the aqueous solution. The production of heptafluoropropane during the bromination and chlorination of perfluoro-*n*-propylzinc iodide presumably was due to reaction with hydrogen halide produced by the halogenation of dioxane at the reaction temperatures employed.[41]

Oxygen.—A solution of 0.114 mole of zinc compound in 90 ml. of dioxane failed to gain weight or show any positive signs of reaction when dry oxygen was bubbled into it at a rate of 0.5 mole per hour at room temperature. Likewise, at 90° after two days no evidence of reaction was observed. One gram, 5%, of heptafluoropropane was evolved during this period. Hydrolysis yielded 15 g. or a total of 16 g., 82%, of heptafluoropropane and the hydrolyzate was free of fluoride ion.[42]

In a parallel experiment with oxygen, 0.144 mole of zinc compound in dioxane was illuminated with eight G.E. 15 watt B.L. fluorescent bulbs placed concentrically around and one inch from the Pyrex reaction flask. No positive evidence of reaction was observed during 48 hr. with the solution at 35° and an oxygen flow of 0.5 mole per hour. The temperature was raised to 90–100° and the oxygen flow continued for five days during which time 18 g. of condensate collected in the Dry Ice trap. The system lost 9 g. in weight, presumably by oxygen entrainment. Separation of the trap material yielded 1.5 g., 6%, of heptafluoropropane, and 11 g., b.p. 40°, n^{20}D 1.3290, identified as perfluoro-*n*-propyl iodide, 26%. Hydrolysis of the reaction mixture, which gave a faint test for fluoride, yielded 3 g., 12%, of heptafluoropropane. Distillation of the hydrolysate from excess silver sulfate yielded only 1.4 meq. of acid.

Carbon Dioxide.—A solution of 0.261 mole of zinc compound was placed in a dry lecture cylinder and 70 g., 1.6 moles, of carbon dioxide was added with the cylinder cooled in Dry Ice. The cylinder was closed with a steel valve and heated in a reciprocating shaker at 106° for 110 hr. Carbon dioxide was vented through a sintered glass disk into 500 ml. of 14*N* caustic to yield 4 g. of heptafluoropropane, 9%, which was free of perfluoropropene as tested by infrared spectrum and acetone permanganate. Water, 50 ml., was added to the bomb which was then heated at 100° for 2 hr. to yield 30 g. of material, b.p. <0°, which on redistillation gave 25 g., 56%, of heptafluoropropane, b.p. −13.0 to −12.5° (740 mm.). No perfluorobutyric acid was obtained by distillation of the hydrolyzate from excess silver sulfate.

Carbonyl Compounds.—The essential technique in the reactions summarized below was to heat the reactants together under the conditions specified. The volatile products were isolated by distillation and the residual salts hydrolyzed in order to estimate the quantity of unchanged zinc compound. The percentage yields listed are regarded as approximate values. Water-insoluble products remaining in the hydrolyzate were partially investigated. Only in the case of perfluoro acid chlorides were detectable quantities of the desired products, ketones, produced. The reaction mixtures in which most of the zinc compound was consumed during the heating period were characteristically dark and tarry. The reaction mixtures in which most of the zinc compound was unchanged, despite the relatively high temperatures employed, remained fairly clean. Varying amounts of ester by-products were shown to be formed by cleavage of dioxane in the reactions with acid halides and anhydrides.

Illustrative results are summarized below. In each case following the name of the organic reagent is given: the number of moles organic reagent per mole of zinc compound, the reaction time and temperature, the percentage heptafluoropropane (I) evolved during the reaction period and the percentage unchanged zinc compound II and/or other products isolated. Percentages are based on the initial concentration of zinc compound.[39]

Perfluoro-*n*-propylzinc Iodide in Dioxane Solution.—*Paraformaldehyde:* 3.3, 5.5 days at 130°, 46% I (containing some formaldehyde), 42% II. *Benzophenone:* 0.82, 18 hr. at 80° plus 7 days at 115°, 8% I, 62% II. *Ethyl perfluoro-n-butyrate:* 1.1, 24 hr. at 80° plus 4 hr. at 105°, I and II were not determined quantitatively, but 75% ethyl perfluoro-*n*-butyrate was recovered. *Benzoyl chloride:* 0.84, 18 hr. at 90°, 14% I, 49% II (β-chloroethyl benzoate, ethylene glycol dibenzoate and possibly β-iodoethyl benzoate were shown to be present). *Perfluoro-n-butyryl chloride:* 1.5, 2 hr. at 60°, 8% I, 76% II. 1.4, 16 hr. at 110°, 63% I (containing some acid chloride), 31% II.

Perfluoro-*n*-propylzinc Iodide Solid Dioxane Solvate.—One to two moles of dioxane plus approximately 0.25 mole of zinc iodide were present per mole of organozinc compound. Complete conversion of the zinc compound took place in each case. *Acetic anhydride:* 5.6, 12 hr. at 110°, 56% I. *Acetyl chloride:* 4.4, 12 hr. at 90°, 78% I. *Benzoyl chloride:* 1.8, 12 hr. at 130–140°, 59% I, 17% heptafluoro-*n*-propyl iodide. *Trifluoroacetyl chloride:* 2.4 (plus chlorobenzene diluent), 15 hr. at 120°, compound I was mixed with trifluoroacetyl chloride and was not determined quantitatively, 6% perfluoro-2-pentanone. *Perfluoro-n-butyryl chloride:* 1.9, 65 hr. at 120°, compound I was mixed with perfluoro-*n*-butyryl chloride; 15% perfluoro-4-heptanone, b.p. 72–74° (738 mm.), yielded a solid ammonia adduct, m.p. 57.5–58.5°, phenylhydrazone, m.p. 35–37°, and formed a liquid hydrate; reported[43] for perfluoro-*n*-heptanone b.p. 75° (740 mm.).

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[41] C. L. Butler and L. H. Cretcher, THIS JOURNAL, **54**, 2987 (1932).

[42] The postulated product, $CF_3CF_2CF_2OZnI$, would be expected to break down to give perfluoropropionic acid and hydrogen fluoride.

[43] A. L. Henne and W. C. Francis, THIS JOURNAL, **75**, 991 (1953).

[CONTRIBUTION FROM THE BAKER LABORATORY OF CHEMISTRY, CORNELL UNIVERSITY]

Preferential Replacement Reactions of Highly Fluorinated Alkyl Halides. I. Preparation of Certain Fluorinated Allyl Iodides[1,2]

BY WILLIAM T. MILLER, JR., AND ARNOLD H. FAINBERG

RECEIVED MARCH 12, 1957

Certain fluorinated allyl chlorides, including 3-chloropentafluoropropene and 2,3-dichlorotetrafluoropropene, have been found to react readily with sodium iodide in anhydrous acetone to yield 3-iodopentafluoropropene and 2-chloro-3-iodotetrafluoropropene, respectively. Other compounds such as 1,1,2,3-tetrachlorodifluoropropene and 1,3-dichlorotetrafluoropropene were completely inert under more rigorous conditions. The resistance of the latter two compounds to substitution suggests that the ready reaction of the first two does not involve direct reaction at the α-carbon atom, but rather anionic attack by iodide ion on the γ-carbon atom, with allylic shift and elimination of chloride ion, an SN2′ mechanism.

As part of a general investigation of the reactivity of X in highly halogenated compounds of the type RCF_2X, $RCFXR'$ and $RR'R''CX$, where $X = Cl$, Br or I, a number of compounds containing the group $CClF_2$ in the allylic and benzylic positions have been prepared. Physical properties for these compounds, and for their precursors and derivatives, are listed in Table I. For the

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[1] Presented at the 119th Meeting of the American Chemical Society, Boston, Mass., April, 1951, Abstracts of Papers, p. 24-M. Based in part on the thesis submitted by Arnold H. Fainberg to the Graduate School of Cornell University in partial fulfillment of the requirements for the Ph.D. degree, June, 1950.

[2] This work has been supported in part by the Office of Naval Research.

TABLE I

PHYSICAL PROPERTIES OF COMPOUNDS

No.	Compound	B.p.[a] (760 mm.), °C.	B. range,[b] °C.	F.p., °C.	F.p. dep.,[c] °C.	n^{20}_D	d^{20}_4	MR^{20}_D Found[d]	MR^{20}_D Calcd.[e]
Ia	$CClF_2CClFCClF_2$	73.9	0.1	“α,” −141.3 “β,” −135.0	<0.1	1.3501	1.6541[g]	30.89	30.97
Ib	$CClF_2CClFCClF_2$	73.7	.1	−142.7[f]		1.3502	1.6545	30.89	
Ic[h]	$CClF_2CClFCClF_2$	73.7	1.0	Glass at −150		1.3504	1.6563	30.87	
	$CClF_2CClFCClF_2$[4]	74.0	..	−72 ± 3		1.3512	1.6631	30.81	
IIa	$CF_2{=}CFCClF_2$	7.3	< .1	−139.8	<0.1	....	1.5152[i]		
IIb	$CF_2{=}CFCClF_2$	7.4	< .1	−143.	..	....	1.5162[i]		
	$CF_2{=}CFCClF_2$[4]	7.5	..	Glass		1.3050[j]	1.5116[j]	20.96[k]	21.09
III	$CBrF_2CBrFCClF_2$	113.1	< .1	−118.0	0.2	1.4028	2.2016	36.15	36.19
	$CBrF_2CBrFCClF_2$[8]	56 (105)	2	−123.1	0.6	1.4029	2.205		
IV	$CClF{=}CFCF_3$	8.0	<0.1	−150.1	Large[l]	....	1.5158[i]		
	$CClF{=}CFCF_3$[5a]	7.9[m]	..	−158.	5[l]	....	....		
	$CClF{=}CFCF_3$[4]	8.4	..	−156.8	2.8[l]	....	....		
Va	$CCl_2FCClFCF_3$	73.4	< .1	−55.1	0.4	1.3530	1.6634	30.95	30.97
Vb	$CCl_2FCClFCF_3$	73.4	.4	−68	Large	1.3532	1.6612	31.00	
	$CCl_2FCClFCF_3$[5a]	73.5[m]	..	Glass	..	1.3529	1.6643	30.92	
VI	$CF_2{=}CFCF_3$	−29.7	1	−155.5	0.1	....	....	...	
	$CF_2{=}CFCF_3$[9]	−29.8	..	−156.2	..				
VII	$C_6H_5CF_3$	102.2	<0.1	−28.9	< .1	1.4148	1.1887	30.77	[n]
	$C_6H_5CF_3$[10]	102.0	.01	−29.14	.02				
VIII	$C_6H_5CClF_2$	140.6	0.1	−49.8	<0.1	1.4648	1.2509	35.92	35.81[o]
	$C_6H_5CClF_2$[11]	142.2		..		1.4697[p]	1.2544[p]	36.17[k]	
IX	$C_6H_5CCl_2F$	94.8 (50)	.1	−26.8	<0.1	1.5126	1.3116	41.00	40.85[o]
	$C_6H_5CCl_2F$[12]	178–180		..		....	....		
X	$C_6H_5CCl_3$	146.9 (100)	< .2	−4.5	<0.1	1.5580	1.3734	45.89	[n]
	$C_6H_5CCl_3$[13]	89 (10)	.5	−4.4	..	1.5579	1.3741	45.86	
XI	$CCl_2{=}CClCCl_3$	141.4 (100)	< .2	−72.9	Large	1.5491	1.7621	44.91	45.1
	$CCl_2{=}CClCCl_3$[14]	211.6[m]				1.5491	1.766	44.82	
XII	$CCl_2{=}CClCCl_2F$	170.3	< .2	−95.5	<0.4	1.5053	1.7075	40.37	40.3
	$CCl_2{=}CClCCl_2F$[5b]	170.2[m]	..	Glass	..	1.5050	1.7041	40.44	
XIII	$CCl_2{=}CClCClF_2$	128.1	< .1	−102.8	0.2	1.4572	1.6562	35.51	35.4
	$CCl_2{=}CClCClF_2$[5b]	128.0[m]		−103.0		1.4573	1.6598	35.44	
XIV	$CCl_2{=}CClCF_3$	88.4	< .1	−114.9	<0.1	1.4094	1.6165	30.52	30.54
	$CCl_2{=}CClCF_3$[5b]	88.3[m]		−114.7		1.4095	1.6188	30.49	
XVa	$CClF_2CCl_2CClF_2$	112.3	< .1	−45.9	1.7	1.3960	1.7184	35.50	35.50
XVb	$CClF_2CCl_2CClF_2$	112.4	< .1	−44.7	1.5	1.3954	1.7181	35.46	
	$CClF_2CCl_2CClF_2$[15]	112.0[m]		−42.9	1.	1.3958	1.7199	35.45	
XVI	$CF_2{=}CClCClF_2$	44.8	< .1	−120.7	0.1	1.3484	1.5399	25.46	25.48
	$CF_2{=}CClCClF_2$[5b]	44.7[m]		−121.2		1.3484	1.5406	25.45	
XVII	$CBrF_2CBrClCClF_2$	86.7 (100)	< .1	−44	[q]	1.4471	2.2480	40.75	40.71
XVIII	$CF_2{=}CFCF_2I$	54.7	.1	“α,” −143.3 “β,” −131.6	0.9	1.3886	2.1093	28.90	29.1
XIX	$CF_2{=}CClCF_2I$	92.4	< .1	−106.6	0.5	1.4409	2.1567	33.59	33.5

[a] Computed from the observed b.p. t_0 at pressure p_0 with the equation $t_{760} = t_0 + 0.043(760 - p_0)$.[6] [b] Boiling range of the center cut on which all other physical properties were taken. [c] F.p. depression with the material half frozen. [d] MR^{20}_D found $= (n^2 - 1)M/(n^2 + 2)d$. [e] Calculated from the group and atomic refractions proposed elsewhere.[7] These refractions are based in part on the data of Table I. [f] “β” phase not obtained. [g] d^{30}_4 1.6310. [h] These properties are substantially identical with those previously reported[8] for a material of the same origin. [i] At 0.0°. [j] At 1.4°. [k] Corrected to 20.0°, assuming the temperature dependence of MR to be +0.015% per °C.[7] [l] Presumably a mixture of *cis–trans* isomers, and therefore not necessarily an indication of the presence of other impurity. [m] Pressure not specified. [n] On the basis that MR^{20}_D for $C_6H_5CH_3 = 31.095$[16] and AR^{20}_D H = 1.029,[16] these data yield AR^{20}_D Cl = 5.96 and AR^{20}_D F = 0.92 in $C_6H_5CX_3$. [o] Based on the data calcd. for $C_6H_5CCl_3$ and $C_6H_5CF_3$.[n] [p] At 13°. [q] See exptl. section.

most part, the present data supplement or substantially revise data previously reported.

3-Chloropentafluoropropene.—This compound was prepared by dechlorination of 1,2,3-trichloropentafluoropropane, and its identity therefore depended on the identity of the latter compound.

(3) W. T. Miller, Jr., J. M. Phelan and A. H. Fainberg, Abstracts of Papers, 119th Meeting of the American Chemical Society, Boston, Mass., April, 1950, p. 23-M.

(4) A. L. Henne and T. H. Newby, THIS JOURNAL, **70**, 130 (1948).

(5) (a) A. L. Henne and T. P. Waalkes, *ibid.*, **68**, 496 (1946); (b) A. L. Henne, A. M. Whaley and J. K. Stevenson, *ibid.*, **63**, 3478 (1941); (c) A. H. Fainberg and W. T. Miller, Jr., unpublished work.

(6) N. A. Lange, "Handbook of Chemistry," 3rd Ed., Handbook Publishers, Inc., Sandusky, Ohio, 1939, p. 667.

(7) A. H. Fainberg and W. T. Miller, Jr., forthcoming publication.

(8) W. T. Miller, Jr., Nat. Nuclear Energy Ser., Div. VII, I, "Prepn., Properties, and Technol. of Fluorine and Org. Fluorine Compds.," McGraw-Hill Book Co., Inc., New York, N. Y., 1951, chap. 32, pp. 567–685.

(9) E. G. Young and W. S. Murray, THIS JOURNAL, **70**, 2814 (1948).

(10) J. C. Potter and J. H. Saylor, *ibid.*, **73**, 90 (1951).

(11) F. Swarts, *Bull. classe sci., acad. roy. Belg.*, [3] **35**, 375 (1898).

(12) F. Swarts, *ibid.*, 414 (1900).

The bulk of the trichloride was prepared by the photochemical addition of chlorine to the chloropentafluoropropene fraction obtained from the high-temperature thermal reaction of chlorotrifluoroethylene.[3,8] The physical properties of this trichloride (compound Ic in Table I) were found to differ markedly from those previously reported in the literature for 1,2,3-trichloropentafluoropropane by Henne and Newby.[4] For this reason, pure samples of the trichloride were synthesized from several compounds of known identity. The purity of these samples (Ia, Table I) was established by cooling curves; in both cases freezing point depressions were less than 0.1°. Repetition of the synthesis of Henne and Newby gave a trichloride Ib with virtually the same properties as Ia. These properties differ markedly from those of the other isomeric trichlorides which can be formed by the addition of chlorine to the isomeric chloropentafluoropropenes, namely, 1,1,2-trichloropentafluoropropane (V) and 1,2,2-trichloropentafluoropropane.[5a–c] On the basis of the physical properties of the pure compounds, it was concluded that Ic was at least 75%, and probably > 90% 1,2,3-trichloride, the impurity being the 1,1,2- and/or the 1,2,2-trichlorides.

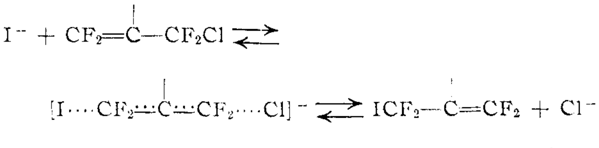
The chloropentafluoropropene IIb obtained by dechlorination of Ic was therefore at least 75% 3-chloropentafluoropropene, the impurity being the 1- and/or 2-chloroölefins.

In view of the similarity of the physical properties, particularly f.p. and density, of the 1,1,2-trichloride (Va) to those reported by Henne and Newby[4] for their 1,2,3-trichloride, it was considered advisable to check their report that 3-chloropentafluoropropene undergoes rearrangement on treatment with antimony trifluorodichloride to form 1-chloropentafluoropropene. Their result was fully confirmed by the present work.

Reactions with Iodide Ion.—α-Chloro-α,α-difluorotoluene, 1,3-dichlorotetrafluoropropene, and 1,1,2,3-tetrachlorodifluoropropene were found to be completely inert to the action of sodium iodide in anhydrous acetone, even at elevated temperatures for prolonged periods of time. In sharp contrast, 3-chloropentafluoropropene and 2,3-dichlorotetrafluoropropene reacted readily at room temperature with the iodide reagent to yield, respectively, 3-iodopentafluoropropene and 2-chloro-3-iodotetrafluoropropene. These reactions have been shown to involve reversible equilibria, in which the allyl chlorides are highly favored over the iodides.[17] That the iodides can be isolated at all is attributed only to the enormously greater solubility of sodium iodide than that of sodium chloride in anhydrous acetone,[18] with consequent displacement of the equilibria toward the iodides.

The resistance of the allylic chlorine in $CClF{=}CFCClF_2$ and $CCl_2{=}CClCClF_2$ to attack by iodide ion suggested that the ready reaction of $CF_2{=}CFCClF_2$ and $CF_2{=}CClCClF_2$ does not involve direct reaction at the α-carbon atom. This is in line with the observation that the chlorine in compounds of the type RCF_2Cl, where R is phenyl or saturated perhaloalkyl, is not capable of substitution by iodine under the same reaction conditions.

On the other hand, an S_N2′ mechanism[20,21,22] involving initial attack by the iodide ion on the far γ-carbon atom with allylic shift and elimination of chloride ion, as shown below, is consistent with the observed differences of reactivity of the allyl chlorides



$$I^- + CF_2{=}\overset{|}{C}{-}CF_2Cl \rightleftarrows [I\cdots CF_2\overset{\cdots}{=}\overset{|}{C}\overset{\cdots}{=}CF_2\cdots Cl]^- \rightleftarrows ICF_2{-}\overset{|}{C}{=}CF_2 + Cl^-$$

Implicit in this formulation is the structural requirement: attack by iodide ion productive of allyl iodide occurs on $CF_2{=}$, but not on $CFCl{=}$ or $CCl_2{=}$. It is considered of direct significance that the identical structural requirement has been found for base-catalyzed additions to fluoroölefins leading to saturated products. Thus, in every case reported to date in which olefins of the type $CF_2{=}CX^1X^2$ (X = H, Br, Cl and/or F) have been treated under basic conditions with BH (B = OAlk,[23 to 31] OAr,[32] NR_2,[25,33] SR[34]), saturated addition products have been reported.[35] Furthermore, these products invariably have the structure

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[13] A. L. Henne and M. S. Newman, THIS JOURNAL, **60**, 1697 (1938).

[14] M. Prober, *ibid.*, **76**, 4189 (1954).

[15] A. L. Henne and M. W. Renoll, *ibid.*, **61**, 2489 (1939).

[16] "Selected Values of Properties of Hydrocarbons and Related Compounds," American Petroleum Institute Research Project 44, Table 21b, April 30, 1954.

[17] A. H. Fainberg and W. T. Miller, Jr., Abstracts of Papers, 120th Meeting of the American Chemical Society, New York, N. Y., Sept., 1950, p. 7-K.

[18] The following solubility data have been reported for sodium iodide and sodium chloride in anhydrous acetone at 18°: NaI, 1.29 mole/l.; NaCl, 5.5×10^{-6} mole/l.[19]

[19] A. Lannung, *Z. physik. Chem.*, **A162**, 262 (1932).

[20] E. D. Hughes, *Trans. Faraday Soc.*, **34**, 185 (1938).

[21] R. E. Kepner, S. Winstein and W. G. Young, THIS JOURNAL, **71**, 115 (1949).

[22] W. G. Young, I. D. Webb and H. L. Goering, *ibid.*, **73**, 1076 (1951).

[23] W. E. Hanford and G. W. Rigby, U. S. Patent 2,409,274, Oct. 15, 1946; *C. A.*, **41**, P982b (1947). Hanford and Rigby were the first to imply the structural requirement.

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

[25] M. D. Hurwitz and W. T. Miller, Jr., Abstracts of Papers, 114th Meeting, American Chemical Society, Washington, D. C., Aug., 1948, p. 4-L.

[26] J. D. Park, *et al.*, THIS JOURNAL, **70**, 1550 (1948).

[27] J. T. Barr, *et al.*, *ibid.*, **72**, 4480 (1950).

[28] J. D. Park, *et al.*, *ibid.*, **73**, 861 (1951).

[29] J. D. Park, *et al.*, *ibid.*, **73**, 1329 (1951).

[30] P. Tarrant and H. C. Brown, *ibid.*, **73**, 1781 (1951).

[31] J. A. Young and P. Tarrant, Abstracts of Papers, 120th Meeting, American Chemical Society, New York, N. Y., Sept., 1951, p. 4-K.

[32] P. Tarrant and H. C. Brown, THIS JOURNAL, **73**, 5831 (1951).

[33] R. L. Pruett, *et al.*, *ibid.*, **72**, 3646 (1950).

[34] K. E. Rapp, *et al.*, *ibid.*, **72**, 3642 (1950).

[35] There are two apparent exceptions; Tarrant and Brown[30] reported the isolation of only unsaturated ethers from the reaction of $CF_2{=}CCl_2$ and $CF_2{=}CClF$ with sodium *t*-butoxide in *t*-butyl alcohol, and Pruett, *et al.*,[33] obtained $CHClFCF{=}NC_4H_9$ from the action of $C_4H_9NH_2$ with $CF_2{=}CClF$. However, in both cases the authors believe that the saturated addition product was actually formed first, and that it subsequently split out HF. This view is partly substantiated by the report of Barr, *et al.*,[27] of the isolation of a saturated ether from the reaction of $CF_2{=}CClF$ with *t*-butyl alcohol in the presence of base; this ether was found to be highly unstable both thermally and in the presence of HF.

$CF_2BCX^1X^2H$,[36] in which the anionic fragment B is attached to the carbon atom bearing the two fluorine atoms.

In sharp contrast to the behavior of the fluoroolefins containing the $CF_2{=}$ group described above, those containing $CClF{=}$ or $CCl_2{=}$ such as $CClF{=}CClF$,[25] $CCl_2{=}CClF$[25] and $CCl_2{=}CClCF_3$[37] are relatively unreactive and do not appear to undergo base-catalyzed addition leading to saturated products. Under conditions resulting in reaction, they tend to give vinyl ethers instead.

A two-stage mechanism which accounts for the phenomenon of base-catalyzed addition and elimination of vinyl and allyl halogen, as well as for the highly preferred orientation of addition, has been proposed by Miller, *et al.*[24,25] In it, the first, rate-controlling step involves nucleophilic attack on $CF_2{=}$. Similarly, the S_N2' mechanism here proposed for the iodide–chloride interchange requires rate-controlling attack at the $CF_2{=}$ group by such relatively mild nucleophiles as iodide and chloride ion.

It is obvious that the allyl chlorides which have been found reactive to the iodide reagent are of such a structure as to yield the same organic iodide by allylic rearrangement as by direct substitution at the allylic carbon atom. For these compounds, it would appear that a definitive proof of mechanism can only be obtained by the use of labeled carbon. However, product analyses and kinetic results are consistent with the proposed S_N2' mechanism for the reactions with halide ions of structures of the type $CF_2{=}CXCCl_2F$, X = F or H.[38]

Properties of the Fluorinated Allyl Iodides.—The fluorinated allyl iodides were obtained as clear, colorless liquids by distillation in the dark under an inert atmosphere (for $CF_2{=}CClCF_2I$ vacuum distillation was necessary, since some thermal decomposition was encountered at the boiling point at atmospheric pressure). In the air and on exposure to light they rapidly turned purple due to liberated iodine, $CF_2{=}CClCF_2I$ being less stable than $CF_2{=}CFCF_2I$. The allyl iodides were found to be strongly lachrymatory, as were also $CF_2{=}CClCClF_2$ and the olefin dibromides.

Some reactions of these iodides have been investigated, and will be reported in a subsequent paper in this series.

Experimental Methods

Dehalogenation.—Dechlorinations were carried out by adding, through an addition funnel, the compound being dechlorinated to a well-stirred refluxing mixture of zinc dust in absolute methyl or ethyl alcohol. Induction periods could be substantially eliminated by the initial addition of a small amount of zinc chloride to the reaction mixture.[39] To take care of the very considerable heat of reaction, water-cooling of the reaction flask was employed. The product was continuously distilled out of the reaction mixture as formed. With these techniques, the rate of reaction for virtually all the dechlorinations run in this Laboratory to date employing zinc dust and methyl or ethyl alcohol as the solvent was found to be very rapid. This is in contrast to several reports in the literature of very sluggish reaction.[40,41]

Products and recovered starting materials were always obtained as minimum boiling azeotropes with the alcohol used as the solvent. Physical properties and compositions of some of the azeotropes encountered are given in Table II.

TABLE II

AZEOTROPES

Component A	Component B	B.p., °C. Pure A[a]	B.p., °C. Azeotrope[b]	Bar. press., mm.	$n^{20}D$ Pure A	$n^{20}D$ Azeotrope	Wt. % B in azeotrope
$CF_2{=}CFCClF_2$	CH_3OH	6.5	5.5	741	....	....	2
$CF_2{=}CFCClF_2$	C_2H_5OH	6.4	6.0	740			<1
$CClF_2CClFCClF_2$	CH_3OH	73.0	51.9	739	1.3501	1.3432	10
$CClF_2CClFCClF_2$	C_2H_5OH	73.7	61.6	756	1.3501	1.3514	20
$CF_2{=}CClCClF_2$	C_2H_5OH	43.9	41.3	739	1.3484	1.3492	6
$CClFCClFCF_2CF_2$	CH_3OH	59.2	45.4	745	1.3342	1.3320	
$CClFCClFCF_2CF_2$	C_2H_5OH	59.0	51.5	739	1.3342	....	6
$CBrFCBrFCF_2CF_2$	C_2H_5OH	132.6	73.0	745	1.3884	....	
$CF{=}CFCF_2CF_2$	C_2H_5OH	0.2	0.1	739	....	....	<1
$CBrF_2CBrF_2$	CH_3OH	46.3	39.8	735	1.3702	1.3662	

[a] B.p. t_c adjusted to barometric pressure p_c at which azeotrope b.p. was taken by use of equation $t_c = t_0 + 0.043(p_0 - p_0)$ where t_0 is observed b.p. of pure compound at pressure p_0.[6] [b] Observed value.

It would appear that azeotrope formation between halogenated compounds and alcohols is a general phenomenon. It has proved to be very useful in the recovery of high-boiling products, since it eliminates having to work up the residue.

For compounds boiling below room temperature, the alcohol was removed by treatment with P_2O_5 and fractional distillation therefrom. Compounds boiling above room temperature were extracted with ice-water, treated with P_2O_5, filtered and fractionally distilled. Distillation from P_2O_5 is not recommended for compounds boiling higher than about 70°, because of decomposition of the products of the P_2O_5–alcohol reaction.

Allylic Fluorination.—Swarts[42] prepared $C_6H_5CCl_2F$ and $C_6H_5CClF_2$ by treating benzotrichloride with SbF_3 for

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[36] Hanford and Rigby[23] in a patent claimed that ethers with the reverse orientation were also formed. However, they cited no experimental evidence for this. They did report that $CF_2{=}CClF$ and $CF_2{=}CHCl$ gave $CHClFCF_2OEt$ and CH_2ClCF_2OEt, respectively, and gave chemical evidence for the structure of the latter. Tarrant and Brown[30] cite the formation of both difluoro- and chlorofluoro- acetamides from $CF_2{=}CClF$ and amines "under certain conditions." These results appear to be in contrast to those of other workers (see above).

(37) J. D. Park, *et al.*, THIS JOURNAL, **74**, 4104 (1952).

(38) W. T. Miller, Jr., J. Fried and M. Gazith, unpublished work.

(39) This effect also has been observed by T. Alfrey, Jr., H. B. Hass and C. W. Lewis, THIS JOURNAL, **73**, 2851 (1951).

(40) A. L. Henne and T. P. Waalkes, *ibid.*, **68**, 496 (1946).

(41) A. L. Henne and W. J. Zimmerschied, *ibid.*, **69**, 281 (1947).

(42) F. Swarts, *Bull. classe sci., Acad. roy. Belg.*, [3] **38**, I 414 (1900).

periods of two weeks or more at room temperature. The method proved unsatisfactory for large-scale preparation, particularly of the monofluoride. In line with previous observation,[43] heating the mixture at atmospheric pressure gave only benzotrifluoride and the reaction was accompanied by much decomposition. However, it was found that rapid reaction between the SbF_3 and benzotrichloride sets in at 100–110°. This is too low a temperature to permit distillation at atmospheric pressure out of the reaction mixture of the intermediate fluorination products ($C_6H_5CClF_2$ boils at 140°, $C_6H_5CCl_2F$ at 180°). By lowering the pressure to 25–50 mm. so as to bring the boiling points of the intermediate fluorination products below the temperature at which reaction sets in, it was found possible to isolate either of the intermediates as the predominant product.

This technique was found to be equally effective in the isolation of the intermediate fluorination products of hexachloropropylene, and will very likely prove applicable to allylic fluorinations in general.

The fluorination products invariably carried over volatile antimony salts with them. These salts were difficult to remove quantitatively by the usual technique of washing with aqueous HCl, nor could they be separated by fractional distillation. It was found that they could be removed quantitatively by treatment of the material with a high-boiling organic base, such as quinoline. An insoluble complex was formed, which could be filtered off; the excess quinoline was then separated by fractional distillation.

Quantitative removal of the volatile antimony salts prior to distillation was found essential in the isolation of the intermediate fluorination products of benzotrichloride, for they were found to cause disproportionation[44,45] of these products to the trifluoride and trichloride. This reaction was also encountered with the intermediate fluorination products of hexachloropropylene.[47]

The formation of a cloudy solution or precipitate on the addition of one drop of quinoline to several ml. of a compound was found to constitute a sensitive test for the presence of antimony halides. Application of this test to other compounds prepared by fluorination with antimony salts revealed that all compounds so prepared boiling higher than 75–100° contained trace amounts of antimony salts. Such compounds were therefore given the quinoline treatment prior to distillation. It is suggested that the rather wide discrepancies between the densities of a number of compounds reported in this paper and those previously reported may be due to the presence of small amounts of antimony salts in the earlier preparations (densities previously reported are consistently higher).

Physical Properties and Analytical Data.—Physical properties were determined as described previously.[7,44] Densities of liquids boiling below room temperature were taken in sealed 10- or 25-ml. pycnometers.

Samples were decomposed for halide analysis by peroxide fusion in a Parr bomb.[48]

Experimental Results

Fluorination of $CCl_3CClFCCl_2F$ and $CCl_2FCClFCClF_2$.—These fluorinations were carried out by the method of Henne and Flanagan.[49] A steel lecture cylinder (Matheson Co.) was charged with 122 g. of HF, 173 g. of HgO (1.60 eq.) and 96 g. of $CCl_3CClFCClF_2$[50] (0.33 mole). The cylinder was sealed with a steel valve and heated to 175° for 40 hours with shaking. The reaction product was steam distilled from the cylinder into an aqueous solution of KOH, separated as the lower layer, dried over P_2O_5, and fractionally distilled to give 54 g. of $CClF_2CClFCClF_2$, b.p. 72–74° (0.23 mole, 70% yield), center cut Ia, b.p. 72.9° (738 mm.).

In a similar manner, 35 g. of $CCl_2FCClFCClF_2$[51] (0.14 mole), 93 g. of HF and 32 g. of HgO (0.30 eq.), held at 175° for 24 hours with shaking, gave 22 g. of $CClF_2CClFCClF_2$, b.p. 72.8–73.3° (0.093 mole, 65% yield); the center cut had physical properties virtually identical with those found for Ia.

In neither of the above runs was anything obtained boiling lower than 72°, thus further demonstrating the resistance of terminal $-CClF_2$ and internal $-CClF-$ groups in saturated perhalo compounds to further fluorination under the reaction conditions employed.[52]

Fluorination of $CCl_3CClFCCl_3$.—The fluorination of $CCl_3CClFCCl_3$ was carried out with SbF_3Cl_2, following the directions of Henne and Newby[4] as closely as possible. The fluorinating agent was prepared by condensing 44 g. of Cl_2 (0.62 mole) in a lecture cylinder containing 216 g. of SbF_3 (1.20 moles), sealing it, and warming to room temperature for 3 hours. By reaction of 160 g. of $CCl_3CClFCCl_3$[54] (0.53 mole) with this fluorinating agent there was obtained 109 g. of material, $n^{20}{}_D$ 1.3489, the bulk of which distilled (from quinoline) at 70–73°. Physical properties of the purest cut, Ib, b.p. 72.7° (737 mm.), are listed in Table I.

Dechlorination of $CClF_2CClFCClF_2$.—In a typical run, 1188 g. of $CClF_2CClFCClF_2$ (5.0 moles, Ic)[55] was dechlorinated with 500 g. of 90% zinc dust in 1400 ml. of absolute ethanol to which 20 g. of $ZnCl_2$ had been added, to give 770 g. of an ethyl alcohol azeotrope (<1% EtOH) of $CF_2{=}CFCClF_2$, b.p. 5.6–6.3°, plateau at 6.3° (743 mm.) (91% conversion, 95% yield), plus 60 g. of material, b.p. 61.6° (756 mm.), shown to be the ethyl alcohol azeotrope of $CClF_2$-$CClFCClF_2$ (*ca.* 20% EtOH). Thus, drowning the latter in water, and treating with P_2O_5, followed by fractional distillation gave $CClF_2CClFCClF_2$, b.p. 73.1° (743 mm.), $d^{20}{}_4$ 1.653, $n^{20}{}_D$ 1.3505. Fractional distillation of the ethyl alcohol–$CF_2{=}CFCClF_2$ azeotrope from P_2O_5 gave IIb, b.p. 6.2° (732 mm.); mol. wt. calcd. 166.5, found 165.

The purest sample of $CF_2{=}CFCClF_2$ obtained, IIa, b.p. 6.5° (741 mm.), was prepared by dechlorination of Ia. It added bromine readily to give $CBrF_2CBrFCClF_2$ (III), b.p. 112.4° (744 mm.).

Reaction of $CF_2{=}CFCClF_2$ with SbF_3Cl_2.—The procedure of Henne and Newby[4] was followed as closely as possible. To a fluorinating agent prepared as described above from 82 g. of SbF_3 (0.61 mole) and 13 g. of Cl_2 (0.18 mole) in a lecture cylinder was added 102 g. of $CF_2{=}CFCClF_2$ (IIb, 0.61 mole). The cylinder was warmed, with shaking, to 95–105° for 21 hours, then 125–130° for 12 hours more. From the cylinder was distilled 98 g. of material, which gave, on fractional distillation, 6 g. of $CF_2{=}CFCF_3$ (VI), b.p. -30.7 to $-29.6°$ (741 mm.) (0.04 mole, 7% yield), plus 64 g. of a C_3ClF_5, b.p. 5.5–7.7° (0.38 mole, 63% yield), center cut b.p. 7.4° (745 mm.), shown to be almost pure $CClF{=}CFCF_3$ (IV) by photochemical chlorination to CCl_2-$FCClFCF_3$ (Va), b.p. 71.1° (737 mm.). Physical properties of a somewhat less pure sample (judging by the respective cooling curves) of $CCl_2FCClFCF_3$ (Vb), b.p. 72.5–.9° (744 mm.), prepared[56] by the addition of F_2 to $CCl_2{=}CClCF_3$, are also listed in Table I for comparison.

Fluorination of $C_6H_5CCl_3$.—In a typical run in which the monofluoride was the desired product, 293 g. of $C_6H_5CCl_3$ (1.5 moles), held at 115–120°, was treated in several portions with 90 g. of SbF_3 (1.5 equiv.) at a pressure of 50 mm., the product being distilled out as formed. It was treated with 10 ml. of quinoline, filtered through charcoal, and fractionally distilled to give 1 g. of $C_6H_5CF_3$, b.p. 46.5–47.5° (100 mm.) (1% yield); 37 g. of $C_6H_5CClF_2$, b.p. 79–81° (100 mm.) (0.23 mole, 19% yield); 101 g. of $C_6H_5CCl_2F$, b.p. 108–113° (100 mm.) (0.56 mole, 46% yield); and 54 g. of $C_6H_5CCl_3$ (0.28 mole, 18% recovered).

The yield of difluoride was improved by using twice the above proportion of SbF_3 and operating at 25 mm.

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[43] A. L. Henne, "Organic Reactions," Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1944, p. 52.

[44] A. H. Fainberg, Ph.D. Thesis, Cornell University, 1950.

[45] This reaction was independently reported by Prober.[46]

[46] M. Prober, THIS JOURNAL, **76**, 4189 (1954).

[47] A similar reaction has been reported for $\overline{CCl{=}CClCF_2CCl_2CF_2}$ by A. L. Henne and W. J. Zimmerschied, *ibid.*, **67**, 1235 (1945).

[48] Analyses were carried out by J. M. Howald.

[49] A. L. Henne and J. V. Flanagan, THIS JOURNAL, **65**, 2362 (1943).

[50] This compound was furnished by G. Gavlin, who prepared it by the addition of F_2 to $CCl_2{=}CClCCl_3$. Physical properties for this sample are listed elsewhere[7]

[51] This compound was furnished by M. D. Hurwitz, who prepared it by addition of F_2 to $CCl_2{=}CClCClF_2$.

[52] Similar results have also been obtained with perhalobutanes.[53]

[53] E. Rutner and W. T. Miller, Jr., unpublished work.

[54] The sample of $CCl_3CClFCCl_3$ used was prepared[7] by chlorination of $CH_3CClFCH_2Cl$.[7]

[55] From the addition of Cl_2 to the C_3ClF_5 fraction from the pyrolysis of $CClF{=}CF_2$.[3,8]

[56] J. M. Phelan and W. T. Miller, Jr., unpublished work.

Refractionation of the above compounds gave center cuts $C_6H_5CF_3$ (VII), b.p. 100.9° (731 mm.); $C_6H_5CClF_2$ (VIII), b.p. 139.7° (739 mm.); $C_6H_5CCl_2F$ (IX), b.p. 94.5° (50 mm.); and $C_6H_5CCl_3$ (X), b.p. 146.9° (100 mm.).

Fluorination of $CCl_2=CClCCl_3$.—Fluorination of $CCl_2=CClCCl_3$ at atmospheric pressure has been reported.[5b] To increase the yields of the intermediate fluorination products, the reduced pressure technique was employed. In a 1-liter 3-neck flask fitted with stirrer, addition funnel, and wide bore take-off tube leading to an ice-cooled receiver was placed 720 g. of SbF_3 (4.0 moles). The reaction flask was immersed in an oil-bath at 200–230°, the pressure lowered to 150 mm., and 1245 g. (5.0 moles) of $CCl_2=CClCCl_3$, (XI), b.p. 141.4° (100 mm.) added over a half-hour period. The stirrer was started up as soon as possible, and a mixture of products distilled out at 100–130 mm. The crude mixture was extracted several times with 1:2 aq. HCl, treated with 20 ml. of quinoline, filtered through charcoal, and given a rapid preliminary fractional distillation at 30 mm. Under these conditions, the following yields were obtained. The variations in yield were determined by the rate of take-off, slower take-off favoring the more highly fluorinated products.

Run	Recovered $CCl_2=CClCCl_3$, %	Yield, %		
		$CCl_2=CClCCl_2F$	$CCl_2=CClCClF_2$	$CCl_2=CClCF_3$
1	6	15	62	7
2	6	39	51	5
3	18	62	29	3
4	34	79	15	1

Refractionation gave the following center cuts: $CCl_2=CClCCl_2F$ (XII), b.p. 169.2° (735 mm.); $CCl_2=CClCClF_2$ (XIII), b.p. 127.1° (738 mm.); and $CCl_2=CClCF_3$ (XIV), b.p. 87.4° (730 mm.).

Preparation of $CF_2=CClCClF_2$.—Dechlorination[5b] of $CClF_2CCl_2CClF_2$ (XVa)[7] with zinc dust in ethanol gave $CF_2=CClCClF_2$ (XVI), b.p. 43.8° (747 mm.), in 90% yield. The cooling curve for the olefin had a freezing point depression of <0.1°, in contrast to the much larger depression of 1.7° found for its precursor XVa, which had been prepared by fluorination of $CCl_3CCl_2CClF_2$.[7] However, photochemical addition of Cl_2 to XVI gave a $CClF_2CCl_2CClF_2$ (XVb), b.p. 111.7° (747 mm.), which had a f.p. depression of 1.5°. Apparently XVa contained a small amount of a dechlorinatable impurity capable of depressing its freezing point, but which, on dechlorination, gave an olefinic impurity in the $CF_2=CClCClF_2$ which formed a solid solution with the latter.

Photochemical addition of Br_2 to XVI gave $CBrF_2CBrClCClF_2$ (XVII) for which a satisfactory cooling curve could not be obtained.

Action of Sodium Iodide in Acetone on $CF_2=CFCClF_2$.—In a typical reaction, 1250 g. of $CF_2=CFCClF_2$ (IIb, 7.5 moles) was treated with 1366 g. of NaI (9.1 moles) in 3500 ml. of anhydrous acetone (prepared by refluxing reagent grade acetone over Drierite, and fractionally distilling therefrom). Reaction occurred at room temperature as evidenced by the precipitation of NaCl (of greater than 98% purity in the early stage of reaction). After ten days at room temperature, the remaining low-boiling material was rapidly distilled off, and the product was worked up by drowning the reaction mixture, in five times its volume of water, washing with several portions of iced dilute aqueous $NaHSO_3$ to remove iodine and acetone, drying over P_2O_5, filtering and fractionally distilling. In this way was obtained 324 g. of recovered C_3ClF_5, b.p. 5.3–6.3° (737 mm.); 1150 g. of $CF_2=CFCF_2I$, b.p. 53.0–53.6° (738 mm.) (4.5 moles, 60% conversion); and 30 g. of higher boiling material, discussed further below. Refractionation of the $CF_2=CFCF_2I$ gave a center cut XVIII, b.p. 53.6° (734 mm.).

Anal. Calcd. for C_3F_5I: I, 49.2; mol. wt., 258. Found: I, 49.2; mol. wt., 264.

Boiling point, molecular weight, iodine analysis, unsaturation to $KMnO_4$ in acetone, and molar refraction support the molecular formula C_3F_5I. The structural formula proposed is consistent with substitution of chlorine in $CF_2=CFCClF_2$ by iodine with or without allylic rearrangement; any other structure would involve rearrangement of carbon–fluorine bonds, which is considered highly unlikely under the conditions of the reaction. In further support of the allylic structure is the fact that a number of reactions[17] of the iodide regenerate, directly or indirectly, the known $CF_2=CFCClF_2$ and $CClF_2CClFCClF_2$.

In another run, using the same quantity of reagents, the reaction was carried out by holding the mixture at reflux. The temperature of the reaction mixture rose asymptotically from 20 to 47° in five days, and remained at 47° for the next five days. In this way, 1250 g. of $CF_2=CFCClF_2$ (7.5 moles, b.p. 6.8° (755 mm.), b. range 0.1°, f.p. −144.2°, f.p. dep. 2°, obtained from dechlorination of Ic) gave 120 g. of C_3ClF_5, b.p. 6.6–7.1° (center cut b.p. 6.6° (743 mm.), b. range <0.1°, f.p. −151°, f.p. dep. very large), plus 980 g. (3.8 moles, 51% conversion) of $CF_2=CFCF_2I$, b.p. 52–54° (center cut b.p. 53.8° (739 mm.), f.p. −130.6°, f.p. dep. 0.2°), plus smaller amounts of several higher boiling by-products which appear to have been formed by substitution of fluorine by iodine. Among these were 55 g. of a compound, b.p. 93–98°, center cut, b.p. 97.5° (744 mm.), b. range 0.1°, d^{20}_4 2.1270, n^{20}_D 1.4010; and 200 g. of another compound, b.p. 70.6° (50 mm.), b. range 0.1°, f.p. −43.6°, f.p. dep. 0.1°, d^{20}_4 2.1691, n^{20}_D 1.4811. In addition, a small amount of a compound b.p. −30° was obtained. Further work on these by-products is in progress.

A portion of the recovered C_3ClF_5 fraction was treated with NaI in acetone, and found to react further, thus demonstrating the presence of $CF_2=CFCClF_2$. However, evidence that at least one other C_3ClF_5 isomer also was present was furnished not only by the physical properties of the material itself, but also by addition of chlorine to another portion of the material to give a $C_3Cl_3F_5$, b.p. 71.5–72.0° (739 mm.), d^{20}_4 1.6606–1.6609, n^{20}_D 1.3512–1.3517. It is believed that the impurity resulted from a concentration of impurity originally present in the starting material, rather than rearrangement of the allyl chloride.

Action of Sodium Iodide in Acetone on $CF_2=CClCClF_2$.—To a solution of 825 g. of NaI (5.50 moles) in 2000 ml. of anhydrous acetone at 22° was added 905 g. of $CF_2=CClCClF_2$ (XVI, 4.94 moles). Reaction occurred at a considerably faster rate than for $CF_2=CFCClF_2$; in half an hour the temperature rose to 32°, then started falling. After 45 hours at room temperature, the reaction product was drowned in water and worked up as described above for $CF_2=CFCF_2I$ to give 160 g. (0.87 mole, 18%) of recovered $CF_2=CClCClF_2$, b.p. 35–45°, center cut b.p. 43.6° (740 mm.), b. range <0.1°, f.p. −120.8°, f.p. dep. 0.1°, d^{20}_4 1.5398, n^{20}_D 1.3483; and 950 g. of $CF_2=CClCF_2I$, b.p. 37–38° (100 mm.), center cut XIX, b.p. 37.5° (100 mm.), 91.4° (737 mm.) (3.5 moles, 70% conversion, 85% yield.)

Anal. Calcd. for C_3ClF_4I: Cl, 12.9; I, 46.3; mol. wt., 274.5. Found: Cl, 12.8; I, 46.4; mol. wt., 274.

Compounds Unreactive to Sodium Iodide in Acetone.—Each of the following compounds was treated with an equivalent amount of sodium iodide in anhydrous acetone at reflux temperature for periods of 24 to 150 hours: $Cl_2=CClCClF_2$, $CClF=CFCClF_2$,[57] $C_6H_5CClF_2$ and $CClF_2CClFCClF_2$. No precipitate formation was observed for any of these compounds, a very sensitive sign of reaction, and they were recovered unchanged in substantially quantitative amounts.

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(57) Isolated from the thermal reaction of $CClF=CF_2$.[3,8]