product dried for one hour at 100° contained alcohol of crystallization.

D. **Demethylation by Sodium Propylate. 2-Methyl-3-ethyl-5-dimethylaminoindole.**—The quaternary ammonium chloride (10 g.) was refluxed with a solution of sodium (4 g.) in *n*-propyl alcohol (250 ml.) for 17 hours. After removal of most of the solvent under reduced pressure, water was added and residual propanol distilled out also under reduced pressure. Finally the water-insoluble oil remaining crystallized and was filtered. The dimethylamino compound so obtained was recrystallized from a concentrated alcoholic solution by slow addition of a little water.

The 5-dimethylaminoindole also was obtained from the 5-aminoindole without purification of the intermediate quaternary salts. Instead of precipitation of a picrate, concentration of the acidified methylation mixture was carried out. The saline residue was carefully dried by repeated concentration with absolute alcohol and final heating *in vacuo* at 50° and 1 mm. This material was then subjected to sodium propylate demethylation as described above. From 20 g. of 2-methyl-3-ethyl-5-aminoindole 19 g. of the 5-dimethylamino compound, m.p. 97–100°, was obtained for an over-all yield of 82%.

2-Methyl-3-β-chloroethyl-5-dimethylaminoindole Picrate.—To 2-methyl-3-β-hydroxyethyl-5-dimethylaminoindole (1.0 g.) dissolved in chloroform (50 ml.) was added a solution of thionyl chloride (1.2 ml.) in chloroform (50 ml.) in one portion. The mixture was refluxed for 45 minutes, then concentrated under reduced pressure with several additions of alcohol. The residue in a little alcohol was added to 5% alcoholic picric acid (60 ml.). The crystals that separated together with a second crop obtained on cautious addition of water were combined and recrystallized from 90% acetone to give 1.5 g., 72%, m.p. 188–189° with slow heating. The m.p. was quite variable with the rate of heating. The Beilstein test for halogen was strong.

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A Study of the Chlorination of Fluorinated Aliphatic Ethers[1]

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RECEIVED OCTOBER 30, 1953

Previous papers[2,3] described the photochemical monochlorination of some fluorinated aliphatic ethers. The present paper reports (with some correction of previous data) a complete study of the products isolated in the stepwise photochemical chlorination of $CH_3\text{–}O\text{–}CF_2CFClH$ and $CH_3CH_2\text{–}O\text{–}CF_2CFClH$ in the liquid phase. The chlorination of $CH_3\text{–}O\text{–}CF_2CFClH$ went easily and stepwise to $CCl_3\text{–}O\text{–}CF_2CFClH$ then, after some lag, to $CCl_3\text{–}O\text{–}CF_2CFCl_2$. Although not all possible chlorinated products of $C_2H_5\text{–}O\text{–}CF_2CFClH$ could be isolated, experimental results indicated that chlorination proceeded in a similar manner. Chlorination first gave the α- and β-monochlorinated ethers, $CH_3CHCl\text{–}O\text{–}CF_2CFClH$ and $CH_2ClCH_2\text{–}O\text{–}CF_2CFClH$ in a ratio of 3:1.

It was previously reported[2] that chlorination of $C_2H_5\text{–}O\text{–}CF_2CFClH$ in a similar manner, yielded $CH_3CCl_2\text{–}O\text{–}CF_2CFClH$ (2 parts) and $CH_2ClCH_2\text{–}O\text{–}CF_2CFClH$ (1 part). The α-chloro ether obtained in the present work was found, by means of physical properties and infrared absorption spectra, to be identical with the compound reported to be $CH_3CCl_2\text{–}O\text{–}CF_2CFClH$. Since repeated chlorine analyses and molar refraction indicated the major fraction to be a monochlorinated product, it now appears that actually $CH_3CHCl\text{–}O\text{–}CF_2\text{-}CFClH$ was obtained instead of the dichlorinated ether.

Continued chlorination of either $CH_3CHCl\text{–}O\text{–}CF_2CFClH$ or $CH_2ClCH_2\text{–}O\text{–}CF_2CFClH$ yielded successively $CH_2ClCHCl\text{–}O\text{–}CF_2CFClH$ and $CHCl_2CHCl\text{–}O\text{–}CF_2CFClH$. Further chlorination gave a mixture of higher chlorinated products which distilled over a range of 65–94° at 10 mm. pressure, with no constant-boiling flat, while the index of refraction rose from 1.4300 to 1.4575. Although the tetra- and pentachlorinated compounds could not be isolated from this high-boiling mixture, cleavage with aluminum chloride, as described below, showed it contained no products resulting from the replacement of the H-atom located in the fluoroalkyl portion of the ether.

Finally, chlorination was allowed to proceed to completion to yield $CCl_3CCl_2\text{–}O\text{–}CF_2CFCl_2$.

These chlorinated ethers proved to be stable compounds undergoing none of the reactions to which alkyl and chloroalkyl ethers are usually susceptible. They did not undergo hydrolysis to esters in the presence of sulfuric acid by the method of Young and Tarrant.[4] The ethers did undergo cleavage with aluminum chloride and aluminum bromide to yield a mixture of alkyl and acyl halides. These cleavage reactions were used extensively in the identification of the chlorinated products.

Experimental

The photochemical liquid-phase chlorination was carried out by bubbling chlorine through the liquid through a sintered glass distributor. The chlorinations proceeded smoothly with evolution of sufficient heat to cause refluxing. However, the reactions became slower as the ether became more highly chlorinated. In each case chlorine was passed into the ether until the gain in weight of the ether indicated that one additional chlorine had been introduced into the molecule. The product was washed with water, dried and fractionated in a precision fractionating column.

Proof of the point of attack of chlorine was found by cleavage of the ethers with aluminum chloride in the following manner. For example: $CH_3\text{–}O\text{–}CF_2CFClH$ upon treatment with aluminum chloride yielded a mixture of methyl chloride, methyl fluoride, CFClHCOF and CFClHCOCl. The acid halides were identified by formation of the known N-phenyl-α-chloro-α-fluoroacetamide,[4] m.p. 86–87°.

Anal. Calcd. for C_8H_7FClNO: C, 51.25; H, 3.76; N, 7.53; Cl, 18.90. Found: C, 51.55; H, 3.86; N, 7.53; Cl, 18.86.

The above methyl halides were identified after separation by low temperature distillation.

It was found, on subsequent use of the above reaction, that the more highly chlorinated the ether the more it resisted cleavage with aluminum chloride. In general, the period of reaction, the temperature at which reaction occurred and the amount of reagent required to bring about effective cleavage increased as the number of chlorine atoms increased. Aluminum bromide was also effective in splitting the chlorinated ethers.

The fact that N-phenyl-α-chloro-α-fluoroacetamide was obtained from all the chlorinated ethers except $CCl_3\text{-}O\text{-}CF_2CFCl_2$ and $CCl_3CCl_2\text{-}O\text{-}CF_2CFCl_2$ indicated that the stepwise chlorination proceeded in accord with the directive influence of the $-CF_2-$ cluster. Cleavage of the fully chlo-

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[1] Presented before the Fluorine Section of the Division of Industrial and Engineering Chemistry, 124th Meeting of the American Chemical Society, Chicago, Ill., Sept. 6–11, 1953. This paper represents part of a thesis submitted by B. Stricklin to the Graduate School, University of Colorado, in partial fulfillment of the requirements for the Ph.D. degree. This work was supported in part by the Office of Naval Research and by a grant-in-aid from the Minnesota Mining and Manufacturing Co., St. Paul, Minn.

[2] J. D. Park, J. R. Lacher, *et al.*, THIS JOURNAL, **74**, 2292 (1952).

[3] K. E. Rapp, J. T. Barr, *et al.*, *ibid.*, **74**, 751 (1952).

[4] J. A. Young and P. Tarrant, *ibid.*, **71**, 2432 (1949).

TABLE I

PHYSICAL PROPERTIES OF THE CHLORINATED FLUOROETHERS

Compound	B.p., °C.	Mm.	d^{20}_4	$n^{20}\text{D}$	MR^a	MR^b	AR_F	Chlorine, % Calcd.	Found
$ClCH_2OCF_2CFHCl^c$	104.5	624	1.5269	1.3768	27.46	27.52	1.12	37.76	38.75
$CHCl_2OCF_2CFHCl$	112.5	626	1.5620	1.3883	31.99	32.40	1.13	48.92	49.09
CCl_3OCF_2CFHCl	131	629	1.6631	1.4090	36.85	37.39	1.17	56.31	56.18
$CCl_3OCF_2CFCl_2$	142	626	1.7141	1.4187	41.73	42.11	1.13	61.91	61.36
$ClCH_2CH_2OCF_2CFHCl^c$	84	100	1.4620	1.3935	32.08	32.44	1.23	36.04	37.15
$CH_3CHClOCF_2CFHCl^c$	63	100	1.4020	1.3755	31.74	32.17	1.14	36.04	35.95
$CH_2ClCHClOCF_2CFHCl$	97	100	1.5426	1.4080	36.61	37.02	1.13	45.95	46.02
$CHCl_2CHClOCF_2CFHCl^c$	85	23	1.6438	1.4291	41.47	41.66	1.06	53.34	53.17
$CCl_3CCl_2OCF_2CFCl_2$	94	10	1.7819	1.4575	56.07	56.00	0.973	67.25	67.02
$CCl_2{=}CClOCF_2CFCl_2$	89	40	1.7054	1.4440	45.97	46.30	1.14	59.42	59.35

[a] Calculated by adding the atomic increments. [b] Observed values, calculated by means of Lorentz-Lorenz equation. [c] Also reported by Rapp, Barr, *et al.*, THIS JOURNAL, **74**, 751 (1952).

rinated ethers and subsequent treatment of the reaction mixture with cold concentrated ammonia produced dichlorofluoroacetamide melting at 125°.

Preparation of $CCl_2{=}CCl{-}O{-}CF_2CFCl_2$.—To a mixture of 27 g. of powdered zinc in ethanol was added slowly 128 g. (0.37 mole) of $CCl_3CCl_2{-}O{-}CF_2CFCl_2$ with efficient stirring. A vigorous reaction occurred with evolution of heat which was removed by cooling in an ice-bath. After the addition of ether was completed, the mixture was refluxed gently for one hour. The reaction mixture was then filtered to remove zinc chloride and the filtrate washed with water and dried.

Fractionation gave 98 g. of $CCl_2{=}CCl{-}O{-}CF_2CFCl_2$ distilling at 89° at 40 mm. pressure. This structure was assigned on the basis of analysis and molar refraction.

Table I summarizes the physical properties of the various chlorination products.

In summary, it may be stated that the initial chlorination of $CH_3{-}O{-}CF_2CFClH$ and $C_2H_5{-}O{-}CF_2CFClH$ takes place exclusively in the alkyl portion of the ether with the hydrogen of the CFClH group being the last to be replaced by chlorine.

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Properties of Some Perfluorinated N-Bromo Amides[1]

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RECEIVED NOVEMBER 2, 1953

The preparation and brominating properties of some halogenated N-bromoacetamides have been previously described[3] and the brominating activity of the N-Br bond related to the infrared intensity of the N-H fundamental band at 2.93 μ.[4]

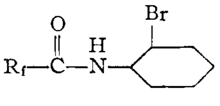
In this work, the N-bromoperfluoramides $CF_3CF_2CONHBr$, $CF_3CF_2CF_2CONHBr$ and $CF_3CF_2CF_2CF_2CONHBr$ were prepared following the method previously described.[3] These three compounds were separately treated with toluene; the percentage side chain bromination was compared to the percentage ring bromination and the absorption coefficient, α, calculated for the N-H fundamental band at 2.93 μ. Table I shows that the correlation found between these two factors falls in line with those previously described.[4]

TABLE I

CORRELATION OF INFRARED ABSORPTION COEFFICIENT, α, WITH BROMINATION STUDIES ON TOLUENE

Compound	α	Ring bromination, %	Side chain bromination, %
$CF_3CF_2CONHBr$	178	69.9	30.1
$CF_3CF_2CF_2CONHBr$	200	73.9	26.1
$CF_3CF_2CF_2CF_2CONHBr$	246	86.7	13.3
$CF_3CONHBr$ (for comparison)	250	88	12

The three N-bromo amides also were treated with cyclohexene which, like toluene, provides an opportunity for bromination to occur by free radical and ionic bromine. Table II shows the results of this study. Along with allylic bromination and addition of bromine across the double bond, some adducts of the type



where R_f = CF_3CF_2–, $CF_3CF_2CF_2$– and $CF_3CF_2CF_2CF_2$–, were isolated in each case.

TABLE II

BROMINATION STUDIES ON CYCLOHEXENE

Compound	3-Bromocyclohexene, %	1,2-Dibromocyclohexane, %	Adduct, %
$CF_3CF_2CONHBr$	17.2	9.5	14.9
$CF_3CF_2CF_2CONHBr$	11.5	9.5	16.9
$CF_3CF_2CF_2CF_2CONHBr$	0	14	14.6

It will be noted from Table II that the percentage of bromination resulting from homolytic cleavage of the N-Br bond decreases and that the total of the two products resulting from heterolytic cleavage of the N-Br bond increases in the same order as the absorption coefficients (Table I) increase. The 3-bromocyclohexene had a b.p. of 77–83° (35 mm.) and $n^{20}\text{D}$ 1.5279 (lit. 80° (35 mm.), $n^{20}\text{D}$ 1.5280). The 1,2-dibromocyclohexane had a b.p. of 100–105° (15 mm.) and $n^{20}\text{D}$ 1.5534 (lit. 99–103° (16 mm.), $n^{20}\text{D}$ 1.5532).

The properties of the various new compounds are given in Table III.

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(1) This work was supported in part by a grant-in-aid from the Minnesota Mining and Manufacturing Co., St. Paul, Minn.

(2) This paper represents in part work done at the University of Colorado in partial fulfillment of the requirements for the Ph.D. degree.

(3) J. D. Park, J. R. Lacher, *et al.*, THIS JOURNAL, **74**, 2189 (1952).

(4) J. R. Lacher, J. D. Park, *et al.*, *ibid.*, **74**, 5578 (1952).