively unreactive olefin with a terminal $CClF{=}$ group and was produced in high yield; eq. 5 and 6.

$$CF_2{=}CHCCl_2F + F^- \longrightarrow CF_3CH{=}CClF \qquad (5)$$

$$CF_2{=}CFCCl_2F + F^- \longrightarrow CF_3CF{=}CClF \qquad (6)$$

In the present work a 90% yield of 1-chloro-1,3,3,3-tetrafluoropropene was obtained from 3,3-dichloro-1,1,3-trifluoropropene[16] with a 74% conversion by reaction with tetraethylammonium fluoride in homogeneous chloroform solution overnight at room temperature. In acetone solution these reactants gave an 86% yield of the same product isolated after fifteen days at room temperature. As will be seen below, the reaction times were very much greater than necessary and demonstrate that any subsequent reaction of $CF_3CH = CClF$ is slow under the conditions used.

Reactions were also carried out between 3,3-dichloro-1,1,3-trifluoropropene and tetraethylammonium chloride, bromide and iodide in chloroform solution at room temperature. The results obtained confirm the order of nucleophilicity previously found for the halide ions in formamide solution with this olefin and the large difference in reactivity between fluoride and chloride ions, $F^- >> Cl^- > Br^-, I^-$.

It was found possible to effect reaction between an olefin with a $CClF{=}$ terminal group and fluoride ion under more vigorous conditions than those utilized with the olefins containing a $CF_2{=}$ terminal group. For example, 1,3-dichloro-1,2,3,3-tetrafluoropropene was treated with potassium fluoride in formamide at 60° and the volatile product allowed to distill out of the reaction mixture. A yield of 52% of 1,1,1,2,3,3,3-heptafluoropropane (b.p −17°) was isolated after three days. This result was interpreted as being due to a sequence of two substitution reactions followed by addition of hydrogen fluoride through the intermediate carbanion $CF_3\bar{C}FCF_3$; eq. 7, 8 and 9.

$$CClF{=}CFCClF_2 + F^- \longrightarrow CClF_6CF{=}CF_2 + Cl^- \qquad (7)$$

$$CClF_2CF{=}CF_2 + F^- \longrightarrow CF_2{=}CFCF_3 + Cl^- \qquad (8)$$

$$CF_2{=}CFCF_3 + F^- \xrightarrow{H^+} CF_3CHFCF_3 \qquad (9)$$

In the above sequence reaction 7 is the slow step. At present the question as to whether vinyl or allyl chlorine is substituted preferentially cannot be answered for this system in which isomeric transition states may be formed from the same atom grouping. Possibly the identity of the two chlorines becomes blurred during reaction 7. Reactions 8 and 9 take place rapidly enough to prevent distillation of the intermediate olefins from the reaction mixture (b.p. 7.4° and b.p. −29.8°)

1,2-Dichlorotetrafluoropropene gave by reaction with the potassium fluoride–formamide reagent a

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(10) E. D. Bergmann and I. Blank, *J. Chem. Soc.*, 3786 (1953).

(11) J. E. Herz, J. Fried, P. Grabowich and E. F. Sabo, THIS JOURNAL, **78**, 4812 (1956).

(12) G. C. Finger and C. W. Kruse, *ibid.*, **78**, 6034 (1956).

(13) Lannung first observed that tetraethylammonium fluoride was soluble in acetone.[14]

(14) A. Lannung, *Z. physik. Chem.*, **161A**, 255 (1932).

(15) A. H. Fainberg and W. T. Miller, Jr., THIS JOURNAL, **79**, 4170 (1957).

(16) An improved synthesis for $CF_2{=}CHCCl_2F$ also was developed. Preparations of $CF_2ICH_2CCl_3$, $CCl_2{=}CHCClF_2$ and of impure $CF_2{=}CHCCl_3$ are also described in the Experimental section.

55% yield of 2-chloro-1,1,1,3,3,3-hexafluoropropane after twenty-seven hours at 60°. This result is consistent with the two reaction steps, 10 and 11.

$$CClF{=}CClCF_3 + F^+ \longrightarrow CF_2{=}CClCF_3 \qquad (10)$$

$$CF_2{=}CClCF_3 + F^- \xrightarrow{H^+} CF_3CHClCF_3 \qquad (11)$$

Direct single step substitution of vinyl chlorine is proposed as the mechanism of reaction 10. A sequence of two SN2′ substitution reactions with initial elimination of allyl fluorine rather than vinyl chlorine is considered unlikely on the basis of the relative strengths of the carbon–chlorine and carbon–fluorine bonds. In addition, convincing evidence for the direct substitution of vinyl halogen by reaction with mercaptide ions has been obtained with $CClF{=}CClCF_3$ and other fluoroölefins.[17] The absence of the hydrogen fluoride addition product 1,2-dichloro-1,1,3,3,3-pentafluoropropane provides experimental evidence against formation of the anion $CClF_2CClCF_3$ followed by loss of chloride ion as an alternative mechanism for reaction 10.[18]

sym-Dichlorodifluoroethylene and tetrachloro-3,3-difluoropropene were resistant to attack by the potassium fluoride–formamide reagent at 60° but reacted slowly at 90°. In each case the initial reaction was presumed to consist of substitution of vinyl chlorine by fluorine, but low conversions and reactions with the solvent prevented the isolation of specific products.

As described above, postulated intermediate olefins containing the highly reactive $CF_2{=}$ terminal grouping could not be isolated under the reaction conditions utilized with the potassium fluoride–formamide reagent due to the rapid addition of hydrogen fluoride. The low solubility of the fluoroolefins in formamide prevented effective use of highly selective reaction conditions. However, it was found possible to isolate the intermediate olefin 2-chloropentafluoropropene formed from 2,3-dichlorotetrafluoropropene by reaction with tetraethylammonium fluoride under homogeneous conditions in chloroform solution. When the reactants, both initially at 0°, were mixed and held at this temperature for approximately five minutes, 52% of the $CF_2{=}CClCClF_2$ was converted into $CF_3CCl{=}CF_2$, the rest of the starting material being recovered. The rate of reaction was impressively fast. At higher temperatures or with longer reaction times $CF_2{=}CClCF_3$ was rapidly converted into the carbanion $CF_3\bar{C}ClCF_3$ by addition of fluoride ion as evidenced by disappearance of the olefin and the formation of $CF_3CHClCF_3$ (11) and other unidentified products.

The reaction of 1,4-dibromohexafluoro-2-butene with potassium fluoride in formamide provided a further result which supports the general reaction scheme presented above of preferential substitution of allyl halogen followed by addition of hydrogen fluoride through an intermediate carbanion. At 60° with excess fluoride ion the principal products were octafluoro-2-butene and its hydrogen fluoride adduct $CF_3CHFCF_2CF_3$. The hydrogen fluoride addition product $CF_3CHFCF_2CBrF_2$ was also isolated and the presence of $CF_3CF{=}CFCBrF_2$ shown by infrared absorption spectra. These results suggest the reaction sequence

$$CBrF_2CF{=}CFCBrF_2 + F^- \longrightarrow CF_2{=}CFCF_2CBrF_2 + Br^- \qquad (12)$$

$$CF_2{=}CFCF_2CBrF_2 + F^- \rightleftarrows CF_3CF{=}CFCBrF_2 + F^- \qquad (13)$$

$$CF_3CF{=}CFCBrF_2 + F^- \longrightarrow CF_3CF_2CF{=}CF_2 + Br^- \qquad (14)$$

$$CF_3CF_2CF{=}CF_2 + F^- \rightleftarrows CF_3CF{=}CFCF_3 + F^- \qquad (15)$$

$$CF_3CF{=}CFCF_3 + F^- \xrightarrow{H^+} CF_3CHFCF_2CF_3 \qquad (16)$$

The isolation of both hexafluoro-2-butene and of its hydrogen fluoride adduct was consistent with the observed lower reactivity of internal perfluoroölefins with fluoride ion as compared with terminal olefins. Reactions 13 and 15 postulate an equilibrium between terminal and internal isomeric olefins which favors the internal olefin. Similarly, lithium chloride in acetone has been found to convert 1,4-dibromohexafluoro-2-butene into an equilibrium mixture consisting very largely of 1,4-dichlorohexafluoro-2-butene.[19]

The hydrogen fluoride adducts $CF_3CHFCF_2CF_3$ and $CF_3CHFCF_2CBrF_2$ could arise from the 2-butenes, $CF_3CF{=}CFCF_3$ and $CF_3CF{=}CFCBrF_2$, and/or from the much more reactive 1-butenes, $CF_2{=}CFCF_2CF_3$ and $CF_2{=}CFCF_2CBrF_2$, which are present in low concentration. The same carbanions, corresponding to the HF adducts, would be formed in either case by addition of fluoride ion. The internal olefin $CF_3CF{=}CFCF_3$ is probably involved to some extent in the formation of $CF_3CHFCF_2CF_3$ but the only significant path to $CF_3CHFCF_2CBrF_2$ is considered to be from $CF_2{=}CFCF_2CBrF_2$. The addition of fluoride ion to $CF_3CF{=}CFCBrF_2$ in competition with reaction 14 seems improbable.

The fluoride ion-catalyzed rearrangement of fluorocarbon olefins was investigated directly with perfluoro-1-heptene. Two isomeric internal olefins would be formed by SN2′ substitution reactions with fluoride ion. An equilibrium mixture of the three

$$CF_3CF_2CF_2CF_2CF_2CF{=}CF_2 \overset{F^-}{\rightleftarrows} CF_3CF_2CF_2CF_2CF{=}CFCF_3 \qquad (17)$$

$$CF_3CF_6CF_6CF_6CF{=}CFCF_3 \overset{F^-}{\rightleftarrows} CF_3CF_2CF_2CF{=}CFCF_2CF_3 \qquad (18)$$

possible perfluoroheptenes, two of which could exist in *cis* and *trans* forms, would result from rearrangement of any one of these olefins. When perfluoro-1-heptene was treated with 0.3 mole of tetraethylammonium fluoride for five minutes at room temperature in chloroform solution it was converted into a mixture of isomeric olefins which contained about 12% of starting perfluoro-1-heptene as determined by infrared absorption. In another experiment with

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[17] W. L. Thompson, Ph.D. Thesis, Cornell University, 1955. For example, $CClF{=}CClCF_3$ and n-BuS$^-$ yielded three parts n-BuSCF$=$CClCF$_3$ and one part n-BuSCCl$=$CClCF$_3$ by reaction at 25° under conditions which would not be expected to dehydrohalogenate n-BuSCClFCHClCF$_3$.

[18] The nucleophilic substitution of vinyl halogen in fluoroölefins was originally proposed as proceeding through an intermediate anion.[6]

[19] W. T. Miller, Jr., and H. F. Kaldon, unpublished work.

1.6 moles of tetraethylammonium fluoride per mole of olefin less than 2% of perfluoro-1-heptene remained after twenty-four hours and a progressive shift in the composition of the mixture of internal olefins had taken place. Analysis of the reaction mixtures demonstrated that rearrangement had occurred with very little addition of fluoride ion.

Addition of Hydrogen Fluoride.—In the olefin–fluoride ion reactions described above where substitution of vinyl or allylic halogen by fluorine or addition to form a carbanion could result from attack on a given unsaturated carbon, substitution was observed to take place first. The resulting more highly fluorinated olefins which contained a terminal $CF_2=$ grouping were then rapidly converted into their hydrogen fluoride adducts while olefins with an internal —CF=CF— group reacted more slowly. When olefins which did not contain replaceable vinyl or allylic halogen other than fluorine and which would not undergo rearrangement by exchange of fluorine (SN2′) were allowed to react with potassium fluoride in formamide the results summarized in Table I were obtained. Dark colored reaction mixtures were formed due to reactions with the solvent.

TABLE I

Olefin	Temp., °C.	Reacn. time,[a] hr.	Product	Yield, %
$CF_2=CClF$	55	30	CF_3CHClF	72
$CF_2=CFCF_3$	25	5	CF_3CHFCF_3	60
$CF_2=CFCF_3$	65	[b]	CF_3CHFCF_3	21[c]
$CF_2=CClCF_3$	25	6	$CF_3CHClCF_3$	61
$CF_3CF=CFCF_3$	81	24	$CF_3CHFCF_2CF_3$	*ca.* 35[d]

[a] In a rocker shaker. [b] Bubbled very slowly through the KF–$HCONH_2$ reagent. [c] Recovered 50% of the $CF_2=CFCF_3$. [d] Estimated; see Experimental section.

As expected, olefins with a terminal $CF_2=$ group readily added hydrogen fluoride while hexafluoro-2-butene which has an internal —CF=CF— group reacted more slowly.

It is important to note that the hydrogen fluoride addition reactions took place in mildly basic media with a high concentration of fluoride ion present. The only consistent mechanism, reaction 1, involves the initial addition of fluoride ion and is analogous to the mechanism proposed for the alkoxide ion-catalyzed addition of alcohols to fluoroölefins.[8] Unfortunately, reaction 1 yields a solvent anion, along with the hydrogen fluoride addition product, which can then react with the fluoroölefin in competition with fluoride ion. This secondary reaction limits the yield of hydrogen fluoride adduct.

The above reaction mechanism was further substantiated by isolation of the hydrogen fluoride adduct CF_3CHFCF_3 from the reaction of hexafluoropropene with an aqueous dioxane solution of potassium fluoride.[20]

$$CF_3CF=CF_2 + F^- \longrightarrow CF_3\bar{C}FCF_3 \qquad (17)$$

$$CF_3\bar{C}FCF_3 + HOH \longrightarrow CF_3CHFCF_3 + OH^- \qquad (18)$$

Fluorocarbanion formation was also shown by hydrogen abstraction when fluoroölefins were allowed to react with the tetraethylammonium fluoride in homogeneous chloroform solution. 2-Chloropentafluoropropene reacted very rapidly. After ten minutes at 15° none of the starting olefin could be recovered. The only product characterized was the hydrogen fluoride adduct, $CF_3CHClCF_3$, obtained in 55% yield. Collapse of the cation and carbanion may have occurred to some extent to form neutral products, but it is considered more probable that protons were largely furnished by water present in the reaction mixture. Hexafluoropropene and chlorotrifluoroethylene also yielded hydrogen fluoride adducts under similar conditions.

Reactions of Fluorocarbanions.—As presented above, abundant evidence has been obtained for the generation of fluorocarbanions by addition of fluoride ion to fluoroölefins. In particular, olefins containing a terminal $CF_2=$ grouping may add fluoride ion with great ease.[22] These observations suggest the application of this general method for producing fluorocarbanions to the study of a broad range of reactions. Syntheses involving the addition of fluorocarbanions to electrophilic carbon and other reactions analogous to those of more conventional organometallic reagents are illustrative.

Acknowledgment.—This work was supported in part by the National Science Foundation for which grateful acknowledgment is made. We also wish to express our appreciation to Mr. H. F. Koch for experimental help.

Experimental Section

Chlorotrifluoroethylene.—A commercial sample of this material (du Pont) was passed through silica gel before use.

3,3-Dichloro-1,1,3-trifluoropropene was prepared by dehydrohalogenation of $CCl_2FCH_2CF_2I$.[1] The properties of a redistilled sample were: b.p. 51.8° (733 mm.), f.p. −103.2° (range 0.4°), n^{20}D 1.3698. The reported properties were: b.p. 52.0–52.2° (741 mm.), f.p. −103.2°.[1]

A sample of $CF_2=CHCCl_2F$ which had been stored for two years and nine months in a glass container was found to have undergone rearrangement to $CClF=CHCClF_2$ and, unexpectedly, $CCl_2=CHCF_3$. The ampule was etched and some oxidation and hydrolysis of oxidation products had probably occurred. In order to demonstrate the feasibility of storing and of handling $CF_2=CHCCl_2F$ in the absence of added halide ion under conditions suitable for reaction studies the following tests were carried out.

A sample of olefin was sealed in glass under nitrogen and stored at Dry Ice temperature for 5 months. No detectable change took place. The recovered olefin had a f.p. of −103.1°, range 0.2°.

Samples of olefin were shaken with 99% formamide, *ca.* 1 to 5, at 36° for 45.5 hours and at 105° for 90 hours. In the first case unchanged olefin as shown by its infrared spectrum was recovered in near quantitative yield; in the second case a tarry mass was formed and no olefin could be recovered.

Samples of olefin were heated in acetone solution in sealed ampules, *ca.* 1 to 5, at 65° for 45 hours and at 105° for 20 hours. In the first case 90% of unchanged olefin was recovered; in the second case a mixture of $CF_2=CHCCl_2F$ and $CClF=CHCClF_2$ was recovered.

1,1-Dichloro-1,3,3-trifluoro-3-iodopropane.—It was found that cleaner reactions and better conversions and yields of $CCl_2FCH_2CF_2I$ could be obtained by using thermal initia-

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[20] In aqueous solution the hydroxide ion produced reacts with $CF_3CF=CF_2$ to yield $CF_3CHFCOO^-$.[21]

[21] W. T. Miller, Jr., Ole Osrunn and P. J. Boesch, unpublished work

[22] It will be seen that ethylenes and propenes, such as the $CF_2=CX_2$'s and $CF_2=CXCF_3$'s, for which loss of the highly reactive $CF_2=$ group by SN2′ rearrangement is impossible, are of especial importance for fluorocarbanion production. In particular, anions of the type $CF_3\bar{C}XCF_3$ appear to be highly stabilized by halogen-hyperconjugation.

tion for the free-radical addition of CCl_2FI to $CH_2=CF_2$ instead of benzoyl peroxide as previously described.[1]

A steel lecture cylinder (Matheson) which was fitted with a steel valve was charged with 209 g., 0.91 mole, of CCl_2FI, cooled with Dry Ice and 60 g., 0.93 mole, of $CH_2=CF_2$ condensed in at 2.5 atm. pressure. The bomb was sealed and heated at 125 ± 5° for 19 hours. It was then cooled and vented to yield 12 g. of unreacted olefin. The liquid products from two runs were combined and distilled to yield 295 g. of $CCl_2FCH_2CF_2I$, b.p. 39° (13 mm.), n^{20}_{D} 1.4655, d^{20}_{4} 2.0978. The reported properties were: b.p. 41.5° (14 mm.), n^{20}_{D} 1.4658, d^{20}_{4} 2.0956.

Attempted Preparation of 3,3,3-Trichloro-1,1-difluoropropene. 1,1,1-Trichloro-3,3-difluoro-3-iodopropane and 1,1,3-Trichloro-3,3-difluoropropene.—The preparation of $CF_2=CHCCl_3$ was attempted by the route: $CCl_3I + CH_2=CF_2 \rightarrow CCl_3CH_2CF_2I \rightarrow CCl_3CH=CF_2$. Trichloroiodomethane has been shown to be a very effective free-radical chain transfer agent with fluoroölefins[23] and the addition of CCl_3I to $CH_2=CF_2$ was smoothly accomplished with thermal initiation by heating the reactants together in the present work. However, initial efforts to prepare the desired olefin, $CCl_3CH=CF_2$, in pure form by dehydroiodination of the addition product, $CCl_3CH_2CF_2I$, were unsuccessful. General decomposition and/or partial rearrangement to form $CCl_2=CHCClF_2$ was observed under the conditions utilized. The high order of reactivity indicated for $CF_2=CHCCl_3$ make it of especial interest for study.

$CCl_3CH_2CF_2I$.—A steel lecture cylinder was charged with 316 g., 1.29 moles, of CCl_3I and 65 g., 1.02 moles, of $CH_2=CF_2$ as described above. The bomb was sealed and heated with rocking at 115 ± 5° for 36 hours. It was then cooled and 2 g. of olefin recovered by venting. The liquid residue was washed with aqueous sodium thiosulfate to remove free iodine, dried and distilled at reduced pressure to yield 53 g. of recovered CCl_3I, 264 g. of $CCl_3CH_2CF_2I$, b.p. 83–84° (29 mm.), and 30 g. of residue. The yield of product was 86.5% based on unrecovered olefin.

The iodide was a clear liquid which rapidly turned pink in the light. A redistilled sample had the properties: b.p. 78.3–78.5° (22 mm.), f.p. −37.5° (range 0.1°), n^{20}_{D} 1.5089, d^{20}_{4} 2.1157; MR_D 43.67, MR_D calcd. 43.42.

The above structure for the iodide was consistent with the orientation of addition observed for other trihalomethyl free radicals with $CH_2=CF_2$[24] and was confirmed by its ultraviolet absorption spectrum and by dehydroiodination to $C_3HCl_3F_2$. In isoöctane solution, 0.67 g./l., a λ_{max} was observed at 270 mμ, ε 379, and λ_{min} at 234 mμ, ε 87. Haszeldine and Osborne have shown that compounds containing the group RCF_2I have λ_{max} at 267–271 mμ, ε *ca.* 300, while those with the group RCH_2I have λ_{max} of 258–262 mμ.[25]

The iodide, $CCl_3CH_2CF_2I$, was readily coupled in ether solution by reaction with powdered zinc to yield 88% $C_6H_4Cl_6F_4$, presumably $CCl_3CH_2CF_2CF_2CH_2CCl_3$, an especially high yield for this type of reaction. The molecular weight found by freezing point depression in benzene was 358; chlorine 58.5%; calculated for $C_6H_4Cl_6F_4$, mol. wt. 365, Cl 58.3%.

Chlorination of the hexane yielded a crystalline solid, m.p. 116.7–118.0°, after recrystallization from alcohol, which contained 70.3% chlorine; calculated for $C_6Cl_{10}F_4$, presumably $CCl_3CCl_2CF_2CF_2CCl_2CCl_3$, Cl 70.5%.

$CCl_2=CHCClF_2$.—The most promising method tried for the dehydrohalogenation of $CCl_3CH_2CF_2I$ consisted of the addition of concentrated aqueous KOH to a hot solution of the iodide in diethylene glycol diethyl ether. An olefinic fraction steam distilled from the reaction mixture. Infrared analysis suggested that this was largely the desired olefin, $CCl_3CH=CF_2$. However, this fraction rearranged during subsequent handling, presumably due to the presence of chloride ion, and the only olefin that was isolated pure was the rearranged isomer $CCl_2=CHCClF_2$.

$$Cl^- + CF_2=CHCCl_3 \longrightarrow CClF_2CH=CCl_2 + Cl^-$$

A solution of 155 g., 0.5 mole, of $CCl_3CH_2CF_2I$ in 400 ml. of peroxide-free diethylene glycol diethyl ether was placed in a 1-l. three-necked flask which was fitted with a dropping funnel and nitrogen inlet, a stirrer and a distillation head. The reaction flask was heated by means of an oil-bath to 150° with a slow stream of nitrogen passing through. A solution of 57 g. of KOH, 1 mole, in 70 ml. of water was then added rapidly with stirring and the distillate collected. The lower layer of the distillate was separated, dried and distilled to yield (1) 28.5 g., b.p. 80–83° (744 mm.), and a residue (2) which consisted largely of solvent. The infrared spectrum of (1) showed a strong peak at 5.75 μ corresponding to $CF_2=CH—$ absorption and a weak peak at 6.12 μ corresponding to $CCl_2=CH—$ absorption.

Several fractions prepared as described above were combined and slowly distilled through a 100-cm. spinning band column, fitted with a stainless steel band. The boiling point rose steadily from 87 to 93°. Redistillation in the same column then gave a large fraction boiling sharply at 95.5° (749 mm.). This material reacted slowly with cold potassium permanganate solution. It had an intense infrared absorption at 6.14 μ but no detectable absorption at 5.75 μ. These data and chlorination of the olefin to form the pentachloro addition product and the known $CCl_3CCl_2CClF_2$ (see below) supported the structure $CCl_2=CHCClF_2$. The properties of the olefin were: b.p. 95.5° (749 mm.), f.p. −96.5° (range <0.1°), n^{20}_{D} 1.4290, d^{20}_{4} 1.5208; MR_D 30.8, MR_D calcd. for $CCl_2=CHCClF_2$ 30.3; Cl, 58.9%, Cl calcd. for $C_3HCl_3F_2$ 58.6%.

1,1,1,2,3-Pentachloro-3,3-difluoropropane.—Photochemical chlorination at atmospheric pressure of 16.1 g. of $CCl_2=CHCClF_2$ until rapid chlorine absorption ceased yielded, after washing with sodium bisulfite solution, drying and distillation, 16.0 g., 72% calcd as $CCl_3CHClCClF_2$, with the properties: b.p. 168–169° (746 mm.), n^{20}_{D} 1.4610, d. (gravitometer) 1.725; MR_D 40.2, MR_D calcd. for $CCl_3CHClCClF_2$ 40.2; Cl 70.2%, Cl calcd. for $C_3HCl_5F_2$ 70.3%.

1,1,1,2,2,3-Hexachloro-3,3-difluoropropane.—Exhaustive photochemical chlorination of 2 g of the $CCl_2=CHCClF_2$ in a sealed tube with 3 g. of chlorine in the presence of 2.5 ml. of water yielded 3.05 g., 96%, of soft waxy crystals, m.p. 51.0–51.2°. Henne and Ladd have reported a m.p. of 50.8° for $CCl_3CCl_2CClF_2$.[26]

1,2-Dichlorotetrafluoropropene, b.p. 47–49° (740 mm.), n^{20}_{D} 1.3514, was prepared by dechlorination of $CCl_2FCCl_2CF_3$ as described by Henne and Waalkes; reported[27] b.p. 47.3° (760 mm.), n^{20}_{D} 1.3511.

1,3-Dichlorotetrafluoropropene was obtained from the dichlorotetrafluoropropene fraction, b.p. 44–49°, available from the pyrolysis of chlorotrifluoroethylene.[28,29] Photochemical bromination at room temperature followed by debromination of the resulting dibromide with zinc in dioxane yielded a $CClF=CFCClF_2$ fraction containing some $CF_2=CClCClF_2$ and $CF_2=CFCCl_2F$ as shown by its infrared absorption spectrum. Treatment of the mixture with lithium chloride in acetone to rearrange $CF_2=CFCCl_2F$ to $CClF=CFCClF_2$[1,4] and with a large excess of sodium iodide in acetone to convert $CF_2=CClCClF_2$ into $CF_2=CClCF_2I$[4] followed by distillation yielded, after recovery and redistillation, a sample of $CClF=CFCClF_2$, b.p. 39.0–48.5° (733 mm.); middle fraction, b.p. 47.0–48.0°, n^{20}_{D} 1.3527. This material contained a small amount of $CF_2=$ impurity, as shown by infrared analysis. A sample of $CClF=CFCClF_2$ previously separated by the above procedure but with final treatment with sodium iodide alone[30] had the properties: b.p. 47.5° (760 mm), formed a glass at *ca.* −160°, n^{20}_{D} 1.3529, d^{20}_{4} 1.5335. Both samples had closely matching infrared absorption in the region 2–15 μ.

The unbrominated portion of the 44–49° boiling fraction from the $CClF=CF_2$ pyrolysis product yielded CCl_2FCClF_2 and impure $CClF=CClCF_3$ by chlorination, distillation, and dechlorination of the higher boiling chlorinated product.

2,3-Dichlorotetrafluoropropene, b.p. 43.0–43.2° (732 mm.), was prepared by dechlorination of $CClF_2CCl_2CClF_2$

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

with zinc in ethanol[4,31]; reported[4] b.p. 44.8° (760 mm.), f.p. −120.7°, n^{20}_{D} 1.3484, d^{20}_{4} 1.5399.

2-Chloropentafluoropropene, b.p. 7° (743 mm.), was obtained by dechlorination of $CF_3CCl_2CClF_2$, b.p. 72° (743 mm.); reported[32,33] b.p. 6.8°.

Hexafluoropropene.—The pyrolysis of sodium perfluorobutyrate according to the method of Hals, *et al.*,[34] yielded 81% perfluoropropene, b.p. −25.5 to −24.5° (uncalibrated system), reported[27] b.p. −29.4°.

1,4-Dibromohexafluoro-2-butene.—Bromination of hexafluorobutadiene with illumination by an incandescent lamp until bromine absorption ceased at room temperature according to the procedure of Miller and Kaldon[35] yielded 90% $CBrF_2CF{=}CFCBrF_2$, b.p. 99.0–100.5° (735 mm.), n^{20}_{D} 1.3924; reported[35] b.p. 98.8–99.4° (737 mm.), n^{20}_{D} 1.3924.

Octafluoro-2-butene was prepared in 73% yield by fluorination of $CClF_2CF{=}CFCClF_2$.[36] The fluorination was performed by heating the reactants in the proportion of 1 mole of olefin to 2 moles of HgO to 4.5 moles of HF at 110° for 4 hours in a steel bomb in a rocker shaker.[37]

Perfluoro-1-heptene, b.p. 80.7–81.0 (744 mm.), was prepared from perfluoroöctanoic acid (Minnesota Mining and Mfg. Co.) as previously described; the reported[38] b.p. was 81°. Its infrared spectrum corresponded to that given by Weiblen[39] with an intense absorption at 5.6 μ. However, gas chromatographic analysis with a 0.25″ × 12′ *n*-hexadecane-on-Celite column indicated the presence of small amounts of isomeric olefins. The major peak corresponded to 87% of the total chromatogram area.

Tetraethylammonium Fluoride.—Lannung[14] has reported the preparation of tetraethylammonium fluoride by reaction of tetraethylammonium iodide with an equivalent amount of silver fluoride in aqueous solution followed by filtration to remove silver iodide, evaporation on a water-bath to crystallization and drying in a vacuum desiccator. The final product was recrystallized from absolute alcohol and dissolved in acetone for conductivity measurements.

Lannung's procedure was utilized in the present work as well as the direct neutralization of tetraethylammonium hydroxide solution with hydrofluoric acid and a modification of Markowitz's[40] general procedure for the preparation of quaternary ammonium salts.

The preferred preparative procedure[41] was to neutralize 48% hydrofluoric acid (Baker and Adamson reagent grade) with 10% aqueous tetraethylammonium hydroxide solution (Eastman) in a polyethylene beaker to a phenolphthalein end-point. The resulting solution was concentrated at 45–50° in a round-bottom flask with a capillary air leak extending to the bottom of the flask with evacuation by an oil-pump until crystals began to form, about 16 hours. The sirupy residue was transferred to an evaporating dish and placed in a large vacuum desiccator over phosphorus pentoxide and drying continued at room temperature for 6 days at <1 mm. The mixture was stirred and broken up twice a day during this time. The product gradually assumed a light purplish hue as drying continued, presumably due to the presence of phenolphthalein, although its aqueous solution was colorless.

The dried salt melted fairly sharply at 115–116° with gas evolution in a sealed melting point tube after becoming moist in appearance and visibly shrinking, 100–112°. It contained 10.1% F and 19.3% H_2O (Karl Fischer) as compared with calculated values of 10.3% F and 19.4% H_2O for $Et_4NF \cdot 2H_2O$. Titration of a 0.5 g. sample required one drop of 0.1 *N* NaOH solution to yield a phenolphthalein end-point.

Further drying of the above salt for two weeks at 42° under vacuum or at 100° for several hours or by azeotropic distillation with benzene yielded lower melting products of increased fluoride content which contained titratable acid, 2 to 10% calculated as HF. There was appreciable weight loss and ethylene and triethylamine were shown to be evolved at 100°. These results suggest the following mode of decomposition: $Et_4NF \rightarrow Et_3NHF + CH_2{=}CH_2$. The residual acidity of the dried salt appeared to be due largely to Et_4NHF_2 formed by the following reaction with removal of the volatile amine: $Et_3NHF + Et_4NF \rightarrow Et_3N \uparrow + Et_4NHF_2$.

Tetraethylammonium fluoride was found to be soluble in ethylene chloride, methylene chloride and chloroform, with chloroform much the best solvent. Its solutions in these solvents became acid and formed chloride ion on standing, as shown by testing water extracts, with the amounts increasing as the temperature was raised. Ethylene and triethylamine were shown to be formed from the dihydrate in chloroform solution and presumably were formed in all cases. Samples of the nearly anhydrous salt prepared by the higher temperature drying procedures were more soluble in the chlorinated solvents than the dihydrate. The observed low temperature decomposition of tetraethylammonium fluoride suggests that quaternary ammonium fluorides may find application for the synthesis of olefins and for degradation studies.

Although there were variations in the composition of the tetraethylammonium fluoride reagent utilized due to differences in the preparative procedure and to its instability, good reproducibility was observed in carrying out the reactions with this reagent reported below in which excess fluoride was ordinarily utilized.

Chlorotrifluoroethylene.—1. A glass ampule was half filled with 32 g., 0.27 mole, of $CClF{=}CF_2$, 24 g., 0.41 mole, of potassium fluoride, and 166 ml. of 95% formamide (du Pont). The ampule was rocked for 30 hours at 55 ± 3° after which time the formamide layer was very dark colored. The darkening of the formamide layer was found to be an indication of HF addition, and of fluorocarbanion production, in this and other similar reactions.

After opening the ampule, 27 g. of low boiling material was collected in a cold trap. This material was mixed with excess bromine and irradiated for 24 hours with a 100 watt incandescent lamp. The excess bromine was removed with sodium sulfite solution and 16 g. of bromine-free liquid recovered, mol. wt. 131, 134 (Dumas); calcd. as C_2HClF_4, yield 46%, mol. wt. 136. The infrared spectrum indicated C–H absorption at 3.34 μ but no absorption between 5 and 7 μ.

The residue from the C_2HClF_4 was washed and dried to yield 13 g., 18%, calcd. as $CBrClFCBrF_2$. Distillation yielded 11 g., b.p. 91–93° (742 mm.), n^{20}_{D} 1.4265, d. (densitometer at 22.5°) 2.219; reported[42] for $CBrClFCBrF_2$, b.p. 92.9° (760 mm.), n^{20}_{D} 1.4272, d^{20}_{4} 2.2318.

The C_2HClF_4 obtained above was shown to be $CHClFCF_3$ by chlorination to the known CCl_2FCF_3. An ampule containing 14.0 g., 0.10 mole, of C_2HClF_4, 18.0 g., 0.25 mole, of chlorine and 8 ml. of water was illuminated 5 days with eight 15-watt G.E. BL fluorescent lamps arranged in a circle. After destroying excess chlorine with sodium sulfite solution, 11.5 g., 68%, of CCl_2FCF_3 was obtained, mol. wt. 171, 175 (Dumas), calcd. mol. wt. 171; f.p. −56.7°, range 0.6°; reported[43] for CCl_2FCF_3, f.p. −56.6°. The other possible HF addition product of $CClF{=}CF_2$, CHF_2CClF_2, would have yielded $CClF_2CClF_2$ by chlorination which is reported[44] to melt at −94°.

2. A steel lecture cylinder (Matheson) was charged with 12 g., 0.106 mole, of $CClF{=}CF_2$, 15.9 g. of tetraethylammonium fluoride in 55 g. chloroform and 20 g. of Dry Ice. The bomb contents were thoroughly mixed and allowed to stand at room temperature for 21 days. Distillation yielded 8.8 g., 0.052 mole, 50%, calcd. as $CHClFCF_3$, b.p. −12 to −10° (738 mm.), infrared spectrum identical with that of an authentic sample of $CHClFCF_3$, saturated to permanganate in acetone. No $CF_3CClFCOOH$ was isolated.

3,3-Dichloro-1,1,3-trifluoropropene.—1. A glass ampule was charged with 4.4 g., 0.027 mole, of $CF_2{=}CHCCl_2F$, 5.5

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(32) A. L. Henne, A. M. Whaley and J. K. Stevenson, *ibid.*, **63**, 3478 (1941).

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g. of tetraethylammonium fluoride and 50 ml. of dry acetone. The tetraethylammonium fluoride was incompletely soluble. The ampule was shaken for 24 hours at room temperature and let stand for 15 days. Its contents were drowned in ice-water, with some loss of olefin, and the water-insoluble fraction separated. Distillation yielded 3.8 g., b.p. 24° (741 mm.), mol. wt. 145 (Dumas), calcd. mol. wt. for C_3HClF_4 148.5, infrared spectrum identical with that of an authentic sample of $CF_3CH{=}CClF$.

The aqueous washings were found to contain 0.024 equivalent of chloride ion.

A 16.5 g., 0.1 mole, sample of $CF_2{=}CHCCl_2F$ was transferred under nitrogen on to 40 g. of tetraethylammonium fluoride and chloroform added to make a total volume of 250 ml. Approximately one-half of the olefin had reacted after 10 minutes as determined by titration of an aliquot for chloride ion. After 12.5 hours at 27° the volatile portion of the reaction mixture was distilled at low pressure into Dry Ice and liquid nitrogen traps placed in series. Redistillation of the trap condensate yielded: (1) 10.4 g., b.p. 24–25°; (2) 1.3 g., b.p. 30–55.2°; and (3) 4.6 g., b.p. 55.2° (737 mm.).

Fraction 1 was found to have a mol. wt. of 147, 151 (Dumas); calcd. for C_3HClF_4 148.4. Its infrared spectrum was identical with that of an authentic sample of $CF_3CH{=}CClF$. Fraction 3 was indicated as largely unchanged $CF_2{=}CHCCl_2F$ and fraction 2 was shown to contain an appreciable amount of this material by infrared and gas chromatographic examination.

2. A solution of 4.0 g., 0.024 mole, of $CF_2{=}CHCCl_2F$ and 10.6 g., 0.064 mole of tetraethylammonium chloride in sufficient chloroform to make a total volume of 60 ml. was let stand at room temperature (*ca.* 27°) for 12.5 hours. The volatile material was removed at low pressure into a cold trap. A gaseous infrared spectrum of the liquid showed that it contained principally unchanged $CF_2{=}CHCCl_2F$, but a weak absorption at 5.95 μ showed the presence of some $CClF{=}CHCClF_2$. Quantitative gas chromatography on a 0.25″ × 4′ dinonyl phthalate-on-Celite column indicated that the rearranged olefin accounted for about 4% of the olefin mixture. Distillation yielded 3.5 g., b.p. 52–53° (739 mm.), shown by its infrared spectrum to be largely recovered $CF_2{=}CHCCl_2F$ contaminated with some $CClF{=}CHCClF_2$.

Similar experiments were carried out with $CF_2{=}CHCCl_2F$ and tetraethylammonium bromide and iodide in chloroform solution at room temperature and at 53.4° for approximately 20 hours. The formation of chloride ion could not be detected in either case at room temperature and not more than trace amounts were produced at the higher temperatures.

1,2-Dichlorotetrafluoropropene.—A mixture of 57 g., 0.30 mole, of $CClF{=}CClCF_3$, 52 g., 0.88 mole, of KF and 500 ml. of formamide was heated under nitrogen with stirring for 27 hours at 60° during which time 39 g. of volatile material distilled into the Dry Ice trap. The volatile product was sealed in a glass ampule with excess bromine and irradiated for two days with a 100-watt incandescent lamp. The excess bromine was removed with sodium sulfite solution and 31 g. of low boiling material, corresponding to 55% of $CF_3CHClCF_3$, isolated by distillation. The infrared spectrum of this material was identical with that of an authentic sample of $CF_3CHClCF_3$ (see below). A residue of 4.5 g., corresponding to 5% $CBrClFCBrClCF_3$, was obtained after washing and drying the non-volatile fraction. Simple distillation yielded 3.0 g., b.p. 148–151° (742 mm.), m.p. 65–67°.

1,3-Dichlorotetrafluoropropene.—A mixture of 81 g., 0.44 mole, of $CClF{=}CFCClF_2$, 87 g., 1.5 moles, of KF and 500 ml. of formamide was brought to 52° and then gradually raised to 65° over a period of 3 days with stirring under nitrogen. During this time most of the fluorinated material was collected in the Dry Ice trap. The small amount remaining in the reaction flask was distilled into the cold trap under reduced pressure. The product was separated into: (1) 48 g. volatile at room temperature, and (2) 10 g. of higher boiling residue. Fraction 2 was indicated as principally unreacted $CClF{=}CFCClF_2$, 12%; distillation through a small helix-packed column yielded a 5-g. center cut, b.p. 46–49° (740 mm.), $n^{20}{}_D$ 1.3520.

Fraction 1 yielded 39 g. saturated bromine-free low boiling material, recovered after bromination, removal of excess bromine and drying. Redistillation from P_2O_5 yielded 35 g. of CF_3CHFCF_3, b.p. −15.5° (718 mm.), f.p. −129.5° (range 0.2°); mol. wt. 167, 173 (Dumas); calcd. for C_3HF_7, mol. wt. 170. The infrared spectra and freezing point of this compound differentiate it from the known $CHF_2CF_2CF_3$, b.p. −17° (735 mm.), f.p. −148.5°.[45]

2,3-Dichlorotetrafluoropropene.—A solution of 40 g., 0.218 mole, of $CF_2{=}CClCClF_2$ in 89 g. of chloroform was cooled in a −5° ice–salt-bath and 28 g. of tetraethylammonium fluoride dissolved in chloroform and cooled to 0° added with stirring over a period of 5 minutes. Heat was evolved. The mixture was quickly distilled at 0° at low pressure into Dry Ice and liquid nitrogen cooled traps placed in series. The trap condensate was combined and distilled to yield: (1) 18.6 g., b.p. 6–7° (735 mm.); and (2) 18.2 g., b.p. 46–48° (741 mm.).

Fraction 1 was shown to be $CF_2{=}CClCF_3$ by its infrared spectrum which was identical with that of an authentic sample of $CF_2{=}CClCF_3$, and by conversion to the dibromide, $CBrF_2CBrClCF_3$, b.p. 109–110° (737 mm.), $n^{20}{}_D$ 1.4091; reported[23] for $CBrF_2CBrClCF_3$, b.p. 110° (760 mm.), $n^{20}{}_D$ 1.4060.

Fraction 2 was shown to be unchanged $CF_2{=}CClCClF_2$ by its infrared spectra and by chlorination to $CClF_2CCl_2CClF_2$, b.p. 111–112° (734 mm.), $n^{20}{}_D$ 1.3977, identical with the material from which the olefin had been prepared.

The yield of $CF_2{=}CClCF_3$, 18.6 g., 0.112 mole, was 95% based on unrecovered starting material; the conversion was 52%. Analysis of residual solids showed that 0.113 equivalent of chloride ion had been produced.

2-Chloropentafluoropropene.—1. An ampule containing 28 g., 0.18 mole, of $CF_2{=}CClCF_3$, 15 g., 0.26 mole, of KF and 165 ml. of 96% formamide was shaken 6 hours at about 25°. Distillation from the ampule yielded 20 g., 61%, calculated as C_3HClF_6. A portion of this material, 18 g., was brominated photochemically. After removing excess bromine, (1) 15.5 g., b.p. 14°; and (2) 1 g. of residue were obtained. Fraction 1 had the properties: b.p. 14°, f.p. −120.8° (range 4.4°), mol. wt. 185, 188 (Dumas); mol. wt. calcd. for C_3HClF_6, 187. The infrared spectrum of this material indicated C–H at 3.36 μ and no unsaturation. The boiling point of $CF_3CHClCF_3$ has been reported[46] as 14.5–15.8°.

The structure $CF_3CHClCF_3$ for the HF addition product was confirmed by chlorination. An ampule containing 15.0 g., 0.08 mole, of fraction 1, 14.0 g., 0.20 mole, of chlorine and 8 ml. of water, was illuminated for 5 days with eight 15 watt General Electric 360 BL fluorescent lamps. After removing excess chlorine 12.0 g., 68%, crude yield of dichloride was obtained; after distillation, 9.0 g., b.p. 32.5–35.5° (733 mm.) f.p. 1.0° (range 0.7°), $n^{20}{}_D$ 1.3042. The freezing point of 1.0° clearly differentiates the product obtained from $CClF_2CClFCF_3$, b.p. 34.7° (760 mm.), f.p. −136° (range 1°), $n^{20}{}_D$ 1.3029.[27] Attempted dehalogenation of fraction 1 with zinc in dioxane did not yield $CF_3CF{=}CF_2$, b.p. −29°.

2. A 10-g., 0.06 mole, sample of $CF_2{=}CClCF_3$ was distilled into an ampule containing 10 g. of tetraethylammonium fluoride and 33 g. of alcohol-free chloroform. After sealing, the ampule was allowed to slowly warm to about 15°, held there for 10 minutes and then chilled in Dry Ice and opened. The solution was homogeneous on melting and yellow in color. The ampule contents were distilled into cold traps at <0° under low pressure. Redistillation yielded 6.2 g., b.p. 14° (735 mm.), mol. wt. 182, 184. The infrared spectra showed no C=C absorption and a C—H absorption at 3.36 μ. Chlorination yielded $CF_3CCl_2CF_3$, b.p. 36–37° (740 mm.), f.p. −1 to 0°, $n^{20}{}_D$ 1.3036.

Hexafluoropropene.—1. An ampule was charged with 21.0 g., 0.14 mole, of $CF_2{=}CFCF_3$, 11.0 g., 0.19 mole, of KF and 85 ml. of 94% formamide and shaken by means of a reciprocating shaker for 5 hours at approximately 25°. The formamide layer was dark brown after this treatment. Distillation yielded 16 g. of low boiling material. This material and an equimolar amount of bromine were sealed into an ampule and illuminated as described above. After removal of excess bromine, 14 g., 59%, of CF_3CHFCF_3 was isolated and identified by means of its infrared spectrum. A small residue, 1 g., presumably the dibromide $CBrF_2CBrFCF_3$, was obtained.

2. A total of 7.0 g., 0.05 mole, of $CF_3CF{=}CF_2$ was bubbled through 500 ml. of 2.0 *M* KF solution in 99% formamide maintained at 65 ± 5° during a 24-hour period. The bubbles

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(45) W. T. Miller, Jr., E. Bergman and A. H. Fainberg, THIS JOURNAL, **79**, 4159 (1957).

(46) E. T. McBee, A. Truchan and R. O. Bolt, *ibid.*, **70**, 2023 (1948).

dispersed by a coarse grade sintered glass disk traversed a length of 3.3″ in passing through the solution. The volatile product, 8.0 g., was collected in a cold trap and treated with 10 g., 0.063 mole, of bromine with illumination for one day. After bubbling the remaining volatile material through sodium sulfite solution, 1.2 g., 21%, of CF_3CHFCF_3 was obtained, identified by its infrared spectrum. A 9.0 g. residue of $CBrF_2CBrFCF_3$ was obtained. Distillation yielded 8.5 g., b.p. 71–72° (740 mm.), n^{20}_D 1.3568; reported[47] for $CBrF_2CBrFCF_3$: b.p. 72–73° (760 mm.), n^{20}_D 1.3588.

3. Hexafluoropropene, 25 g., 0.16 mole, and Dry Ice, 23 g., were added to a steel lecture cylinder containing 28.2 g. of tetraethylammonium fluoride, in 50 ml. of chloroform at Dry Ice temperature. The bomb was sealed and held at room temperature for 7 days. It was then vented to a cold trap and the liquid which was collected distilled to give 23 g., 84%, of CF_3CHFCF_3, b.p. −16 to −14° (740 mm.), identified by its infrared spectra.

4. Hexafluoropropene, 21 g., 0.14 mole, was condensed into a steel lecture cylinder containing a solution of 17.4 g., 0.30 mole, of KF in 100 ml. of water plus 100 ml. of peroxide-free dioxane. The bomb was sealed and shaken at room temperature for 12 days. On venting into a trap, 4 g. of volatile product was obtained. The product was completely saturated to $KMnO_4$, had a mol. wt. of 171 (Dumas), and its infrared spectra corresponded to that for CF_3CHFCF_3.

1,4-Dibromohexafluoro-2-butene.—A mixture of 90 g., 1.66 moles, of KF, 500 ml. of redistilled formamide and 100 ml. of benzene was dried by distilling out a portion of the benzene and formamide, and then treated with 100 g., 0.31 mole, of $CBrF_2CF{=}CFCBrF_2$. The mixture was maintained at 60° by means of an oil-bath and stirred for 3 days. During this period 52 g. of material collected in the Dry Ice trap. An additional 1 g. of insoluble material was obtained on diluting the reaction mixture with water. The trap condensate was distilled through a 14 × 500 mm. glass helix-packed column to yield: (1) 18.5 g., b.p. 2–4° (749 mm.), mol. wt. 212, 214 (Dumas), strong infrared absorption at 5.77 μ; (2) 7.0 g., b.p. 4–6° (749 mm.); (3) 17.0 g., b.p. 6–10° (749 mm.), mol. wt. 220, 223 (Dumas); (4) 8.0 g., residue.

Fractions 1 and 2, presumed to be a mixture of CF_3-$CHFCF_2CF_3$ and $CF_3CF{=}CFCF_3$ on the basis of molecular weight and infrared absorption, were treated with excess bromine for 1 day. The unbrominated material remaining volatile at room temperature was washed with basic sodium sulfite solution to yield 14 g., 21%, of $CF_3CHFCF_2CF_3$, f.p. −129.0° (range < 0.3°). The structure of $CF_3CHFCF_2CF_3$ was based on the identity of its infrared absorption spectrum with that of the HF addition product of $CF_3CF{=}CFCF_3$. Further, the observed infrared absorption was different from that of the known $CF_3CF_2CF_2CHF_2$.[48] Residual material from the bromination was washed free of excess bromine and dried to yield: (5) 20 g., 18%, calculated as CF_3CBr-$FCBrFCF_3$. Distillation of 5 yielded: (6) 4 g., b.p. 90–95.0 (727 mm.), n^{20}_D 1.3501; (7) 12.0 g., b.p. 95.0–96.0 (727 mm.), n^{20}_D 1.3568; reported[49] for $CF_3CBrFCBrFCF_3$, b.p. 96.0° (760 mm.), n^{20}_D 1.3574; (8) 1 g., b.p. 96.0° (727 mm.).

Fraction 3 was shown to be largely $CF_3CHFCF_2CF_3$ by its infrared spectra and the results described above. Fraction 4 was indicated as mostly $CF_3CHFCF_2CBrF_2$ but containing some $CF_3CF{=}CFCBrF_2$ as shown below.

In an experiment carried out as described above but with omission of benzene drying, 70 g., 0.22 mole, of $CBrF_2CF{=}CFCBrF_2$, 36 g., 0.61 mole, of KF and 200 ml. of 99% formamide was heated at 60° with stirring for 3 days. At the end of this period 18.5 g. had collected in the Dry Ice trap. Distillation yielded: (1) 12.5 g., b.p. −2.5° to +2.5°; and (2) 5 g. residue. Fraction 1 was shown to be a mixture of $CF_3CHFCF_2CF_3$ and $CF_3CF{=}CFCF_3$ which contained a small amount of $CF_2{=}CFCF_2CF_3$ by infrared examination, absorption at 3.36, 5.60 and 5.75 μ corresponding to C—H, $CF_2{=}CF{-}R_x$ and $R_xCF{=}CFR_x$, respectively.

Steam distillation of the reaction mixture yielded 23 g. of water-insoluble material from which 17.5 g., b.p. 57–60° (743 mm.), n^{20}_D 1.3086, mol. wt. 272 (cryoscopic in benzene), was obtained. This material had a weak infrared absorption at 5.78 μ indicating the presence of $CF_3CF{=}CFCBrF_2$ in addition to $CF_3CHFCF_2CBrF_2$.

Another sample of material, b.p. 57–60°, obtained similarly by reaction of $CBrF_2CF{=}CFCBrF_2$ with KF in formamide was redistilled through a glass helix-packed column to yield: (9) 7.5 g., b.p. 51–57° (745 mm. n_{20D} 1.3069; (10) 12.5 g., b.p. 57.0–59.0° (745 mm.), f.p. −94° (range 4.2°), n^{20}_D 1.3064, d^{20}_4 1.8397, MR_D 29.1; mol. wt. 279, 283; Br 28.5, 28.8%; calcd. for $CF_3CHFCF_2CBrF_2$, MR_D 29.2, mol. wt. 281, Br 28.5%; (11) 1.5 g., b.p. 59.0° (745 mm.), n^{20}_D 1.3060; (12) 0.5 g. residue. The infrared spectrum of fraction 10 indicated a small amount of unsaturated impurity absorbing at 5.74 μ, most probably due to $CF_3CF{=}CFCBrF_2$. The unsaturated impurity could be removed by shaking with basic aqueous permanganate. Distillation of a fraction similar to (10) which had been subjected to this treatment yielded: (13) 3.0 g., b.p. 56.0–59.0° (733 mm.), n^{20}_D 1.3045; (14) 6.0 g., b.p. 59.0° (733 mm.), n^{20}_D 1.3048; (15) 2.0 g., b.p. 59.0° (733 mm.), n^{20}_D 1.3050; (16) 1.0 g. of residue, n^{20}_D 1.3142.

The structure of $CF_3CHFCF_2CBrF_2$ was confirmed by chlorination. An ampule containing 17 g., 0.06 mole, of this compound, 16 g., 0.23 mole, of chlorine and 10 ml. of water was allowed to stand with illumination for 34 days. After destroying excess chlorine 17.5 g. of material was recovered. Distillation yielded: (17) 15.5 g., b.p. 78–80°, largely b.p. 79–80 (740 mm.), n^{20}_D 1.3305; (18) 2.0 g. of residue. Attempted dehalogenation of fraction 17 with zinc in dioxane yielded only reduced and coupled products but no butene as determined by infrared absorption. This result showed that the chlorine and bromine were not vicinal and hence that only $CClF_2CF_2CF_2CBrF_2$ and $CF_3CClFCF_2CBrF_2$ were possible structures. Only the latter structure is consistent with the observed orientation of anionic attack on fluoroolefins.

Octafluoro-2-butene.—A glass ampule was charged with 37 g., 0.19 mole, of $CF_3CF{=}CFCF_3$, 16 g., 0.27 mole, of KF and 150 ml. of redistilled formamide and rocked at 81 ± 3° for 24 hours. After opening the ampule, 26 g. of distillate was condensed into a cold trap. This material was sealed with 21 g. of bromine and illuminated for 1 day with a 100 watt incandescent lamp. After destroying excess bromine, 10 g., 17%, of $CF_3CHFCF_2CF_3$ was obtained (see above, only $CF_3CHFCF_2CF_3$ can be formed from $CF_3CF{=}CFCF_3$ by addition of HF). Another 15 to 20% of $CF_3CHFCF_2CF_3$ was lost during transfer. A residue of 10 g., 10%, of $CF_3CBrFCBrFCF_3$ was also isolated. Distillation of this material yielded 8 g., b.p. 95–100° (735 mm.), n^{20}_D 1.3555.

Perfluoro-1-heptene.[41] A solution of 5.0 g., 0.014 mole, of perfluoro-1-heptene in 50 ml. of chloroform (Mallinckrodt analytical grade, washed with sulfuric acid and water to remove alcohol, and dried) was added to a solution of 0.86 g. of tetraethylammonium fluoride, m.p. 115–116° dec., in 20 ml. of chloroform. After exactly 5 minutes the chloroform solution was quickly chilled to about 0° and carefully extracted with two 50-ml. portions of water and then with 30 ml. of water. A total time of 20 minutes had elapsed at this point. On distillation of the chloroform solution the perfluoroheptene was found to azeotrope with the chloroform and two phases formed in the distillate. The first fraction of 20.2 g. yielded 4.5 g. of lower fluorocarbon layer after cooling. This material had two weak infrared absorption bands at 5.61 and 5.84 μ (24 mm. sample pressure in a 10-cm. cell). The 5.61 μ band corresponded to about 12% of unchanged perfluoro-1-heptene in the mixture and the 5.84 μ band to less strongly absorbing internal olefins.

A second reaction mixture consisting of 5.0 g. of perfluoro-1-heptene and 3.5 g. of tetraethylammonium fluoride in 130 ml. of chloroform was let stand for 24 hours. After washing and distillation, a 4.0-g. fluorocarbon fraction was separated. This material showed a very weak infrared absorption at 5.61 μ (40 mm. pressure, 10-cm. cell) corresponding to 1 to 2% perfluoro-1-heptene.

Gas chromatographic analysis of the above perfluoroheptene products with a 0.25″ × 12′ n-hexadecane-on-Celite column showed three principal fractions corresponding to the terminal olefin and to two new products. The 5-minute reaction product in addition to the starting olefin consisted largely of a single new fraction, 68% based on chromatogram area. The 24-hour product consisted principally of this fraction plus a major additional product, 21 and 66% based on chromatogram areas. The internal olefins had shorter retention times than the terminal olefin.

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(47) Reference 28, p. 664.

(48) Reference 38, footnote 8, p. 4525.

(49) Reference 28, p. 670.

Chlorination of the above products yielded a mixture of high boiling chlorides which were distinguishable from the dichloride of perfluoro-1-heptene but which had similar retention times. Analysis of aliquots of the combined aqueous extracts from the above reactions accounted for 85% of the fluoride utilized in the first reaction and 95% of that utilized in the second reaction. Small amounts of chloride ion were also detected.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PURDUE UNIVERSITY]

The Configurational Relationship of α-Phenylnitroethane and α-Phenylethylamine

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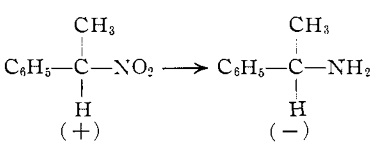
Contrary to an earlier report[3] by Kornblum and Fishbein, reduction of dextrorotatory α-phenylnitroethane gives levorotatory α-phenylethylamine. The earlier report[3] that dextrorotatory 2-nitroöctane gives dextrotatory 2-aminoöctane has been confirmed.

Recently,[2] the observation was made that dextrorotatory α-phenylnitroethane yields levorotatory α-phenylethylamine on reduction by iron and acetic acid. Inasmuch as Kornblum and Fishbein[3] had previously reported that (+)-α-phenylnitroethane gives (+)-α-phenylethylamine on hydrogenation over platinum oxide, this was a most unexpected result. The whole matter has, therefore, been reinvestigated.



$$C_6H_5-\underset{\underset{(+)}{H}}{\overset{CH_3}{C}}-NO_2 \longrightarrow C_6H_5-\underset{\underset{(-)}{H}}{\overset{CH_3}{C}}-NH_2$$

Catalytic reduction of α-phenylnitroethane over platinum oxide in acetic acid had previously been carried out a total of four times.[3] Despite the use of a relatively large amount of catalyst—one gram of platinum oxide for six to eight grams of the nitro compound—no difficulty was reported in obtaining pure α-phenylethylamine (55–61% yields).[3] In the present study a total of thirteen experiments was carried out. When platinum oxide was used in amounts corresponding to that employed by Kornblum and Fishbein[3] no α-phenylethylamine could be isolated. In one run an amine whose $n^{20}D$ and b.p. corresponded to those of α-cyclohexylethylamine[4] was obtained. In another experiment almost twice the amount of hydrogen required for reducing the $-NO_2$ to $-NH_2$ was absorbed and a neutral product, which had the properties of ethylcyclohexane, was isolated.

Efforts to stop the reduction at the α-phenylethylamine stage by using less platinum oxide and operating at lower pressures gave erratic results. Usually the α-phenylethylamine was contaminated with another amine (probably α-cyclohexylethylamine[4]) and the yields of basic material varied all the way from 4 to 69%, the average being 23%.

In two early experiments racemic α-phenylnitroethane gave pure α-phenylethylamine. Attempts at repetition with the optically active nitro compound were, however, less than total successes. One experiment, however, is worth discussing. Here α-phenylnitroethane of $\alpha^{30}D$ − 9.58° gave dextrorotatory α-phenylethylamine ($\alpha^{26}D$ + 9.48°) rather than the levorotatory α-phenylethylamine previously reported.[3] This α-phenylethylamine of $\alpha^{26}D$ + 9.48° was contaminated with an amine and if, as is probable, the contaminant was α-cyclohexylethylamine, it was present to the extent of *ca.* 6%. Since α-cyclohexylethylamine and α-phenylethylamine of the same configuration have opposite signs of rotation, the possibility that the discrepancy between the present results and those of Kornblum and Fishbein derives from contamination by α-cyclohexylethylamine was considered. However, when a sample of α-phenylethylamine ($\alpha^{27}D$ + 32.37°) was hydrogenated over platinum oxide in acetic acid it gave α-cyclohexylethylamine of $\alpha^{25}D$ − 2.77°.[5] Clearly then contamination by 6% of α-cyclohexylethylamine would not reverse the sign of rotation of α-phenylethylamine.

TABLE I

REDUCTIONS OF OPTICALLY ACTIVE α-PHENYLNITROETHANE[a]

	α-Phenylnitroethane				α-Phenylethylamine	
Expt.	α^tD	t, °C.	Method of reduction	Yield, %	α^tD	t, °C.
1	+ 0.88°	26	Fe + gl. HOAc	54	− 0.92°	26
2	− 1.48	26	Fe + gl. HOAc	64	+ 1.64	27
3	− 9.58	30	Fe + gl. HOAc	81	+10.32	29.5
4	+10.85	26	$SnCl_2$ + HCl	36	−11.68	26
5	+11.11	24	$SnCl_2$ + HCl	42	−11.54	25
6	− 9.58	30	H_2 + PtO_2 in gl. HOAc	16	+ 9.48[b]	26

[a] All rotations taken on the pure liquid in a 1-dm. tube; α^tD represents observed rotation. [b] This sample of α-phenylethylamine probably contains 6% of α-cyclohexylethylamine.

α-Phenylethylamine and α-cyclohexylethylamine pick up carbon dioxide very rapidly and one could envision the possibility that carbonate (and/or carbamate) formation might be the source of the discrepancy.[6] Consequently, the rotations of samples of α-phenylethylamine and α-cyclohexylethylamine were determined before and after

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(1) Ethyl Corporation Fellow, 1956–1957.

(2) D. E. Hardies, Ph.D. Thesis, Purdue University, June, 1957.

(3) N. Kornblum and L. Fishbein, THIS JOURNAL, **77**, 6267 (1955); L. Fishbein, Ph.D. Thesis, Purdue University, 1954.

(4) The reduction of α-phenylethylamine to α-cyclohexylethylamine in 82% yield occurs under the conditions employed in these catalytic hydrogenations (*cf.* Experimental).

(5) This is in agreement with W. Leithe (*Ber.*, **65**, 660 (1932)) who reduced α-phenylethylamine of $[\alpha]^{15}D$ −40.3° to α-cyclohexylethylamine of $[\alpha]^{15}D$ +3.2° using platinum oxide and aqueous acetic acid.

(6) L. E. Young and C. W. Porter, THIS JOURNAL, **59**, 1438 (1937).