aliphatic but not aromatic esters. A differential between these two rates was observed earlier by Sudborough[13] and was used in the laboratory in connection with the study of the polymerization of α-methylstyrene.[23] In the present instance the usual condition was in the amounts or proportions of 0.0025 mole of carboxylic acid, 5 ml. of methanol, and 0.2 ml. of concentrated sulfuric acid. During 16 hr. (overnight) α-phenylisobutyric and phenylacetic acid were esterified 100%. Cuminic acid, however, was esterified only 50%; after 72 hr. it was esterified 100%. Phthalic acid was esterified 100% after 16 hr.

These conditions were applied to the two isomeric acids from *p*-cymene. In 72 hours the 2-carboxyl isomer yielded 11% of the half ester and 68% of the diester. The 3-carboxyl isomer yielded 26% of the half ester and 33% of the diester.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF COLORADO]

Stepwise Chlorination of 1,1,2,2-Tetrafluoroethyl Ethyl Ether[1]

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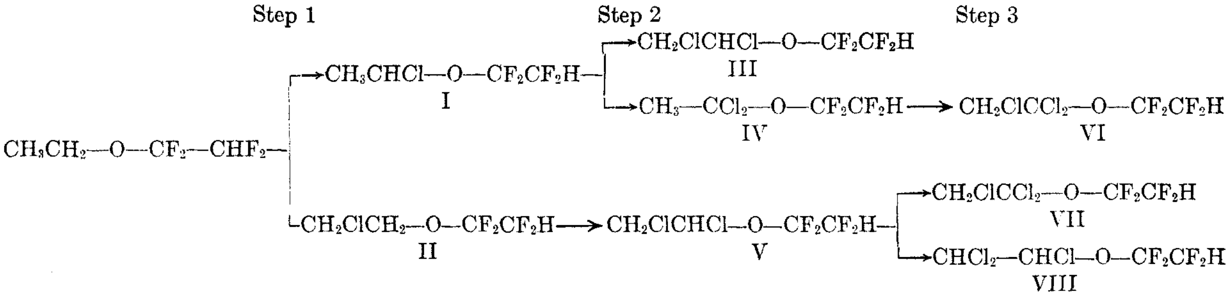
The stepwise photochemical chlorination of $CHF_2CF_2—O—CH_2CH_3$ was carried out and the products isolated and identified.

Previous papers[2-4] described the photochemical chlorination of some fluorinated aliphatic ethers. The present paper reports a study of the products isolated in the stepwise photochemical chlorination of 1,1,2,2-tetrafluoroethyl ethyl ether carried out in the liquid phase. As indicated by our previous studies,[2,3] the directive effect was such that the replacement of the hydrogen atoms took place preferentially in the unfluorinated portion of the ether.



Monochlorination of $CH_3CH_2—O—CF_2CF_2H$ yielded $CH_3—CHCl—O—CF_2CF_2H$ (I) and $CH_2Cl-CH_2—O—CF_2CF_2H$ (II) in the ratio of 7:1. Chlorination of (I) to the dichloride stage yielded $CH_2ClCHCl—O—CF_2CF_2H$ (III) and $CH_3CCl_2—O—CF_2CF_2H$ (IV) in the ratio of 1:1. Stepwise chlorination of II yielded only one dichloride $CH_2Cl—CHCl—O—CF_2CF_2H$ (V). Further stepwise chlorination of (IV) yielded only one trichloride, $CH_2ClCCl_2—O—CF_2—CF_2H$ (VI) and similar chlorination of (V) yielded $CH_2ClCCl_2—O—CF_2CF_2H$ (VII) and $CHCl_2CHCl—O—CF_2CF_2H$ (VIII) in the ratio of 2:1. Continued chlorination of (VI) and (VIII) under the influence of actinic light to obtain more highly chlorinated products was unsuccessful.

The tendency of chlorine to attack the α-hydrogen atoms in preference to the β-hydrogen atoms is not surprising and has been plausibly explained in previous papers.[2,5]

The chlorinated ethers proved to be stable compounds and quite resistant to hydrolysis[6] in the presence of sulfuric acid. However, they did undergo cleavage with aluminum chloride, the products of which were used in the identification of the chlorinated fluoroethers.

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TABLE I

PHYSICAL PROPERTIES OF THE CHLORINATED FLUOROETHERS

Compound	B.P./Mm. Hg	n_D^{20}	d_4^{20}	MR[a]	MR[b]
$CH_3CHCl—O—CF_2CF_2H$	82/615 36.8/100	1.364	1.3349	27.18	27.36
$CH_2ClCH_2—O—CF_2CF_2H$	59.5/100	1.424	1.349	27.18	27.17
$CH_2ClCHCl—O—CF_2CF_2H$	71.4/100	1.5228	1.3726	32.05	32.14
$CH_3—CCl_2—O—CF_2CF_2H$	51.9/100	1.4760	1.3621	32.05	32.32
$CH_2ClCCl_2—O—CF_2CF_2H$	140/632	1.3980	1.6102	36.916	37.39
$CHCl_2CHCl—O—CF_2CF_2H$	160/630	1.4250	1.7337	36.91	36.79
$CH_2{=}CCl—O—CF_2CF_2H$	58–60/630	1.3410^{19}	1.3206^{19}	26.715	27.68
$CHCl{=}CH—O—CF_2CF_2H$	65/632	1.3925	1.5373	26.715	27.1

[a] Calculated by adding atomic and structural increments. [b] Experimental values, calculated from Lorentz-Lorenz equation.

EXPERIMENTAL

The tetrafluoroethylene was made by the pyrolysis of $CHClF_2$ according to the procedure of Park *et al.*[7] and the ether $CH_3CH_2—O—CF_2CF_2H$ obtained by the base-catalyzed addition of ethanol to $CF_2{=}CF_2$ under autogenous pressure.[8] The chlorination and work-up of the ethers were carried out according to methods previously described.[2,3]

Chlorination studies. Chlorination of 184.6 g. of $C_2H_5—O—CF_2CF_2H$ yielded 112.5 g. of $CH_3CHCl—O—CF_2CF_2H$ (I) and 12.9 g. of $CH_2ClCH_2—O—CF_2CF_2H$ (II) in the ratio of 7:1. Total yield 93%.

Anal. Calcd. for $C_4H_5ClF_4O$. Compound I: Cl, 19.66. Found: Cl, 19.4. Compound II: Cl, 19.66. Found: Cl, 19.63.

Proof of the point of attack of chlorine was found by cleavage of (I) and (II) with aluminum chloride and the formation of CHF_2CONH_2, m.p. 50.6° (Lit.[9]: m.p. 50.2°).

Anal. Calcd. for $C_2H_3F_2NO$: C, 25.2; F, 40. Found: C, 25.3; F, 40.2.

These cleavage studies carried out with all of the chlorinated products always indicated that the $—CF_2—CF_2H$ portion of the ethers always remained unattacked by chlorine in the compounds reported in this work as shown by the formation of CHF_2CONH_2.

The structure of (II) was proved by an independent synthesis of $CH_2ClCH_2—O—CF_2CF_2H$. The interaction of CH_2OHCH_2OH and $CF_2{=}CF_2$ yielded $CH_2OH—CH_2O-CF_2CF_2H$[4] which upon further reaction with PCl_5 yielded $CH_2ClCH_2O—CF_2CF_2H$. The physical properties and infrared spectrum of this latter compound were found to be identical with those of (II). On this basis, compound (I) was assigned the structure $CH_3CHCl—O—CF_2CF_2H$. Chlorination of 33.9 g. of (II) yielded only one fraction (V), b.p. 71.3° (100 mm.); yield 93%.

Anal. Calcd. for $C_4H_4Cl_2F_4O$: Cl, 32.7; Found: Cl, 32.6.

The physical properties and infrared spectrum of this compound (V) were found to be identical with one of the two dichlorinated products obtained in the chlorination of (I). (Step 2.)

In the chlorination of 74.4 g. of (I) (Step 2) to the dichloride, two fractions, (III) and (IV), were obtained in the ratio of 1:1. One fraction (IV), b.p. 51.9° (100 mm.) had properties different from compound (V). Since compounds III and V are identical, the only possible structure compatible for the dichloride is $CH_2ClCHCl—O—CF_2CF_2H$. Compound IV, then by an elimination process is assigned the structure $CH_3CCl_2—O—CF_2CF_2H$ (IV).

Anal. Calcd. for $C_4H_4Cl_2F_4O$: Cl, 25.2; F, 40.0. Found: Cl, 25.3; F, 40.2.

Controlled chlorination of 42 g. of (IV) gave 40.5 g. of only one product $CH_2Cl—CCl_2—O—CF_2CF_2H$ (VI), b.p. 140° (630 mm.); yield 81%.

Anal. Calcd. for $C_4H_3Cl_3F_4O$: Cl, 42.68; H, 1.2; C, 19.23. Found: Cl, 42.7; H, 1.3; C, 19.16.

The structure of VI was proved in the following manner. Compound IV ($CH_3CCl_2—O—CF_2CF_2H$) was dehydrochlorinated to $CH_2{=}CCl—O—CF_2CF_2H$ (IX).

Anal. Calcd. for $C_4H_3ClF_4O$: C, 26.91; H, 1.68; F, 42.6. Found: C, 26.81; H, 1.60; F, 42.35.

Compound IX upon reaction with chlorine yielded a trichloride identical with VI. The two infrared spectra were found to be superimposable. Dechlorination of VI gave the same product (IX) which was obtainable from the dehydrochlorination of IV.

Controlled chlorination of 104 g. of V gave two fractions; 45 g. of VII and 19 g. of VIII with the general formula $C_4H_3Cl_3F_4O$ which were obtained in the ratio of about 2:1. VII was found to be identical to VI obtained from the chlorination of IV.

The structure of VIII was arrived at by elimination and by dechlorination of VIII to $CHCl{=}CH—O—CF_2CF_2H$. This latter compound was different from the olefin obtained from the dechlorination of VII.

Anal. Calcd. for $C_4H_3ClF_4O$: C, 26.91; H, 1.68; F, 42.6. Found: C, 26.75; H, 1.61; F, 42.47.

In the chlorination of diethyl ether at room temperature according to Hall *et al.*[10] the α-hydrogen is replaced first, then the three β-hydrogens successively, and only then is the second α-hydrogen attacked. In direct contrast, the chlorination of $CH_3CH_2O—CF_2CF_2H$ proceeds in such a manner to yield $CH_3CHCl—O—CF_2CF_2H$ and $CH_2ClCH_2—O—CF_2CF_2H$ after which the remaining α-hydrogen is attacked to yield $CH_3CCl_2—O—CF_2CF_2H$ and $CH_2Cl—CHCl—O—CF_2CF_2H$. These differences[11] in the mode of radical chlorination may be due to the interplay of radical stability and polar factors. The fluorinated alkoxy group studied here does not provide sufficient activation of the alpha chlorine atom to permit elimination; consequently radical substitution proceeds undisturbed.

The physical properties of the various chlorinated ethers are tabulated in Table I.

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