and in part by the National Science Foundation (G-6580). In addition, the assistance of Dr. William L. Masterton of this department with the kinetics and of Dr. F. W. McLafferty of the Eastern Research Laboratory of the Dow Chemical Company with the mass spectrographic analyses is gratefully acknowledged.

The Synthesis of Highly Fluorinated Compounds by Use of Potassium Fluoride in Polar Solvents

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Fluorination of highly chlorinated compounds of three or more carbon atoms by the action of potassium fluoride in polar solvents—*e.g.*, N-methyl-2-pyrrolidone—has been found to give fair to excellent yields of highly fluorinated products. Dechlorination and dehydrochlorination of the substrate appear to be first steps in the mechanism, often followed by addition of the elements of hydrogen fluoride, and finally replacement by fluorine of all but highly hindered chlorine atoms. For example, the three-carbon substrates octachloropropane, heptachloropropane, and hexachloropropane yield $CF_3CCl_2CF_3$, $CF_3CHClCF_3$, and $CF_3CH_2CF_3$, in mixtures of varying proportions that can be controlled to some degree by choice of conditions. Hexachlorobutadiene yields the new fluoroölefins *cis-* and *trans*-$CF_3CH{=}CFCF_3$. Cyclic compounds are particularly responsive to this technique—*e.g.*, perfluorocyclopentene is obtained in high yield from perchlorocyclopentene.

The synthesis of organic compounds containing isolated fluorine atoms by the action of anhydrous potassium fluoride on compounds having suitably reactive chlorine atoms has long been known.[1] Glycol solvents have often been used,[2] and more recently the polar amide solvents have been employed, often in more complex exchange reactions.[3] Henne and Sedlak[4] recently showed that vinylic chlorine atoms can be replaced with fluorine by the action of potassium fluoride in polar solvents if they are flanked by highly fluorinated structures. Miller[5] and co-workers have postulated nucleophilic substitution of vinylic chlorine atoms by potassium fluoride in formamide, although the existence of the direct substitution products was obscured by the fact that only saturated hydrogen fluoride addition products could be isolated under the conditions employed.

We have now found, in a study of new routes to highly fluorinated organic compounds, that wholesale replacement of chlorine in highly chlorinated compounds of more than two carbon atoms can be readily accomplished with reactive alkali fluorides in certain polar solvents. Among the most useful solvents are N-methyl-2-pyrrolidone and dimethyl sulfone. The reactions have been carried out at about 200° in ordinary open glass laboratory equipment and are so rapid that even starting materials boiling substantially lower than the reaction mixture can be successfully converted to highly fluorinated products.

Results and Discussion

One- and Two-carbon Compounds.—The reactions of one- and two-carbon compounds were not found to yield useful quantities of fluorinated products, although the observations made with these substrates are helpful in understanding the reaction mechanisms involved in systems of this sort. Table I summarizes the reactions observed.

TABLE I

REACTIONS OF CHLORINATED ONE- AND TWO-CARBON COMPOUNDS WITH KF IN N-METHYL-2-PYRROLIDONE[a]

Starting material	Products	Yield, %
	One-carbon compound	
CCl_4	$CHCl_3$	53
	CHF_3	Minor
	Two-carbon compounds	
CCl_3CCl_3	$CCl_2{=}CCl_2$	54–80
$CHCl_2CCl_3$	$CCl_2{=}CCl_2$	65
$CCl_2{=}CCl_2$	CF_3CHCl_2	5
$CHCl{=}CCl_2$	$CCl{\equiv}CCl$	?
	$CHF{=}CCl_2$	15
	$CHF{=}CClF$	?
$CH_2{=}CHCl$	$CH{\equiv}CH$	?

[a] Where yields are indicated as minor or in question, identification was qualitative, based on infrared absorption spectra.

The data of Table I show that solvent attack on chlorocarbon substrates is an important step in reactions in this system. The reduction of carbon tetrachloride to chloroform and the dechlorination of hexachloroethane to tetrachloroethylene suggest that abstraction of the elements of chlorine by the solvent is involved. N-Methylpyrrolidone alone converted hexachloroethane to tetrachloroethylene in 40% yield, although the yield was as high as 80% when potassium fluoride was also present. In the latter case the inorganic salts isolated from the reaction mixture contained substantial amounts of potassium bifluoride. Apparently abstracted chlorine can react with a solvent proton to yield hydrogen chloride, which then reacts with potassium fluoride to give hydrogen fluoride. This hydrogen fluoride can add to olefinic bonds as shown by Fried and Miller[3c] and as will be discussed later. The fate of the solvent involved in this reaction has not been determined.

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(1) A. L. Henne, *Org. Reactions*, **II**, 49 (1944).

(2) (a) F. W. Hoffman, *J. Org. Chem.*, **15**, 425 (1950); (b) F. L. M. Pattison and J. J. Norman, *J. Am. Chem. Soc.*, **79**, 2311 (1957), and other papers in this series.

(3) (a) I. Blank, Br. Patent 727,768 (April 6, 1955); (b) G. C. Finger and C. W. Kruse, *J. Am. Chem. Soc.*, **78**, 6034 (1956); (c) J. Fried and W. T. Miller, Jr., *ibid.*, **81**, 2078 (1959).

(4) (a) A. L. Henne and J. Sedlak, Abstracts of Papers, 138th National Meeting of the American Chemical Society, New York, N. Y., September 11–16, 1960; (b) A. L. Henne, U. S. Patent 3,024,290, (March 6, 1962).

(5) W. T. Miller, J. Fried, and H. Goldwhite, *J. Am. Chem. Soc.*, **82**, 3091 (1960).

(6) Made by sulfur tetrafluoride treatment of choranil.

Dehydrochlorination can occur when the structure of the substrate is suitable, as shown by the conversion of pentachloroethane to tetrachloroethylene, of trichloroethylene to dichloroacetylene, and of vinyl chloride to acetylene. This was also seen in the conversion of hexachlorocyclohexane to 1,2,4-trichlorobenzene in 84% yield by the system potassium fluoride/N-methylpyrrolidone.

This ability of the system to attack chlorinated compounds with abstraction of the elements of chlorine and hydrogen chloride, while not leading to useful products in one- and two-carbon compounds, has made possible a variety of remarkable conversions with higher chlorocarbons. Reactions observed with open chain three- to six-carbon compounds are summarized in the following sections.

Compounds from the Three-carbon Series.—The most extensively examined group of reactants was the three-carbon compounds containing six or more chlorine atoms. The interplay of all of the reactions observed in one- and two-carbon compounds can be clearly seen in the product pattern obtained from the chlorinated propanes and propenes, as illustrated in Fig. 1. For purposes of discussion, these can be conveniently considered as members of three groups—*i.e.*, Group A, octachloropropane; group B, the heptachloropropanes and hexachloropropene; and group C, the hexachloropropanes and pentachloropropenes. Observed reactions are indicated by solid arrows, and hypothetical intermediate steps are shown by broken arrows.

The most highly chlorinated substrate, octachloropropane (A), gave 2,2-dichlorohexafluoropropane (I) as the major product in yields of about 60%, with minor amounts of a mixture of low-boiling partially fluorinated propanes and propenes (II), and a very small yield of 2,2-dihydrohexafluoropropane (III). The least chlorinated group, the hexachloropropanes and pentachloropropene (C), gave III as the major product in yields of about 20%, with smaller amounts of Group II compounds. The hypothetical tetrachloroallene appears to be the common intermediate through which the group C compounds yield III. Group B, the heptachloropropanes and their dehydrochlorination product, hexachloropropene, gave a mixture of all products I, II, and III. These reactions can be rationalized as involving an interrelated series of chlorination, dechlorination, dehydrochlorination, and hydrofluorination steps followed by ultimate displacement of terminal chlorine atoms by fluorine. Both S_N2 and S_N2' displacements may be involved. I can be assumed to be the normal product from A, II from B, and III from C.

Formation of both I and III from hexachloropropene can be visualized as resulting from dechlorination to the hypothetical tetrachloroallene, leading to III, and addition of the elements of chlorine thus made available to part of the propene, yielding A. A then gives I on fluorination. This hypothesis was strengthened by carrying out the reaction of hexachloropropene in the presence of an excess of a compound known to be dechlorinated by this system—*i.e.*, hexachloroethane. I became the exclusive product from hexachloropropene under these conditions. The formation of Group II and III compounds was completely suppressed when the reaction of octachloropropane (A) was carried out in the presence of hexachloroethane. The relatively poor yields obtained from group C compounds probably result from losses due to degradation and resinification of the highly unsaturated intermediates that are involved in these cases.

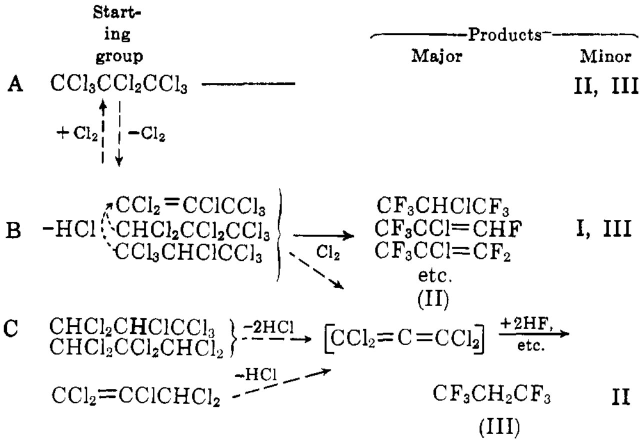


Fig. 1.—Fluorination products of three-carbon chloro-compounds.

Products from Four-carbon Compounds.—The most interesting conversion in this group, as shown in Table II, was the synthesis in good yield of 2-H-heptafluorobutene from hexachlorobutadiene. This reaction appears first to involve the 1,2-addition of one mole of hydrogen fluoride derived from initial attack of solvent and potassium fluoride on the chloro compound. A series of S_N2' displacements of chlorine by fluorine follows in the fashion seen by Fried and Miller[3c] in their studies of the replacement of Cl by F in the propene series. The observed heptafluorobutene is the end product of such a series of reactions. Once initiated, this series of displacements tends strongly to go to completion. When the reaction was carried out at lower temperatures—*e.g.*, 150–160°, yields of the heptafluorobutene were small and a large proportion of the hexachlorobutadiene was recovered unchanged. Compounds of an intermediate degree of fluorine substitution were not obtained in any significant amount.

Table II

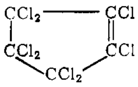
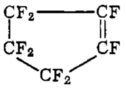
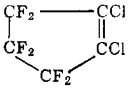
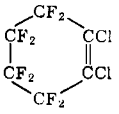
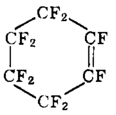
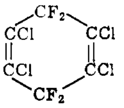
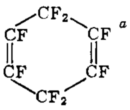
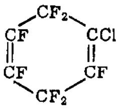
Reactions of Four-carbon Compounds with KF in N-Methyl-2-pyrrolidone

Starting material	Major products	Yield, %
$CCl_2{=}CClCCl{=}CCl_2$	$CF_3CH{=}CFCF_3$	65
$CCl_3CCl{=}CClCCl_3$	$CF_3CH{=}CFCF_3$	20
$CF_3CCl_2CCl_2CF_3$ $CF_3CClFCCl_2CF_3$	$CF_3CClFCClFCF_3$	70
	$CF_3CF{=}CFCF_3$	Minor
	$CF_3CCl{=}CFCF_3$	Minor

Cyclic Compounds.—The rapid and complete conversion of perchlorocyclopentene to its perfluoro analog is perhaps the most surprising reaction observed in the system potassium fluoride/N-methylpyrrolidone. 1,2-Dichlorohexafluorocyclopentene, the normal product of antimony fluoride treatment of the perchloro compound, gave the same product, as shown in Table III. This is striking evidence of the desirability of operating in an open system, in view of Henne's[4a] observation that replacement of the second chlorine is slow when the reaction is carried out in a closed system. The analogous reactions were observed with 1,2,4,5-tetrachlorotetrafluorocyclohexadiene-1,4[6] and 1,2-dichlorooctafluorocyclohexene.[7] Products from the diene were a mixture of isomers, and this reaction has been studied in detail by Dr. W. H. Powell of the Organic Chemicals Department of our company as will be reported in a separate communication. Hexachlorocyclopentadiene, on the other hand, yielded only intractable resinous products, even though analysis of the reaction mixtures showed that a high proportion of the chlorine had been displaced. Under forcing conditions—*i.e.*, 240° in dimethyl sulfone—a small yield of perfluorocyclopentene was obtained from the diene. This undoubtedly resulted from partial chlorination of the diene to perchlorocyclopentene with chlorine abstracted from a portion of the substrate, as in the case of hexachloropropene, and constitutes further evidence for the mechanisms proposed in the three-carbon series. The conversion of hexachlorocyclopentadiene to perfluorocyclopentene could probably be carried out in good yield in the presence of a chlorine source, although this has not been attempted.

TABLE III

REACTIONS OF CHLORINATED CYCLIC COMPOUNDS WITH KF IN N-METHYL-2-PYRROLIDONE

Starting material	Product	Yield, %
		72
	same	76
		71
		~10
		~10
C_6Cl_6	*sym*-$C_6Cl_3F_3$	23
	$C_6Cl_2F_4$	34
	C_6ClF_5	Small

[a] B.p. 56–59°, $n^{20}D$ 1.3132. Single infrared double bond band at 5.68 μ. [b] B.p. 86–89°, $n^{20}D$ 1.3562. Two infrared double bond bands at 5.59, 5.82 μ.

Hexachlorobenzene was converted to *sym*-trichlorotrifluorobenzene, m.p. 57–61°, by the action of potassium fluoride in polar solvents in earlier work by Finger and co-workers.[3b] We have found this is also the major product in the system potassium fluoride/N-methylpyrrolidone, although significant amounts of dichlorotetrafluorobenzene and a small yield of chloropentafluorobenzene, identified from its infrared absorption spectrum, were also obtained. Yields indicated in Table III are those obtained by retreating all fluid fractions from an initial fluorination of hexachlorobenzene. It was not possible to push the reaction all the way to hexafluorobenzene.

Choice of Solvent.—Mixtures of potassium fluoride with any of a wide variety of polar solvents were found to attack chlorocarbons with more or less complete conversion of chlorine to water-soluble chloride form. Table IV lists the solvents tested in order of apparent reactivity in attacking hexachloropropene. In these scouting experiments, no attempt was made to isolate and identify products other than chloride ion. Thus, although many solvents were found to be active for this type of reaction, N-methylpyrrolidone was preferred because of its stability at the required temperature, its high boiling point, its low volatility, and its ready availability. Dimethyl sulfone, while not among those solvents tested in the series of Table IV, appears to be essentially equivalent in action to the pyrrolidone. Its principal disadvantage is that it is a solid at room temperature.

TABLE IV

REACTION OF HEXACHLOROPROPENE WITH POTASSIUM FLUORIDE IN POLAR SOLVENTS

Solvent	Temp., °C.	Time, hr.	Cl displaced, %
Formamide	150	1	71
N-Methylacetamide	150	1	61
N-Methylformamide	100	1	20
Ethylene carbonate	140–180	2	61
Tetramethylene sulfone	150	2	43
Dimethylformamide	145	4	54
N-Methylpyrrolidone	100	3	13
N-Methylpyrrolidone	190–200	3	80
Dimethylacetamide	100	3	11
Nitroethane	114	5	12
α-Butyrolactone	150	2	26
Acetylacetone	140	1	19
Ethyl acetoacetate	150	1	19
Cyclohexanone	160	4	15
Nitropropane	130	4	7
Diglyme	164	4	7
Acetonylacetone	150	1	5
Acetonitrile	82	4 1/2	<1
Nitrobenzene	200	2	<1

Experimental

General Procedure.—Reactions were carried out in three-necked glass flasks fitted with stirrer, thermometer, gas inlet, and a Claisen still head carrying a dropping funnel for addition of the chlorocarbon. The receiver was vented to traps cooled in Dry Ice for collection of low boiling products. In some cases it was found convenient to use a cold finger condenser cooled with Dry Ice, on which volatile products condensed and were collected in a graduated cylinder also so cooled, thus making it possible to observe the course of product formation.

Reagent grade anhydrous potassium fluoride was dried at least two hours in a 150° vacuum oven. N-Methylpyrrolidone was redistilled before use. In the usual procedure, a 100% excess of potassium fluoride over the theoretical requirement was used, although as little as a 20% excess was found adequate in those reactions that were studied in detail. Potassium fluoride has a solubility of about 3% in N-methylpyrrolidone at 190–200°.[8] Salt and solvent were brought to 195°, a gentle flow of dry nitrogen introduced to carry over volatile products, and the chlorocarbon added over a 1–3 hr. period. If the chlorocarbon was a solid, it was added as a concentrated solution in the solvent. If the reactant had a low boiling point—*e.g.*, 1,2-dichlorohexafluorocyclopentene, b.p. 90°, a short length of tubing or a short water-cooled condenser was inserted below the Claisen head to reflux the reactant. Optimum results were in general not obtained at temperatures below 190°.

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(7) E. T. McBee, P. A. Wiseman, and G. B. Bachman, *Ind. Eng. Chem.*, **39**, 415 (1947).

(8) H. L. Jackson, private communication.

Products were distilled in appropriate spinning band stills and characterized by refractive index, infrared absorption spectroscopy, and n.m.r. spectroscopy. Most of the compounds prepared in this work are well characterized in the literature. The preparation and characterization of those which are new are described here.

Synthesis of 2,2-Dichlorohexafluoropropane.—Three hundred and twenty grams (1 mole) of octachloropropane in 400 ml. of N-methyl-2-pyrrolidone was added over 2.5 hr. to a stirred mixture of 522 g. (9 moles) of anhydrous potassium fluoride and 1250 ml. of N-methyl-2-pyrrolidone at 195°. Product distilled as the octachloropropane was added, and its formation was complete 0.5 hr. after addition was finished. There were obtained 151.7 g. (69%) of crude $CF_3Cl_2CF_3$. Residual solvent was distilled and reused in a second run of the same size to give a total of 316 g. of product. This was distilled to yield 35 g. of foreshot, b.p. 24–31°, a main cut at 31–34°, and a small residue. Redistillation of the product gave b.p. 32.2–33.6°, m.p. 3°, $n^{20}D$ 1.3032. The n.m.r. absorption spectrum agreed with the symmetrical structure suggested by the high melting point. Analysis of such a low boiling compound is difficult, but the results agreed fairly well with this composition. Calcd. for $C_3Cl_2F_6$: C, 16.25; Cl, 32.4; F, 51.4; Found, C, 17.45; Cl, 31.5; F, 49.4. Infrared absorption bands were seen at 7.85 and 8.05 μ (C–F), 10.62 and 10.98 μ (C–Cl), and 14.13 μ (CF_3).

Synthesis of 2-H-Heptafluoro-2-butene.—Two hundred and sixty-one grams (1 mole) of hexachlorobutadiene was added to 522 g. of potassium fluoride in 1500 ml. of N-methyl-2-pyrrolidone as above. Yield of low boiling product was 114 g. (65%). On distillation this boiled almost entirely in the range 8.5–15°. After storage in a stainless steel cylinder for about a month, on redistillation this product was found to boil sharply at 7–8°, with only a small tail at 8–10°. Vapor phase chromatography analysis of the main cut showed it to be 95.3% one component, with an adjacent second component accounting for 2.3% of the whole. Infrared and n.m.r. studies agreed with the structure $CF_3CH{=}CFCF_3$, and it is assumed that the *trans* form is the major product, with some higher boiling *cis* form that tends to isomerize to *trans* on standing. Infrared bands were seen at 3.38 μ (C—H), 5.68 μ (C═CF), 7.10, 7.31, 8.18, and 8.35 μ (C—F), 11.55 μ (?), and 13.55 μ (CF_3). In the 40-Mc. n.m.r. spectrum, using CF_3COOH as the standard, doublets at +39 c.p.s. and +620 c.p.s. accounted for two different CF_3 groups, the doubling being attributed to *cis-trans* isomerism. A single fluorine atom was indicated by a peak at −1682 c.p.s.

Additional Observations.—Potassium fluoride is the most practical salt for this reaction, although cesium fluoride was found at least as effective, and rubidium fluoride would undoubtedly also be active. Potassium bifluoride was active but very corrosive in glass equipment. Sodium fluoride showed little activity, as all workers in this field have found. With mixtures of potassium and sodium fluoride, the yield of product could be accounted for entirely by the potassium salt, in agreement with the observation of Finger.[3b] Micropulverization of the salt seemed to help in the sense that less tar formation occurred, but yields were not significantly improved. Addition of glass beads to give a grinding action on the salt made little difference in yields. Addition of various agents in an effort to catalyze the reaction was ineffective, although it was found that those which could be expected to interfere with the chlorine-solvent interaction—*e.g.*, zinc oxide—prevented the reaction entirely.

Determination of the amount of chlorine ion formed was made by filtering precipitated salts from the reaction mixture, washing with acetone, and dissolving them to a known volume in water. An aliquot was then titrated for chloride ion. The presence of substantial amounts of potassium acid fluoride was frequently indicated by the strongly acidic nature of this salt solution, which was neutralized with potassium carbonate to prevent attack on the glass equipment used.

The reactions with the lower boiling chloroethylenes were carried out in a Hastelloy rocker bomb.

Conclusions

The combination of anhydrous potassium fluoride with stable polar solvents, of which N-methyl-2-pyrrolidone is the most convenient, has been found to be an exceedingly powerful agent for the synthesis of highly fluorinated organic compounds from highly chlorinated starting materials. Frequently, more extensive conversions can be accomplished in simple glass equipment with this system than with difficultly handled fluorination systems such as hydrogen fluoride and antimony halides. The reactions that occur in potassium fluoride systems are complex and often result in formation of products with a substantially different structure from that of the starting materials, although in special cases, as in the cyclopentenes, displacement of chlorine by fluorine appears to be straightforward. This latter case may, of course, involve intermediate stages of hydrofluorination and dehydrochlorination that are not apparent from the over-all result. It should be pointed out that displacement of a single chlorine atom by fluorine is readily accomplished by this technique. N-Octyl chloride gave an excellent yield of the corresponding fluoride when treated by the procedure described under Experimental.

These systems give most useful results with compounds in the three- to six-carbon range. One- and two-carbon compounds have not given useful yields of fluorocarbons, and larger compounds are likely to be degraded or to yield complex mixtures. Perchloro-1,5-hexadiene, for example, gave the same products as the hexachloropropanes. A cleavage at the 3,4-position seems to be followed by reaction steps again suggesting the hypothetical tetrachloroallene as an intermediate. Many of the products obtained are of synthetic interest, and a variety of useful conversions to second-stage products can be visualized.

Acknowledgment.—This work was initiated on the strength of a suggestion by Prof. A. L. Henne that potassium fluoride in polar solvents should be expected to accomplish unusual displacements of chlorine by fluorine. Helpful discussions with Dr. R. G. Arnold, Dr. P. A. Roussel, and Prof. J. D. Roberts are also gratefully acknowledged. The interest of Dr. W. H. Powell in this reaction and his further studies of it will be reported in another paper. N.m.r. spectra and interpretations were kindly carried out by Dr. T. E. Beukelman of the Organic Chemicals Department of the Du Pont Company.