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Preferential Replacement Reactions of Highly Fluorinated Alkyl Halides. II.[1] Some Reactions of Fluorinated Allyl Iodides[2,3]

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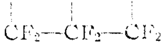
The preferential replacement of iodine in 3-iodopentafluoropropene and in 2-chloro-3-iodotetrafluoropropene by reaction with chlorine and bromine and with chloride and bromide ions is described. Ionic and free radical type reaction mechanisms which involve initial reagent attack at the double bond rather than at the allylic carbon atom are proposed for these reactions. The reactions with halide ion are shown to be reversible. Treatment of the above compounds with metallic zinc results in the replacement of iodine by hydrogen or in the formation of dimeric products with elimination of iodine. The dimerization reaction furnishes a method for the preparation of perfluoro and other highly halogenated 1,5-hexadienes. Perfluoro-1,5-hexadiene on heating undergoes an unusual isomerization to form a saturated compound which is formulated as perfluorobicyclo[2,2,0]hexane.

Introduction

The fluorinated allyl iodides are highly reactive materials which have been found to be versatile intermediates for the preparation of a variety of fluorinated compounds. Illustrative reactions of 3-iodopentafluoropropene and 2-chloro-3-iodotetrafluoropropene are described below. The clean-cut character of the reactions of these compounds, which do not contain hydrogen, is particularly noteworthy. In most cases products of high purity are isolated readily in high yields, without formation of tars and intractable residues. Table I lists

TABLE I

PHYSICAL PROPERTIES OF COMPOUNDS[a]

No.	Compound	B.p., 760 mm.,[b] °C.	B. range,[c] °C.	F.p., °C.	F.p. dep.,[d] °C.	$n^{20}D$	d^{20}_4	$MR^{20}D$ Found[e]	$MR^{20}D$ Calcd.[f]
Ia	$CF_2{=}CFCBrF_2$	26.5	<0.1	Glass at −165	..	1.3322	1.812	23.89	23.9
Ib	$CF_2{=}CFCBrF_2$	26.5	< .05	Glass at −160	..	1.3320	1.8139	23.86	
II	$CF_2{=}CClCBrF_2$	64.5	< .1	105.0	0.3	1.3829	1.8735	28.31	28.3
III	$CBrF_2CBrClCBrF_2$	87.0 (50)	.2	−54.5	< .1	1.4719	2.4955	43.44	43.43
IV	$CBrF_2CBrFCBrF_2$	133.6	< .2	−99.9	< .2	1.4284	2.4570	38.86	38.91
Va	$CClF_2CClFCClF_2$[g]	73.8	< .1	"α" −141.5 "β" −134.7	< .1	1.3502	1.6540	30.90	30.97
Vb	$CClF_2CClFCClF_2$	73.7	.1	"α" −141.4 "β" −134.8	< .2	1.3501	1.6546	30.88	
VI	$CClF_2CClFCBrF_2$	93.2	< .1	−134.8	.2	1.3768	1.9294	33.59	33.69
VII	$CBrF_2CClFCBrF_2$	113.1	< .1	−106.2	.2	1.4026	2.1903	36.32	36.41
VIII	$CF_2{=}CFCHF_2$	1.8	< .1	−101.2	< .1	....	1.4607[h]		
IX	$CBrF_2CBrFCHF_2$	95.9	.2	−98.2	.8	1.3898	2.2004	31.43	31.3[l]
X	$CClF_2CClFCHF_2$[i]	56.3	< .1	−91.1	.2	1.3295	1.5886	26.03	26.1[l]
XI	$C_2H_5OCOCH_2COOC_2H_5$[j]	134.4 (100)	< .2	−52.3	.4	1.4139	1.0534	37.99	
XII	$CF_2{=}CFCF_2CH_2CF{=}CF_2$	59.6	< .1	−70.0	< .1	1.296	1.6090	30.08	30.1
XIII	$CClF_2CClFCH_2CF_2CClFCClF_2$	89 (50)	1	.....	..	1.3683	1.8132	50.18	50.21
XIVa	$(C_2H_5OCOCF_2\text{—})_2$[k]	96 (20)	.4	−48.4	.2	1.3670	1.2794	43.20	42.9[m]
XIVb	$(C_2H_5OCOCF_2\text{—})_2$[k]	95 (20)	< .2	−47.9	< .1	1.3670	1.2773	43.27	42.9[m]
XV		43.8		41					
XVI	$CF_2{=}CClCF_2CF_2CCl{=}CF_2$	113.9	< .2	−34.1	.3	1.3613	1.6789	38.9	38.90

[a] Compounds V, X, XI and XIV have been reported previously. [b] Computed from the observed boiling point t_0 at pressure p_0 (given in the Experimental section) with the equation $t_{760} = t_0 + 0.043(760 - p_0)$.[4,6] [c] The boiling range of the center cut on which all other physical properties were taken. [d] The freezing point depression with the material half frozen.[5,6] [e] MR found $= (n^2 - 1)M/(n^2 + 2)d$. [f] Calculated from the atomic and group increments proposed elsewhere.[6] These increments were based in part on the data of Table I. [g] Previously reported[1] b.p. 73.9° (760 mm.), f.p. "α" −141.3°, "β" −135.0°, f.p. dep. <0.1°, $n^{20}D$ 1.3501, d^{20}_4 1.6541. [h] At 0.0°. [i] Previously reported b.p. 56.0°, $n^{20}D$ 1.3288, "may contain $CHClFCClFCF_3$."[7] [j] Reported b.p. 198.9° (760 mm.),[8] f.p. −49.9°,[8] $n^{20}D$ 1.4142,[9] d^{20}_4 1.0554,[9] $MR^{20}D$ 37.94. [k] Reported[10] b.p. 89° (15 mm.), $n^{20}D$ 1.3690, $n^{23.2}D$ 1.3642,[11] d^{20}_4 1.2640, $MR^{20}D$ 43.94. [l] Using a tentative value for $AR^{20}D$ H of 1.0. [m] Calculated for $MR^{20}D$ 42.39 for diethyl succinate,[12] by subtracting 4H and adding 4F (H = 1.029, F = 1.165).[6]

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[1] Preceding paper in this series, W. T. Miller, Jr., and Arnold H. Fainberg, THIS JOURNAL, **79**, 4164 (1957).

[2] Presented at the 120th Meeting of the American Chemical Society, New York, N. Y., Sept., 1951, Abstracts of Papers, p. 7-K.

[3] This work has been supported by the Office of Naval Research and by a grant-in-aid made by E. I. du Pont de Nemours and Co. to the Department of Chemistry, Cornell University.

(4) N. A. Lange, "Handbook of Chemistry," 3rd ed., Handbook Publishers, Inc., Sandusky, Ohio, 1939.

(5) Essentially as described by A. R. Glasgow, A. J. Streiff and F. D. Rossini, *J. Research Nat. Bur. Standards*, **35**, 355 (1945); A. H. Fainberg, Ph.D. Thesis, Cornell University, 1950.

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

(7) M. Hauptschein and L. A. Bigelow, THIS JOURNAL, **73**, 1428 (1951).

(8) J. Timmermans, *Bull. soc. chim. Belg.*, **25**, 300 (1911).

(9) C. Contzen-Crowet, *ibid.*, **35**, 165 (1926).

(10) A. L. Henne and W. J. Zimmerschied, THIS JOURNAL, **69**, 281 (1947).

(11) M. Hauptschein, C. S. Stokes and A. V. Grosse, *ibid.*, **74**, 1976 (1952).

(12) C. P. Smyth and W. S. Walls, *ibid.*, **53**, 527 (1931).

the physical properties of the compounds involved, most of which are new.

Reactions with Halide Ions.—In the preceding paper in this series was described the preparation of the allylic iodides 3-iodopentafluoropropene and 2-chloro-3-iodotetrafluoropropene by treatment of the corresponding fluorinated allyl chlorides with sodium iodide in acetone. The consistent recovery of unreacted allyl chloride in the earlier work suggested that an equilibrium reaction is involved, equation 1, which is displaced toward the formation

$$NaI + CF_2{=}CXCClF_2 \xrightarrow[\text{acetone}]{\text{anhydrous}} ICF_2CX{=}CF_2 + NaCl \downarrow \quad (1)$$

of allyl iodide by virtue of the extremely low solubility of the sodium chloride in the anhydrous acetone.

This equilibrium has been confirmed in the present work. Thus, treatment of perfluoroallyl iodide with sodium chloride in anhydrous acetone gave perfluoroallyl chloride under conditions in which the more volatile chloride was progressively distilled out of the reaction mixture. Furthermore, the rate of formation of the allyl chloride was increased markedly by the addition of water to the acetone; the water increases the solubility of the sodium chloride in the solvent.

In addition, it was shown that the allyl chloride is thermodynamically favored over the bromide. The allyl bromide reacted under equilibrium conditions with lithium chloride in anhydrous acetone, equation 2, to give perfluoroallyl chloride in high yield. Substantially complete reaction occurred

$$Cl^- + CF_2{=}CFCBrF_2 \rightleftarrows CClF_2CF{=}CF_2 + Br^- \quad (2)$$

in less than five minutes at 0°. Likewise, treatment of the allyl iodide with lithium bromide in acetone, equation 3, gave a 90% yield of 3-bromopentafluoropropene of high purity.

$$Br^- + CF_2{=}CFCF_2I \rightleftarrows CBrF_2CF{=}CF_2 \uparrow + I^- \quad (3)$$

All of the above reactions are postulated to proceed *via* an SN2′ mechanism,[1] equation 4. This

$$Y^- + CF_2{=}CFCF_2X \rightleftarrows [Y\cdots CF_2 \overset{\cdots}{-} CF \overset{\cdots}{-} CF_2\cdots X]^- \rightleftarrows YCF_2CF{=}CF_2 + X^- \quad (4)$$

mechanism involves rate-controlling attack by halide ion Y^- on the terminal vinyl carbon atom, with allylic shift and elimination of halide ion X^-. It is striking that such usually mild nucleophiles as chloride and bromide ion are so effective in these reactions with fluoroallyl halides.

Reactions with Elemental Bromine and Chlorine.—3-Iodopentafluoropropene and 2-chloro-3-iodotetrafluoropropene reacted rapidly with bromine in the dark at room temperature to yield the corresponding allyl bromides almost quantitatively. Similarly, perfluoroallyl iodide reacted with chlorine in diffuse light to give the allyl chloride in high yield. In none of the above reactions was any trace of saturated compounds produced.

Heptafluoropropyl iodide does not react with bromine under the same conditions.[13] This result supports the view that the allyl iodides are attacked by the halogen, not at the allylic carbon atom, but at the terminal vinyl carbon atom, a reaction path analogous to that proposed for the reactions with halide ions (4). Inasmuch as some free iodine was always present at the start of these reactions, due to the instability of the allyl iodides, it is considered likely that reaction proceeds largely *via* the inter-halogen compounds, by an SN2′ type of mechanism as shown in equations 5 and 6. A cyclic transition state may be involved which

$$X_2 + I_2 \longrightarrow 2IX \quad (5)$$

$$\overset{\delta+}{I}{-}\overset{\delta-}{X} + CF_2{=}CX'CF_2I \longrightarrow CF_2XCX'{=}CF_2 + I_2 \quad (6)$$

yields an iodine molecule directly.[14]

Perfluoroallyl bromide did not appear to undergo a dark reaction with chlorine corresponding to that obtained with the allyl iodide. However, photochemical chlorination gave appreciable amounts of at least three other perhalopropanes, in addition to the expected chlorine adduct; see Table II.

TABLE II

PRODUCTS OF THE PHOTOCHEMICAL CHLORINATION OF $CF_2{=}CFCBrF_2$

Compound	Yield, %
$CClF_2CClFCClF_2$	22
$CBrF_2CClFCClF_2$	52
$CBrF_2CBrFCClF_2$	7
$CBrF_2CClFCBrF_2$	14
$(CBrF_2CBrFCBrF_2)$	*ca.* 1
Total	96

These products clearly establish that a large amount of carbon–bromine bond cleavage took place, with the formation of bromine atoms. The reaction may well represent the free radical counterpart of the dark reaction of chlorine with perfluoroallyl iodide, as shown in equations 7, 8 and 9.

$$Cl_2 + h\nu \longrightarrow 2Cl\cdot \quad (7)$$

$$Cl\cdot + CF_2{=}CFCBrF_2 \longrightarrow CClF_2\dot{C}FCBrF_2 \quad (8)$$

$$CClF_2CFCBrF_2 \longrightarrow CClF_2CF{=}CF_2 + Br\cdot\text{, etc.} \quad (9)$$

Reactions with Zinc.—Perfluoroallyl iodide, on treatment with zinc dust in methanol, reaction 10, gave the reduction product

$$CF_2{=}CFCF_2I + Zn + MeOH \longrightarrow CF_2{=}CFCHF_2 + Zn(OMe)_2 \quad (10)$$

1,1,2,3,3-pentafluoropropene in high yield. This latter compound added chlorine and bromine readily at low temperatures in the presence of light with no evidence of hydrogen substitution. It was necessary to raise the temperature *ca.* 40° in order to further chlorinate the $CClF_2CClFCHF_2$ to the known trichloride. This sequence of reactions thus constitutes a proof of structure for the initial reduction product and its halogen adducts.

In anhydrous dioxane, the perfluoroallyl iodide reacted with zinc dust to give a good yield of the coupled product, decafluoro-1,5-hexadiene. This diene added two moles of chlorine to give a saturated tetrachloride. The 1,5-positions of the double bonds was proved by oxidation of the diene

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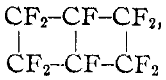
(13) A. H. Fainberg and W. T. Miller, Jr., unpublished work.

(14) The relationship of entering and departing groups has been shown to be *cis* for SN2′ reactions of some cyclohexene derivatives; G. Stork and W. N. White, THIS JOURNAL, **75**, 4119 (1953); **78**, 4609 (1956).

to tetrafluorosuccinic acid, isolated as the diethyl ester; see Table I.

Thermal reaction of the diene resulted in the formation of a remarkable isomeric compound, m.p. 41°, boiling only 3° higher, for which the structure decafluorobicyclo[2.2.0]hexane,  $\begin{array}{ccccc} CF_2 & - & CF & - & CF_2 \\ | & & | & & | \\ CF_2 & - & CF & - & CF_2 \end{array}$, is proposed. The application of this new ring closure reaction to longer chain terminally unsaturated dienes is under investigation.

Experimental Results

Physical Properties.—Physical properties were determined as previously described.[1,6] Structure assignments were tested in all cases by correlation of physical properties and *MR*D in addition to the other evidence cited.

Apparatus.—Unless otherwise indicated, all reactions were carried out in a three-neck round-bottom flask fitted with an all-glass stirrer, thermometer, addition funnel, and a 25 cm. × 1.5 cm. i.d. glass helix packed column surmounted by a water-cooled variable take-off head connected to a receiver and traps cooled in ice and in Dry Ice.

$CF_2{=}CFCF_2I + NaCl$ **in Acetone.**—Redistilled $CF_2{=}CFCF_2I$,[1] 129 g., was added to a suspension of 58 g. of NaCl in 500 ml. of anhydrous acetone and the mixture heated to reflux with stirring for ten days. Slow but continuous evolution of $CF_2{=}CFCF_2Cl$ occurred to yield a total of 23 g., b.p. 5–9°, center cut b.p. 6.2° (738 mm.), f.p. −141°; previously reported[1] b.p. 7.3° (760 mm.), f.p. −139.8°. In another run, the addition of 1% by wt. H_2O, which increases the solubility of NaCl in acetone by a factor of 10, speeded up the rate of formation of the $CF_2{=}CFCClF_2$ by a factor of more than 3.

$CF_2{=}CFCF_2I + LiBr$ **in Acetone.**—To a well-stirred solution of 104 g. of LiBr (1.2 moles) in 800 ml. of anhydrous acetone at 20° was added, over a ten-minute period, 258 g. of $CF_2{=}CFCF_2I$ (1.0 mole), which had been cooled to 0°. The temperature rose to 27° during mixing. The reaction mixture was heated to reflux and 204 g. of material, b.p. 27–28°, distilled out during seven hours (180 g. during three hours). Redistillation of the volatile product from 7 g. of P_2O_5 yielded 190 g., 90%, of $CF_2{=}CFCBrF_2$, b.p. 25.5–25.7°, center cut Ia, b.p. 25.5° (738 mm.).

$CF_2{=}CFCBrF_2$.—Compound Ia contained bromine, was unsaturated to $KMnO_4$ in acetone, and added one mole of bromine to give a saturated tribromide. The same compound was obtained from the action of bromine on the perfluoroallyl iodide, see below. Molecular weight, molar refraction and boiling point support the molecular formula C_3BrF_5. The allylic position of the bromine was demonstrated by the ready interconvertibility of the compound with the known allyl chloride and iodide.

$CF_2{=}CFCBrF_2 + LiCl$ **in Acetone.**—To 400 ml. of anhydrous acetone in a 500-ml. Pyrex bottle was added 25.4 g. of LiCl (0.60 mole, a 20% excess). The mixture was equilibrated at 0°, thus giving a saturated solution in which *ca.* 20 g. of LiCl was present as a solid phase.[15] To this mixture was added 105.5 g. of $CF_2{=}CFCBrF_2$ (0.50 mole), also at 0°. The bottle was tightly stoppered and shaken vigorously. Within five minutes, almost all of the solid phase had gone into solution, about 1 g. of LiCl remaining undissolved. There was no further change during the next three hours. The solution was poured on cracked ice in a separatory funnel with some loss of volatile product. The lower layer was fractionally distilled to give 65 g., 80%, of $CF_2{=}CFCClF_2$, b.p. 6.3° (739 mm.), f.p. −141°. No trace of unreacted starting material, b.p. 25°, was found.

$CF_2{=}CFCBrF_2$ **and** $CF_2{=}CClCBrF_2 + NaI$ **in Acetone.**—In a qualitative test, $CF_2{=}CFCBrF_2$ was found to react readily with 10% NaI in anhydrous acetone, a heavy precipitate of NaBr forming in one minute at room temperature. Under the same conditions, $CF_2{=}CClCBrF_2$ gave a precipitate instantaneously.

$CF_2{=}CFCF_2I + Br_2$.—To 985 g. of $CF_2{=}CFCF_2I$ (3.8 moles) in a one-liter reaction flask at room temperature in the dark was added, with stirring, 400 g. of bromine (2.5 moles) during one hour. Characteristic sharp cracking sounds were produced during the reaction and sufficient heat of reaction was developed to distil about a quarter of the product, b.p. 25 to 30°, out of the reaction flask. The flask then was warmed gently to drive over the rest of the product, leaving free iodine behind. The volatile product was washed with iced aqueous KOH and fractionally distilled to give 730 g., 90% conversion, 95% yield, of $CF_2{=}CFCBrF_2$, b.p. 25.8–25.9°, center cut Ib, b.p. 25.9° (745 mm.); mol. wt. calcd. 211, found 214. Fifty grams, 5%, of unreacted $CF_2{=}CFCF_2I$, b.p. 55°, was recovered. No material boiling higher than 55° was found.

$CF_2{=}CClCF_2I + Br_2$.—To 147 g. of $CF_2{=}CClF_2I$[1] (0.53 mole) in a 200-ml. flask in the dark was slowly added 50 g. of Br_2 (0.30 mole). As with the $CF_2{=}CFCF_2I$, sharp cracking sounds were produced during the addition. The evolution of a large amount of heat necessitated cooling in an ice-bath; most of the reaction was carried out at 30–35°. The reaction mixture, almost solid at this point, was treated with dilute aqueous KOH. The lower layer was separated and fractionally distilled to give 5% of recovered starting material and 100 g., 82% conversion, 87% yield, of $CF_2{=}CClCBrF_2$, b.p. 63.0–63.5°, center cut II, b.p. 63.5° (736 mm.); mol. wt. calcd. 227.5, found 231.5.

The $CF_2{=}CClCBrF_2$ added one mole of bromine slowly at room temperature, with illumination furnished by a 100 w. lamp, to give $CBrF_2CBrClCBrF_2$ (III), b.p. 86.9–87.1° (50 mm.).

$CF_2{=}CClCBrF_2$ and $CBrF_2CBrClCBrF_2$.—The olefin II contained fluorine, chlorine and bromine, but no iodine. Its molecular formula C_3BrClF_4 is supported by its molecular weight, molar refractivity and boiling point as well as by the molar refractivity of its bromine adduct III. Any structures other than $CF_2{=}CClCBrF_2$ for II and $CBrF_2CBrClCBrF_2$ for III would necessitate postulating rearrangements for which no analogous cases exist.

$CF_2{=}CFCF_2I + Cl_2$.—A solution of 108 g. of $CF_2{=}CFCF_2I$ (0.42 mole) in 200 g. of CCl_2FCClF_2 was placed in a 500-ml. three-neck flask fitted with gas inlet tube, thermometer and Dry Ice-cooled reflux condenser connected to an ice-cooled and a Dry Ice-cooled trap. Chlorine was passed into the solution rapidly in diffuse room light (no light directly on flask). After about four minutes during which the initial purple iodine color was bleached, the liquid became opaque black and evolved sufficient heat to raise the temperature from 30 to 45°. A low-boiling liquid ($CF_2{=}CFCClF_2$, b.p. +7°) started refluxing back into the flask. The temperature of the reaction mixture fell slowly with the continued rapid addition of chlorine, as the low boiling product built up, and a large amount of free iodine crystallized out of solution. Finally, the solid iodine liquefied rather suddenly (ICl formed), and the chlorine input was stopped. The reaction flask was warmed on a water-bath to distil out material boiling up to the boiling point of the solvent CCl_2FCClF_2 (47°). The product, a clear, light amber colored liquid was shaken with a small amount of mercury to remove traces of free halogen and fractionally distilled to give 58 g. of $CF_2{=}CFCClF_2$, b.p. 6–8° (85% yield), center cut b.p. 6.3° (739 mm.), f.p. −141°.

$CF_2{=}CFCBrF_2 + Br_2$.—The $CF_2{=}CFCBrF_2$ (Ib) added bromine initially rather slowly at its reflux temperature with illumination furnished by a 100-w. incandescent lamp, the bromine being only sparingly soluble in the olefin. The rate of reaction increased rapidly as the product built up, and the reflux temperature rose. The product, obtained in substantially quantitative yield, was the expected tribromide $CBrF_2CBrFCBrF_2$ (IV), b.p. 132.4° (733 mm.); mol. wt. calcd. 371, found 365; Br calcd. 64.7, found 65.0, 64.9.[17]

$CF_2{=}CFCBrF_2 + Cl_2$.—The $CF_2{=}CFCBrF_2$ did not appear to react with chlorine at room temperature in diffuse light. It did, however, react rapidly with chlorine when illuminated with 2–15 w. G.E. 360 BL ultraviolet fluorescent lamps. The chlorination product from 422 g. of $CF_2{=}CFCBrF_2$ (Ib, 2.00 moles) was let stand overnight with dissolved chlorine and illumination. After washing to remove excess chlorine, distillation yielded: 54 g., 13%, of recovered $CF_2{=}CFCBrF_2$, b.p. 19–25°,

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[15] The solubility of LiCl in acetone at 0° is 1.73 g./100 g. of acetone.[16]

[16] W. R. G. Bell, *J. Chem. Soc.*, 1927 (1930).

[17] Analyses for halogen were carried out by J. M. Howald.

b.p. plateau 25.5° (734 mm.); 91 g., 22% yield, of $CClF_2CClFCClF_2$, b.p. 72–74°, center cut Va, b.p. 73.1° (743 mm.); 257 g., 52% yield, of $CBrF_2CClFCClF_2$, see below, b.p. 91–93°, center cut VI, b.p. 92.7° (749 mm.); 120 g., 21% yield, of $C_3Br_2ClF_5$'s, b.p. 111–112°, see below, center cut, b.p. 111.9° (732 mm.); and about 1% higher b.p. material, possibly $CBrF_2CBrFCBrF_2$.

$CBrF_2CClFCClF_2$.—Fraction VI above was shown to have the molecular formula $C_3BrCl_2F_5$. Its cooling curve indicated a single substance. These observations supported the conclusion that it was the expected chlorine adduct $CClF_2CClFCBrF_2$. In addition, VI was found not to react with sodium iodide in acetone. Other work[13] has shown that bromine in terminal $-CBrF_2$ groups is inert toward iodide ion in acetone while internal $-CBrF-$ is readily attacked.

$CBrF_2CBrFCClF_2$ **and** $CBrF_2CClFCBrF_2$.—The fraction of b.p. 112° formed by chlorination of $CF_2{=}CFCBrF_2$ was saturated to permanganate in acetone and contained bromine, chlorine and fluorine. It had the following physical properties: b.p. 113.1° (760 mm.), b. range <0.1°, f.p. −115.8°, f.p. depression very large, n^{20}_D 1.4026, d^{20}_4 2.1935. The large freezing range showed that the fraction was a mixture of isomers. Its boiling point supports the molecular formula $C_3Br_2ClF_5$. Excluding rearrangement of carbon–fluorine bonds the components of the mixture could be only $CBrF_2CBrFCClF_2$ and $CBrF_2CClFCBrF_2$. It was predicted, on the basis of observations made with other structures,[13] that while the 1,2-dibromide would react with NaI in acetone to give $CF_2{=}CFCF_2Cl$ plus free iodine the 1,3-dibromide would not react at all under the same conditions. Verification of this prediction, see below, led to the isolation of 1,3-dibromide (VII) in pure form.

The composition of the $C_3Br_2ClF_5$ fraction was thus shown to be about one-third $CBrF_2CBrFCClF_2$ and two-thirds $CBrF_2CClFCBrF_2$.

$CBrF_2CClFCBrF_2$. **Debromination of** $CBrF_2CBrFCClF_2$ **with NaI in Acetone.**—To a solution of 120 g. of NaI (0.80 mole) in 500 ml. of anhydrous acetone was added 116.5 g. (0.36 mole) of the $C_3Br_2ClF_5$ fraction, b.p. 112°, see above. The solution, initially clear, became cloudy within a minute and a white precipitate settled out on standing. After six days at room temperature, during which time a small amount of low boiling material appeared in the Dry Ice trap, the solution was drowned in ice-water. Titration of the solution with standard aqueous $Na_2S_2O_3$ showed 0.125 mole of free I_2 present. The organic layer was washed with iced aq. $NaHSO_3$ and fractionally distilled to give: 11 g. of material b.p. below room temperature, assumed to be $CF_2{=}CFCClF_2$, 18% yield; 9 g., 10%, $CF_2{=}CFCF_2I$, b.p. 51–53°, plateau 53.1° (732 mm.); 68 g., 59%, $CBrF_2CClFCBrF_2$, b.p. 110–112°, center cut VII, b.p. 112.0° (735 mm.), mol. wt. calcd. 326, found 319. The physical properties of $CBrF_2CBrFCClF_2$ differentiate it from $CBrF_2CClFCBrF_2$; previously reported for $CBrF_2CBrFCClF_2$[1] b.p. 113.1° (760 mm.), f.p. −118.0°, n^{20}_D 1.4028, d^{20}_4 2.2016.

$CF_2{=}CFCF_2I$ + **Zn in** CH_3OH. $CF_2{=}CFCHF_2$.—To a well-stirred suspension of 120 g. of Zn dust in 700 ml. of anhydrous methyl alcohol in a one-liter flask at reflux was added slowly 194 g. of $CF_2{=}CFCF_2I$ (0.75 mole). Reaction started immediately, as evidenced by heat evolution, and material boiling from below room temperature up to the boiling point of the methyl alcohol was collected. Distillation of the product gave three fractions: A, b.p. 1.3° (749 mm.); B, b.p. 35.0° (749 mm.); C, b.p. 45° (746 mm.).

Fraction B was tentatively identified as the methyl alcohol azeotrope of $CF_2{=}CFCF_2OCH_3$, obtained in 0 to 16% conversion. It appeared to undergo decomposition with the evolution of acid fumes when distilled from P_2O_5, and was not treated further. Fraction C appeared to be the methyl alcohol azeotrope of unreacted $CF_2{=}CFCF_2I$; about 3% was so recovered.

Redistillation of fraction A from P_2O_5 gave $CF_2{=}CFCHF_2$, center cut VIII, b.p. 1.2° (746 mm.); mol. wt. calcd. 132, found 133 (74% to 90% conversion).

The $CF_2{=}CFCHF_2$ added bromine rapidly with illumination at its boiling point to give $CBrF_2CBrFCHF_2$ (IX), b.p. 95.0–95.2° (741 mm.); mol. wt. calcd. 292, found 292; Br calcd. 54.8, found 55.0, 55.0.

Addition of 35 g. of Cl_2 (0.49 mole) to 73 g. of $CF_2{=}CFCHF_2$ (0.55 mole) with illumination at 0 to 10°, resulted in rapid reaction without evolution of HCl. Fractionation of the product gave 7 g., 10%, of recovered $CF_2{=}CFCHF_2$, b.p. below room temperature; and 96 g., 92% yield, of $CClF_2CClFCHF_2$, b.p. 52–55°, center cut X, b.p. 55.2° (735 mm.), mol. wt. calcd. 203, found 203. There was no sign of higher boiling material.

Chlorination of $CClF_2CClFCHF_2$ occurred slowly at 45 to 55°, to give in substantially quantitative yield $CClF_2CClFCClF_2$ (Vb), b.p. 72.7° (736 mm.). The formation of this well characterized compound substantiated the structures of compounds VIII and X.

$CF_2{=}CClCF_2I$ + **Zn in** C_2H_5OH.—To a well-stirred suspension of 120 g. of zinc dust in 500 ml. of absolute ethyl alcohol at reflux was added, over a half-hour period, 274.5 g. of $CF_2{=}CClCF_2I$ (1.00 mole). Reaction occurred with sufficient heat evolution to require external cooling during the addition. A low-boiling fraction A, 41 g., slowly accumulated in the Dry Ice trap during the addition and for three hours thereafter. A second fraction B boiling from 40 to 77° was then distilled out of the reaction flask leaving a residue, fraction C, a thick slurry.

Fraction A was fractionally distilled from P_2O_5, with which it appeared to react, for only a trace of material boiling below room temperature was obtained, b.p. <17°. The bulk of the material, 32 g., 25% yield, as yet unidentified, b.p. 32.9–33.6° (745 mm.), center cut b.p. 33.4° (738 mm.), b. range <0.1°, f.p. −105°, f.p. dep. <1.3°, d^{20}_4 1.1980, n^{20}_D 1.3342, mol. wt. found 125, MR^{20}_D found 21.5, contained fluorine and chlorine, was unsaturated to $KMnO_4$ in acetone and burned with a smoky flame.

Fraction B, 40 g., was found to be an azeotropic mixture of ethyl alcohol and higher boiling products, all unsaturated to $KMnO_4$ in acetone. It was not treated further.

Fraction C, the residue, was dissolved in water, acidified with HCl, and extracted with benzene using a continuous liquid–liquid extractor. Fractional distillation of the benzene extract gave 60 g., 37% yield, of diethyl malonate, b.p. of center cut XI, 134.4° (100 mm.). The diethyl malonate, in which all that is left of the original perhaloolefin is the three carbon skeleton, may have arisen from hydrolysis of a diether $C_2H_5OCF_2CH_2CF_2OC_2H_5$. The latter would have been produced by a series of basic displacements and base-catalyzed additions accompanying reduction. These interesting reactions are under further investigation.

$CF_2{=}CFCF_2I$ + **Zn in Anhydrous Dioxane.** $CF_2{=}CFCF_2CF_2CF{=}CF_2$.—To a well-stirred suspension of 200 g. of Zn dust in 1500 ml. of anhydrous dioxane (refluxed with and fractionally distilled from Na) at reflux was slowly added 1032 g. of $CF_2{=}CFCF_2I$ (4.00 moles). Rather sudden heat evolution was observed after about one-third of the iodide was added. From this point on,[18] reaction proceeded smoothly. The reaction mixture was held slightly below reflux for several hours, after which material boiling from 52 to 100° was distilled out. The residue contained no water-insoluble material. Redistillation of the volatile product gave 4% of unreacted starting material and an 83% yield of $CF_2{=}CFCF_2CF_2CF{=}CF_2$, b.p. 57–59°, center cut XII, b.p. 58.4° (733 mm.), iodine-free; mol. wt. calcd. 262, found 264.

The 1,5-position of the two double bonds in XII was demonstrated by its oxidation, described below, to the known tetrafluorosuccinic acid.

Photochemical addition of chlorine to XII yielded $CClF_2CClFCF_2CF_2CClFCClF_2$ (XIII), b.p. 89° (50 mm.); mol. wt. calcd. 404, found 405; Cl calcd. 35.1, found 34.8, 35.0.

Oxidation of $CF_2{=}CFCF_2CF_2CF{=}CF_2$.—To a well-stirred mixture of 274 g. of $KMnO_4$ (1.7 moles) and 358 g. of $NaHCO_3$[19] (4.3 moles) in 800 ml. of water cooled to 10°, in a 3-l. 3-neck r.b. flask fitted with a Dry Ice-cooled reflux condenser, was added 200 ml. of reagent grade acetone.[20]

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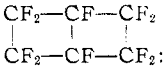
[18] The induction period probably can be eliminated by the initial addition of some $ZnCl_2$ to the reaction mixture.

[19] The use of $NaHCO_3$ instead of NaOH or KOH with $KMnO_4$ for oxidation of perhaloölefins has been found generally advantageous in that degradation of the oxidation products is reduced, R. T. Carroll and W. L. Miller, Jr., unpublished work.

[20] On one occasion uncontrolled oxidation of the acetone occurred when the temperature was allowed to rise on mixing. However, no difficulty was encountered when the reaction mixture was kept below 20° after the acetone was added.

To this mixture was added 141.5 g. of $CF_2{=}CFCF_2CF_2CF{=}CF_2$ (0.5 mole) during about one hour with the temperature kept below 20°.[20] Stirring was continued for an additional three hours until the evolution of carbon dioxide ceased. The oxidation mixture was worked up by reducing with SO_2 until there was no further lightening in color, filtering the slurry, acidifying the filtrate with 120 ml. of concd. H_2SO_4, and distilling out material up to the boiling point of water, mostly CO_2, SO_2 and acetone. The residue was extracted with diethyl ether in a continuous liquid-liquid extractor. The ether was then removed and the residue treated with 300 ml. of absolute ethyl alcohol. The excess alcohol was distilled off at atmospheric pressure, and the product fractionally distilled to give 75 g., 60% yield, of $C_2H_5OCOCF_2CF_2COOC_2H_5$ (XIVa), b.p. 96° (20 mm.). The physical properties of this material differed substantially from those reported by Henne and Zimmerschied[10]; see Table I, footnote *k*. For this reason, another sample of $C_2H_5OCOCF_2CF_2COOC_2H_5$ was prepared from $CF{=}CFCF_2CF_2$.[10]

Oxidation of $CF{=}CFCF_2CF_2$.—The oxidation of this compound, b.p. 0.2° (740 mm.), was carried out at atmospheric pressure, and the diethyl ester of perfluorosuccinic acid isolated by the technique described above for the oxidation of XII. The olefin, 81 g. (0.50 mole), was distilled into the reaction flask containing 137 g. of $KMnO_4$, 179 g. of $NaHCO_3$, 200 ml. of acetone and 800 ml. of water. No external cooling was required, since the refluxing olefin kept the mixture below 12°. Most of the olefin had reacted in 9 hours. From the resulting mixture was obtained 85 g., 70% yield, of $C_2H_5OCOCF_2CF_2COOC_2H_5$ (X), center cut (XIVb) b.p. 95° (20 mm.). The physical properties of XIVb were substantially identical with those of XIVa; see Table I.



$$\begin{array}{ccccc} CF_2 & - & CF & - & CF_2 \\ | & & | & & | \\ CF_2 & - & CF & - & CF_2 \end{array}$$

: Thermal Reaction of $CF_2{=}CFCF_2CF_2CF{=}CF_2$.—The diene XII was metered from a constant head dropping funnel into a copper coil vaporizer immersed in an oil-bath held at 100° and the vapor passed into a 45 cm. × 3.8 cm. i.d. electrically heated nickel reactor tube. A thermocouple well extended into the center of the reactor tube. The mixture of product and unreacted starting material was condensed by a water-cooled copper condenser with receiver connected to Dry Ice and liquid air-cooled traps. Before and after each run the system was swept out with dry nitrogen. The product, boiling 17° lower than the starting material, was separated readily by fractional distillation. In the first run, 0.84 mole of XII was passed through the tube at 350° with a contact time of two minutes to give less than 1% conversion to product; 97% of the starting material was recovered. In the second run, the temperature was raised to 450°; 0.62 mole of XII gave a 60% conversion to product and 37% of the starting material was recovered. In the third run, with the temperature at 450°, the contact time was increased to 6 minutes; 0.46 mole of XII gave a 70% conversion to product, and 27% of the starting material was recovered.

The product, compound XV, a solid melting at 41°, b.p. 42.6° (732 mm.), mol. wt. calcd. 262, found 262, was saturated to chlorine plus light and to $KMnO_4$ in acetone. It formed an azeotrope with CCl_4, b.p. 41.6° (737 mm.).

The structure proposed for this compound, perfluorobicyclo[2.2.0]hexane, is based on the following considerations. The formation of a single product from the diene XII with the same molecular weight and with more than 97% total weight recovery indicated that XV was formed from XII by thermal isomerization, a process which requires only an electronic rearrangement. The loss of two double bonds necessitates a bicyclo structure for XV. The relatively high freezing point and very small liquid range (about 3° at atmospheric pressure) suggest a high degree of symmetry. The marked ease of formation of four-membered rings by thermal reaction of a variety of olefins containing the terminal $CF_2{=}$ structure is well known. In addition, a compound analogous to XV, which contains three fused four membered rings, perfluorotricyclo[4.2.0.0^{2,5}]-octane, is known to be formed by thermal reaction of perfluoro-1,3-butadiene.[21]

An X-ray investigation of XV[22] failed to shed much light on the structure, because the material was found to show rotational disorder.

$CF_2{=}CClCF_2I$ + Zn in Anhydrous Dioxane: $CF_2{=}CClCF_2CF_2CCl{=}CF_2$.—To a well-stirred suspension of 100 g. of Zn dust in 400 ml. of anhydrous dioxane at reflux was added 169 g. of $CF_2{=}CClCF_2I$ (0.62 mole) over a half-hour period. There was no noticeable heat effect at any time; the mixture was held near reflux for 6 hours, and material was distilled out to the boiling point of dioxane, 100.7° (747 mm.). The distillate contained nothing boiling below room temperature. It contained a small amount of unidentified material boiling at 45°, having a very pungent odor, but was principally a dioxane azeotrope, b.p. 98.5° (747 mm.), n_D^{20} 1.3989, *ca.* 54% dioxane by wt., which gave on drowning in water a 32% yield of $CF_2{=}CClCF_2CF_2CCl{=}CF_2$ (XVI), b.p. 112.8° (735 mm.). The structure proposed for this material is based on analogy with that demonstrated for XII.

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Methyl-fluorinated Methyldiarylcarbinols and Related Compounds

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Nine methyl-fluorinated derivatives of diphenylmethylcarbinol have been prepared by the Grignard reaction from suitable substitution products of ethyl fluoroacetate or acetophenone. The ultraviolet and infrared spectra of these carbinols are discussed. Some of the above acetophenones also have been reduced and the corresponding secondary alcohols condensed with chlorobenzene in the presence of fuming sulfuric acid. The chemical reactions of the new substances have been studied. Ethyl fluoroacetate is α-chlorinated by sulfuryl chloride in the presence of benzoyl peroxide.

The interesting biological properties[1-3] of the diaryl-(trifluoromethyl)-carbinols[4,5] made a study of

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