[Contribution from the Department of Chemistry, University of Colorado]

The Stability of Some Fluorochloropropyl Ethyl Ethers[1]

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The preparation and stability of some fluorochloropropylethyl ethers are discussed. The physical properties of various esters produced from the hydrolysis of the ethers are given. This latter reaction is a novel method of preparation not heretofore given in the literature.

It is known that the substitution of fluorine atoms in alkyl halogenated ethers produced compounds which are quite stable to heat. Park, Lacher, *et al.*[2,3] and Hanford and Rigby[4] and others have added alkanols to such fluorinated olefins as $CF_2{=}CF_2$ and $CF_2{=}CFCl$ producing saturated ethers of the type $ROCF_2CF_2H$ and $ROCF_2CHFCl$ which are quite stable to heat.

However, it is known[5,6,7] that ethers of the type $ROCCl_2CHCl_2$ and $ROCCl_2CH_2Cl$ are very sensitive to heat and will easily decompose to an acid chloride and ethyl chloride in the absence of water or to an ester and hydrogen chloride in the presence of water.

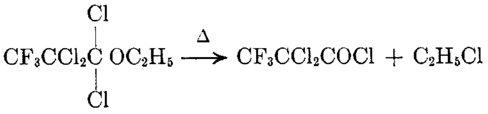
Since the trifluoromethyl group and the fluorine atom are strongly electronegative, the placement of these substituents in various positions should improve the stability of this type of compound.

Thus $CF_3CCl_2CCl_2OC_2H_5$ may be considered as being an analog of $CHCl_2CCl_2OC_2H_5$ in which the hydrogen in the $-CHCl_2$ group is replaced by the $-CF_3$ grouping which is more electronegative in character. This CF_3- grouping is known to influence by induction the stability of adjacent groupings. In this case, it should have a slight shortening effect on the length of the carbon-chlorine bond, thereby affecting its stability.

$CF_3CCl_2CCl_2OC_2H_5$ (I) may be prepared by the addition of chlorine to $CF_3CCl{=}CClOC_2H_5$.

Although $CHCl_2CCl_2OC_2H_5$ can be easily hydrolyzed to the ester $CHCl_2CO_2C_2H_5$ by the addition of water, prolonged boiling with water of I gave negative results.

However on being heated, I readily underwent decomposition to CF_3CCl_2COCl and C_2H_5Cl.



$$CF_3CCl_2\overset{\overset{\displaystyle Cl}{|}}{\underset{\underset{\displaystyle Cl}{|}}{C}}OC_2H_5 \xrightarrow{\Delta} CF_3CCl_2COCl + C_2H_5Cl$$

The ethyl chloride was caught in a trap and identified by its boiling point on a Podbielniak column and by its molecular weight.

The CF_3CCl_2COCl was fractionated on a glass helix-packed column in order to obtain a reasonably pure sample. Its molar refraction checked closely with the theoretical value for this structure. The infrared spectrogram showed the presence of a strong peak in the carbonyl region and it was converted to the acid $CF_3CCl_2CO_2H$ (whose neutral equivalent compared closely with the calculated value). The corresponding amide $CF_3CCl_2CONH_2$ and the anilide $CF_3CCl_2CONHC_6H_5$ showed by nitrogen analysis that CF_3CCl_2COCl is the correct structural assignment.

A new series of fluorochloropropionic esters were also prepared by reacting methyl, ethyl, *n*-propyl, and *n*-butyl alcohol with CF_3CCl_2COCl.

An examination of the physical properties of each one of these esters, *i.e.*, the density, refractive index, molar refraction, magnetic susceptibility, infrared spectrogram, and carbon-hydrogen analyses shows them to be members of a homologous series.

Chaney[8,9,10] in a series of patents assigned to the American Viscose Company described the preparation of fluorochloroacid chlorides and their derivatives by the introduction of a mixture of oxygen and chlorine into a fluorochloroolefin under the influence of actinic light.

The decomposition of saturated fluorochloroethers to fluorochloroacid chlorides is not reported in the literature and represents a new method of preparing fluorochloroacid chlorides or fluorides and their derivatives.

Hydrogen chloride was also added to the double bond of $CF_3CCl{=}CClOC_2H_5$ and this adduct on heating was found to decompose to $CF_3CHClCOCl$ and C_2H_5Cl. $CF_3CHClCOCl$ although not obtained

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[1] Abstracted from a thesis submitted by W. M. Sweeney in partial fulfillment of the requirements for the Ph.D. degree, University of Colorado, June 1953.

[2] Park, Lea, Vail, and Lacher, *J. Am. Chem. Soc.*, **70**, 1550 (1948).

[3] Park, Snow, and Lacher, *J. Am. Chem. Soc.*, **73**, 861, 862 (1951).

[4] Hanford and Rigby, U. S. Patent 2,409,274 [*Chem. Abstr.*, **41**, 982 (1942)].

[5] Crompton and Triffitt, *J. Chem. Soc.*, **119**, 1874, 1875 (1921).

[6] McKie, *J. Chem. Soc.*, **123**, 2213–2217 (1923).

[7] Imbert, German Patent 222,194 [*Chem. Zentr.*, **II**, 1999 (1910)].

[8] Chaney, U. S. Patent 2,456,768 [*Chem. Abstr.*, **43**, 4683 (1949)].

[9] Chaney, U. S. Patent 2,439,505 [*Chem. Abstr.*, **42**, 7315 (1948)].

[10] Chaney, U. S. Patent 2,514,473 [*Chem. Abstr.*, **44**, 9474 (1950)].

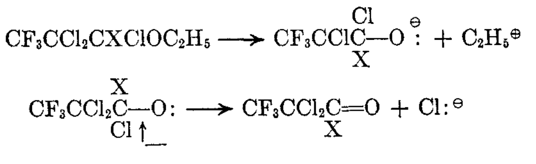
in a pure enough form to obtain exact physical data, was identified by its conversion to the amide $CF_3CHClCONH_2$ and the anilide $CF_3CHClCONHC_6H_5$ whose nitrogen analyses compared closely with the calculated values.

Since ethers of the type $ROCF_2R$ do not ordinarily decompose to form acid fluorides and alkyl fluorides because of the greater stability of the carbon fluorine bond, it was thought that the substitution of a fluorine atom for one of the *alpha* or *beta* chlorine atoms in $CF_3CCl_2CCl_2OC_2H_5$ might result in greater heat stability, and if the ether did decompose, a new method of preparing fluorochloroacid fluorides might be developed since upon cleavage it is more likely that the *alpha* chlorine atom rather than the *alpha* fluorine atom would eliminate and combine with the alkyl group to form the alkyl halide.

Chlorine was added to $CF_3CCl{=}CFOC_2H_5$ to yield $CF_3CCl_2CFClOC_2H_5$. Physical properties and carbon-hydrogen analyses checked with the theoretical values. This saturated fluorochloroether proved to be much more stable than $CF_3CCl_2CCl_2OC_2H_5$. It could be fractionated under reduced pressure without decomposition, and, as in the case of $CF_3CCl_2CCl_2OC_2H_5$, could not be hydrolyzed to the ester by boiling with water.

On heating to its boiling point at atmospheric pressure, however, $CF_3CCl_2CFClOC_2H_5$ was not stable enough to maintain its entity but decomposed mainly to CF_3CCl_2COF and C_2H_5Cl. The structure, CF_3CCl_2COF, was proved by its conversion to the amide and anilide whose physical properties checked with those prepared from CF_3CCl_2COCl above.

The following mechanism is proposed to explain the decomposition. (X is chlorine or fluorine).

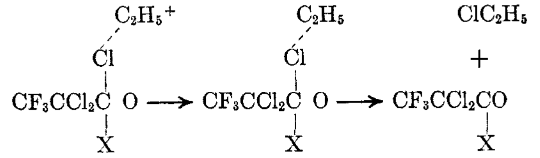


$$CF_3CCl_2CXClOC_2H_5 \longrightarrow CF_3CCl\overset{Cl}{\underset{X}{C}}{-}\overset{\ominus}{O}: + C_2H_5^{\oplus}$$

$$CF_3CCl_2\overset{X}{\underset{Cl\uparrow\_}{C}}{-}O: \longrightarrow CF_3CCl_2\underset{X}{C}{=}O + Cl:^{\ominus}$$

$$Cl^{\ominus} + C_2H_5^{\oplus} \longrightarrow C_2H_5Cl$$

It is possible that the *alpha* chlorine atom is removed by the attack of the ethyl carbonium atom.



$$CF_3CCl_2\overset{\overset{C_2H_5^+}{\vdots}}{\underset{X}{\overset{Cl}{C}}}\ O \longrightarrow CF_3CCl_2\overset{\overset{C_2H_5}{\vdots}}{\underset{X}{\overset{Cl}{C}}}\ O \longrightarrow CF_3CCl_2\underset{X}{C}O + ClC_2H_5$$

No work was done to prove or disprove these mechanisms. A free radical type mechanism was discarded because of the absence of such by-products as chlorine, hydrogen chloride, ethylene, or butane which could have been formed under free radical conditions.

EXPERIMENTAL

Preparation of CF_3CCl_2COCl from $CF_3CCl{=}CClOC_2H_5$.[11] Chlorine (22 g.) was bubbled, in the absence of light through 70 g. of $CF_3CCl{=}CClOC_2H_5$ kept below 0° at a rate slow enough to prevent the temperature from rising above 0°.

The unreacted olefin was stripped from the reaction mixture under reduced pressure. Attempts to further purify the crude saturated ether by fractional distillation under reduced pressure resulted in its decomposition. Chlorine was added in a similar manner to the methyl, *n*-propyl, and *n*-butyl ethers. The dichlorides of these ethers also decomposed when attempts were made to purify them by fractionation.

Eighty g. of crude $CF_3CCl_2CCl_2OC_2H_5$ was refluxed under atmospheric pressure for two hours. Ethyl chloride, one of the products of decomposition, was caught in a Dry Ice trap. After two hours of refluxing, the residue was fractionated on a small glass helix-packed column. About 39 g. of CF_3CCl_2COCl, boiling point 80° (630 mm.) (yield of 62%) was obtained. n^{2}_{D} 1.3850, d^{20}_{4} 1.600.

Anal. Calc'd for $C_3Cl_3F_3O$: C, 16.7; F, 26.5. Found: C, 16.9; F, 27.1.

The ethyl chloride was identified by its boiling point during fractionation on a low temperature Podbielniak column and by molecular weight determinations. Molecular weight; calculated: 64.5, found: 63.5. About 8.5 g. (71% yield) of ethyl chloride was recovered. Some tar formation and handling losses account for the rest of the material. The methyl, *n*-propyl, and *n*-butyl ethers decomposed in the same way. In the case of the *n*-propyl and *n*-butyl ethers the alkyl halide is removed from the acid chloride by fractionation.

Preparation of $CF_3CCl_2CO_2H$. The above CF_3CCl_2COCl was converted to the acid $CF_3CCl_2CO_2H$ by alternate treatment with base and a strong acid. From 20 g. of CF_3CCl_2COCl, 5 g. (23% yield) of $CF_3CCl_2CO_2H$ was obtained, b.p. 155–156° (625 mm.), n^{20}_{D} 1.3855, d^{20}_{4} 1.630. Neutral equivalent; calc'd: 197.0, found: 196.0.

Preparation of the esters of $CF_3CCl_2CO_2H$. The acid chloride, CF_3CCl_2COCl (34.5 g.) was placed in a 100-cc. flask immersed in an ice-bath, and equipped with a stirrer, dropping-funnel, and a reflux condenser. A tube led from the top of the condenser to a trap.

About 13.0 g. of methyl alcohol was added, with stirring, at a rate slow enough to keep the temperature from rising much above room temperature. When the last of the alcohol had been added the mixture was stirred an additional hour. The ester was separated from the excess alcohol by washing several times with water. After drying over calcium chloride, the product was fractionated. The fraction boiling at 116–117° (625 mm.) was $CF_3CCl_2CO_2CH_3$. The yield was 21.6 g. (64%), n^{20}_{D} 1 3806, d^{20}_{4} 1.5092.

Anal. Calc'd for $C_4H_3Cl_2F_3O_2$: H, 1.54; C, 24.62. Found: H, 1.63; C, 25.00.

Yields of these esters are as follows, using in each case 34.5 g. of acid chloride and an excess of alcohol.

Ethyl alcohol, gave 24.5 g., 67.0% yield of the ethyl ester, $CF_3CCl_2CO_2C_2H_5$, b.p. 128.5° (625 mm.), n^{20}_{D} 1.3822, d^{20}_{4} 1.4116.

Anal. Calc'd for $C_5H_5Cl_2F_3O_2$: H, 2.49; C, 24.62. Found: H, 2.54; C, 28.86.

n-Propyl alcohol, gave 15.5 g., 40.0% yield of the ester $CF_3CCl_2CO_2C_3H_7$, b.p. 144.5° (625 mm.), n^{20}_{D} 1.3888, d^{20}_{4} 1.3531.

Anal. Calc'd for $C_6H_7Cl_2F_3O_2$: H, 3.14; C, 32.28. Found: H, 3.29; C, 32.16.

n-Butyl alcohol, gave 23.9 g., 58.8% yield of the ester $CF_3CCl_2CO_2C_4H_9$, b.p. 165.0° (625 mm.), n^{20}_{D} 1.3592, d^{20}_{4} 1.3075.

Anal. Calc'd for $C_7H_9Cl_2F_3O_2$: H, 3.80; C, 35.44. Found: H, 3.90; C, 36.35.

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[11] Park, Halpern, and Lacher, *J. Am. Chem. Soc.*, **74**, 4104–4105 (1952).

Preparation of $CF_3CCl_2CFClOC_2H_5$. The ether, CF_3-$CCl{=}CF{-}OC_2H_5$[12] (53 g.) was placed in a test tube containing a glass frit. A tube led from the top of the test tube to a Dry Ice trap. Chlorine gas was introduced through the glass frit until the theoretical amount of the weight was gained. Unreacted chlorine was removed from the system by blowing air through the reaction mixture. The reaction mixture then was fractionated under reduced pressure. The fraction boiling at 34° (8 mm.) was $CF_3CCl_2CFClOC_2H_5$; 51 g. (65% yield) was obtained, n^{20}_D 1.3907, d^{20}_4 1.4965.

Anal. Calc'd for $C_5H_5Cl_3F_4O$: H, 1.89; C, 27.19. Found: H, 2.05; C, 27.00.

A few grams of this ether boiled with an equal amount of water for an hour gave a negative test with silver nitrate solution.

Preparation of CF_3CCl_2COF *from* $CF_3CCl_2CFClOC_2H_5$. The saturated ether, $CF_3CCl_2CFClOC_2H_5$ (50 g.), was allowed to reflux for three hours at atmospheric pressure. The material then was fractionated, the decomposition proceeding more rapidly as the lower-boiling liquids are removed from the still pot permitting a higher temperature there to effect a faster reaction.

A fraction boiling at 41° (627 mm.) was CF_3CCl_2COF of which 10 g., (26% yield) was obtained; n^{20}_D 1.3343, d^{20}_4 1.528. The identity of this compound was proved by conversion to $CF_3CClCONH_2$.

Anal. Calc'd for $C_3H_2Cl_2F_3NO$: N, 7.14. Found: N, 7.17.

A higher-boiling fraction gave a copious test for chloride with silver nitrate solution. Not enough of the material was available for determination of physical properties; but from a comparison of boiling points and odors, it was gathered that it was a mixture of CF_3CCl_2COCl and other organic material.

Preparation of $CF_3CCl_2CONH_2$ *from* CF_3CCl_2COF *or* CF_3CCl_2COCl. The acid chloride, CF_3CCl_2COCl (2 g.) was carefully added to four times its volume of ice cold concentrated ammonium hydroxide. The solid amide instantly precipitated from the aqueous solution. On completing the addition of the acid chloride, the mixture was stirred briefly and filtered. The precipitate was washed several times with water to remove the ammonium chloride, dried, and then purified by sublimation to yield $CF_3CCl_2CONH_2$. Melting point (sealed tube) 80.0–81.0°. In using CF_3CCl_2COF the same process was used yielding the same amide, m.p. 80–81°.

Preparation of $CF_3CCl_2CONHC_6H_5$ *from* CF_3CCl_2COF *or* CF_3CCl_2COCl. Either halide, CF_3CCl_2COF or CF_3CCl_2COCl (2 cc.), was added to an excess of aniline cooled in an ice-bath, water was added to the resulting oily solid, and the mixture was filtered. The solid was washed several times with dilute hydrochloric acid and crystallized twice from ethanol-water mixture. The dried anilide, $CF_3CCl_2CONHC_6H_5$, prepared from the two acid halides had the same melting points, m.p. 83.5–84.5°.

Anal. Calc'd for $C_9H_6Cl_2F_3NO$: N, 5.15. Found: N, 5.31.

Preparation of $CF_3CHClCCl_2OC_2H_5$. The unsaturated ether $CF_3CCl{=}CClOC_2H_5$ (64 g.), and 50 g. of glacial acetic acid were placed in a large test tube. The test tube was equipped with a glass frit and a reflux condenser. A tube led from the top of the condenser to a trap. Hydrogen chloride was introduced through the frit until the correct weight had been added (11 g.). Unreacted hydrogen chloride was removed by blowing air through the solution.

The glacial acetic acid was stripped off under reduced pressure. All attempts to obtain pure $CF_3CHClCCl_2OC_2H_5$ resulted in its decomposition to the foul smelling CF_3CCl-$HCOCl$ and ethyl chloride. $CF_3CHClCOCl$ was identified by its conversion to the amide $CF_3CHClCONH_2$ by means of aqueous ammonium hydroxide, m.p. 117°.

Anal. Calc'd for $C_3H_3ClF_3NO$: N, 8.67. Found: N, 8.90.

Further identification was carried out by conversion to the anilide $CF_3CHClCONHC_6H_5$, m.p. 125.5–126.5°.

Anal. Calc'd for $C_9H_7ClF_3NO$: N, 6.22. Found: N, 5.92.

BOULDER, COLORADO

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(12) Park, Sweeney, Hopwood, Jr., and Lacher, *J. Am. Chem. Soc.*, **78**, in press (1955).