

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

The Preparation and Properties of Some Fluorochloropropyl Alkyl Ethers¹BY J. D. PARK, W. M. SWEENEY, S. L. HOPWOOD, JR.,² AND J. R. LACHER

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The base-catalyzed reaction of alkanols and some fluorochloropropenes of the type $\text{CF}_3\text{CX}=\text{CX}_2$, where X is F or Cl, was found to yield saturated and unsaturated ethers of the types $\text{CF}_3\text{CXH}-\text{CX}_2\text{OR}$ and $\text{CF}_3\text{CX}=\text{CXOR}$ depending upon the positions of X in $\text{CF}_3\text{CX}=\text{CX}_2$. The physical properties of these new ethers are reported.

The base-catalyzed addition of alkanols to fluorinated ethenes to form ethers has been previously reported by us.³⁻⁶ These ethers were of the general type $\text{ROCF}_2-\text{CX}_2\text{H}$ (where X is F, Cl or H) in which the two fluorine atoms alpha to the ether linkage have no tendency to dehydrofluorinate in alcoholic base. However, under similar conditions with $\text{CF}_3\text{CCl}=\text{CCl}_2$ ⁷ and $\text{CF}_3-\text{CCl}=\text{CCl}-\text{CF}_3$,⁸ unsaturated ethers $\text{CF}_3\text{CCl}=\text{CCl}(\text{OR})$ and $\text{CF}_3-\text{CCl}=\text{C}(\text{OR})\text{CF}_3$ were obtained as the principal products. These results seem to indicate that the stability of the ethers may be due to the presence of the CF_3 - group or the substituents attached to the carbon containing hydrogen.

The present study is concerned with the base-catalyzed addition of alkanols to $\text{CF}_3\text{CCl}=\text{CFCl}$ (I), $\text{CF}_3\text{CCl}=\text{CF}_2$ (II), $\text{CF}_3\text{CF}=\text{CCl}_2$ (III), $\text{CF}_3-\text{CF}=\text{CF}_2$ (IV) and $\text{CF}_2\text{ClCF}=\text{CCl}_2$ (V) in an effort to determine the effect, if any, of the fluorine atoms (in the terminal or internal vinylic positions) on the formation of saturated and/or unsaturated ethers.

In the case of II, III, IV and V, stable saturated fluoroethers of the type $\text{CF}_3\text{CXH}-\text{CX}_2\text{OEt}$ were obtained as the main products.

From this and earlier works, it is now concluded that the formation of saturated or unsaturated chlorofluoroalkyl ethers from $\text{CF}_2\text{XCX}=\text{CX}_2$ (where X is Cl or F) and alcoholic base is dependent upon the substituents present in the internal or terminal vinylic positions. These may be summarized in the following form.

In order to form saturated alkyl ethers in the presence of a base, the perhalopropene must have one of the following features. (1) A $-\text{CF}_2-$ group alpha to the ether linkage after addition of the alkanol. (2) A F- atom attached to the carbon on the internal vinylic position. In the absence of these features, unsaturated ethers will result.

These saturated fluoroethers were identified by their physical properties and by analyses. In many cases the ethers were hydrolyzed to the corresponding esters of the type $\text{CF}_3\text{CHXCOOEt}$ by means of sulfuric acid by the method of Tarrant and Young.⁹

(1) Presented before the Fluorine Subdivision of the Division of Industrial and Engineering Chemistry, 124th Meeting of the American Chemical Society, Chicago, Ill., September -11, 1953. This paper represents parts of the theses submitted by W. M. Sweeney and S. L. Hopwood, Jr., to the Graduate School, University of Colorado, in partial fulfillment of the requirements for the Ph.D. degree.

(2) E. I. du Pont de Nemours Predoctoral Fellow 1952-1953.

(3) J. D. Park, K. R. Lea, D. K. Vail and J. R. Lacher, *THIS JOURNAL*, **70**, 1550 (1948).

(4) J. D. Park, C. M. Snow and J. R. Lacher, *ibid.*, **73**, 861 (1951).

(5) J. D. Park, W. R. Lycan and J. R. Lacher, *ibid.*, **73**, 711 (1951).

(6) W. H. Breen, unpublished work, University of Colorado.

(7) J. D. Park, E. Halpern and J. R. Lacher, *THIS JOURNAL*, **74**, 4104 (1952).

(8) P. W. Trott, unpublished work, University of Colorado.

(9) J. A. Young and P. Tarrant, *ibid.*, **71**, 2432 (1949).

In the case where the unsaturated ether $\text{CF}_3-\text{CCl}=\text{CFOC}_2\text{H}_5$ was the principal product a small amount of $\text{CF}_3\text{CCl}=\text{CClOC}_2\text{H}_5$ was also isolated. In this case, the presence of a fluorine atom on the carbon alpha to the ether linkage of a fluorochloropropyl ether (hypothetical $\text{CF}_3\text{CHClCFClOC}_2\text{H}_5$) is not strong enough to prevent the formation of $\text{CF}_3\text{CCl}=\text{CClOC}_2\text{H}_5$ or $\text{CF}_3\text{CCl}=\text{CFOC}_2\text{H}_5$ by the elimination of HX in a basic solution. One should also note in this case, the greater strength of the C-F bond as compared to the C-Cl bond which allows only a small amount of HF to be eliminated to yield $\text{CF}_3\text{CCl}=\text{CClOC}_2\text{H}_5$.

This reaction is not new and has its counterpart in the reaction of alkanols and trichloroethylene in the presence of a base which also results in the formation of unsaturated ethers.^{10,11}

Experimental

Preparation of Fluoroolefins.—All the olefins used in this study were prepared by the method of Henne and Waalkes.¹² The unsaturated and saturated ethers were prepared from the olefins by methods previously described.^{7,8}

Preparation of $\text{CF}_3\text{CCl}=\text{CFOC}_2\text{H}_5$.—Starting with $\text{CF}_3-\text{CCl}=\text{CFCl}$, about 56.3 g. (33.9% of theory) of $\text{CF}_3\text{CCl}=\text{CFOC}_2\text{H}_5$ was obtained; b.p. 105.5° (628 mm.), n_D^{20} 1.3630, d_4^{20} 1.3391; molar refraction, 31.33 calcd., 31.97 found. *Anal.* Calcd. for $\text{C}_5\text{H}_5\text{ClF}_4\text{O}$: C, 31.43; H, 2.60. Found: C, 31.39; H, 2.72.

A small amount of liquid having the physical properties of $\text{CF}_3\text{CCl}=\text{CClOC}_2\text{H}_5$ (b.p. 130° at 612 mm., d_4^{20} 1.3945, n_D^{20} 1.4058) was obtained at a higher temperature. Thus it is shown that, in the case of the intermediate $\text{CF}_3\text{CHClCFClOC}_2\text{H}_5$ hypothesized in this preparation, hydrogen chloride is split out by base much more readily than hydrogen fluoride.

Preparation of $\text{CF}_3\text{CHClCF}_2\text{OC}_2\text{H}_5$.—The following fractions were obtained from $\text{CF}_3\text{CCl}=\text{CF}_2$ and ethanolic base: (a) $\text{CF}_3\text{CHClCF}_2\text{OC}_2\text{H}_5$: b.p. 88° (630 mm.), n_D^{20} 1.3333, d_4^{20} 1.3348; molar refraction 31.23 calcd., 32.5 found. *Anal.* Calcd. for $\text{C}_5\text{H}_5\text{ClF}_3\text{O}$: C, 28.25; H, 2.83. Found: C, 28.17; H, 2.95. (b) $\text{CF}_3\text{CHClCO}_2\text{C}_2\text{H}_5$: b.p. 118° (630 mm.), n_D^{20} 1.3636, d_4^{20} 1.3215. *Anal.* Calcd. for $\text{C}_5\text{H}_5\text{ClF}_3\text{O}_2$: C, 31.49; H, 3.15. Found: C, 31.24; H, 3.17. (c) A higher boiling fraction, b.p. 132.5° (41 mm.), n_D^{20} 1.4305, d_4^{20} 1.1951, had the same physical properties as $\text{CHCl}(\text{CO}_2\text{C}_2\text{H}_5)_2$; literature value b.p. 137°, 50 mm., n_D^{20} 1.4327 and d_4^{20} 1.2040.

Preparation of $\text{CF}_3\text{CHF}_2\text{OC}_2\text{H}_5$.—The following reaction products of the potassium hydroxide-catalyzed addition of ethanol to $\text{CF}_3\text{CF}=\text{CF}_2$ were obtained. (a) $\text{CF}_3-\text{CHF}_2\text{OC}_2\text{H}_5$: b.p. 65.5° (628 mm.), n_D^{20} 1.2950, d_4^{20} 1.3016. *Anal.* Calcd. for $\text{C}_5\text{H}_5\text{F}_3\text{O}$: C, 30.60; H, 3.06. Found: C, 31.09; H, 2.96. (b) $\text{CF}_3\text{CHF}_2\text{OC}_2\text{H}_5$: b.p. 103.0° (629 mm.), n_D^{20} 1.3288, d_4^{20} 1.2884. *Anal.* Calcd. for $\text{C}_5\text{H}_5\text{F}_3\text{O}_2$: C, 34.48; H, 3.45. Found: C, 34.73; H, 3.50.

Preparation of $\text{CF}_3\text{CHFClOCH}_3$.—This was obtained from the reaction of $\text{CF}_3\text{CF}=\text{CCl}_2$ with methanolic base.

(10) G. Imbert, German Patent 210,502, *Chem. Zentr.*, **80**, **II**, 78 (1909); German Patent 216,940, *Chem. Zentr.*, **81**, **I**, 308 (1910).

(11) H. Crompton and P. L. Vanderstickele, *J. Chem. Soc.*, **117**, 691 (1920).

(12) A. L. Henne and T. P. Waalkes, *THIS JOURNAL*, **68**, 496 (1946).

Distillation yielded $\text{CF}_3\text{CFHCCl}_2\text{OCH}_3$, b.p. 50° (94 mm.), n_D^{20} 1.3717, d_4^{20} 1.5096. *Anal.* Calcd. for $\text{C}_4\text{H}_4\text{Cl}_2\text{F}_4\text{O}$: C, 22.30; H, 1.86; Cl, 33.3. Found: C, 22.14; H, 1.82; Cl, 33.72.

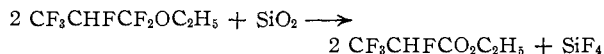
Preparation of $\text{CF}_2\text{CICFHCCl}_2\text{OCH}_3$.—This was obtained from $\text{CF}_2\text{CICF}=\text{CCl}_2$ and methanolic base. $\text{CF}_2\text{CICFHCCl}_2\text{OCH}_3$, b.p. $78-80^\circ$ (91 mm.), n_D^{20} 1.4120, d_4^{20} 1.5510. *Anal.* Calcd. for $\text{C}_4\text{H}_4\text{Cl}_2\text{F}_3\text{O}$: C, 20.3; H, 1.73; Cl, 45.99. Found: C, 21; H, 1.8; Cl, 45.87.

Preparation of $\text{CF}_3\text{CHClCO}_2\text{C}_2\text{H}_5$.—About 5 g. of $\text{CF}_3\text{CHClCF}_2\text{OC}_2\text{H}_5$ was added cautiously to twice its volume of 90% sulfuric acid, according to the method of Young and Tarrant.⁹ When the addition was completed, the reaction product was cooled to room temperature and poured over a small amount of ice. The oily layer which separated was washed with ice-water and dried over anhydrous calcium chloride. Its physical properties compared closely with those of $\text{CF}_3\text{CHClCO}_2\text{C}_2\text{H}_5$ given above (n_D^{20} 1.3637, d_4^{20} 1.3222).

Preparation of $\text{CF}_3\text{CHF}_2\text{OC}_2\text{H}_5$.—Two methods were used to accomplish the hydrolysis of $\text{CF}_3\text{CHFCF}_2\text{OC}_2\text{H}_5$ to $\text{CF}_3\text{CHF}_2\text{OC}_2\text{H}_5$. In the first, about 100 g. of 90% sulfuric acid was placed in a three-neck flask containing a stirrer, dropping funnel and a reflux condenser. About 19.6 g. of $\text{CF}_3\text{CHFCF}_2\text{OC}_2\text{H}_5$ was dropped into the flask at a rate slow enough to prevent the reaction from getting out of hand. The evolved hydrogen fluoride gas was led from the top of the reflux condenser to a trap. When the last of the ether had been added, the reaction mixture was hydrolyzed by adding an excess of ice-water with continued stirring and cooling of the flask with an ice-bath. The oily layer was then separated, washed twice with ice-water, dried over anhydrous sodium sulfate and fractionated. The fraction boiling $103-104^\circ$ (629 mm.) was $\text{CF}_3\text{CHF}_2\text{OC}_2\text{H}_5$, yield 10.0 g. (57.4% of theory), n_D^{20} 1.3288, d_4^{20} 1.2884.

The second method developed from an attempt to decompose the $\text{CF}_3\text{CHFCF}_2\text{OC}_2\text{H}_5$ to $\text{CF}_3\text{CHF}_2\text{OCF}$ and $\text{C}_2\text{H}_5\text{F}$ by heating in a sealed tube. The desired products were not obtained and the only product which could be identified was $\text{CF}_3\text{CHF}_2\text{OC}_2\text{H}_5$.

It is suggested that the fluoroether reacted with the silicon dioxide present in the walls of the sealed tube to form the ester and silicon tetrafluoride.



About 20 g. of $\text{CF}_3\text{CHFCF}_2\text{OC}_2\text{H}_5$ was placed in a thick-walled Pyrex tube and carefully sealed. The tube was heated at 150° for 12 hours, then permitted to cool to room temperature. The tube was chilled by immersion in a Dry Ice-acetone-bath and opened. A considerable amount of non-condensable gas escaped, assumed to be silicon tetrafluoride. The remaining liquid was distilled directly from the opened tube, washed several times with ice-water to remove acid present, dried over anhydrous sodium sulfate and fractionated. The fraction boiling $103-104^\circ$ (629 mm.) was $\text{CF}_3\text{CHF}_2\text{OC}_2\text{H}_5$. About 8 g. was obtained which is 46% yield. Tar formation in the sealed tube and handling losses accounted for the rest of the material.

Preparation of $\text{CF}_3\text{CHClCO}_2\text{C}_2\text{H}_5$.—About 10 g. of $\text{CF}_3\text{CCl}=\text{F}_2\text{OC}_2\text{H}_5$ was hydrolyzed with 90% sulfuric acid in the same method used to hydrolyze the series of ethers $\text{CF}_3\text{CCl}=\text{CClOR}$ as described in the preparation of $\text{CF}_3\text{CHClCO}_2\text{C}_2\text{H}_5$ from $\text{CF}_3\text{CHClCF}_2\text{OC}_2\text{H}_5$ above. An ester, $\text{CF}_3\text{CHClCO}_2\text{C}_2\text{H}_5$, prepared elsewhere in this paper, was isolated, n_D^{20} 1.3634, d_4^{20} 1.3215.

Preparation of $\text{CF}_3\text{CHFCONH}_2$.— $\text{CF}_3\text{CHF}_2\text{OC}_2\text{H}_5 + \text{NH}_4\text{OH} \rightarrow \text{CF}_3\text{CHFCONH}_2 + \text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O}$. About 2 g. of $\text{CF}_3\text{CHF}_2\text{OC}_2\text{H}_5$ was treated with ammonium hydroxide and purified in the same manner as $\text{CF}_3\text{CHClCO}_2\text{C}_2\text{H}_5$ above. The amide isolated, $\text{CF}_3\text{CHFCONH}_2$, had a melting point of 57.0° . *Anal.* Calcd. for $\text{C}_3\text{H}_5\text{F}_3\text{NO}$: N, 9.65. Found: N, 9.51.

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BOULDER, COLORADO

[CONTRIBUTION FROM THE DOW CORNING CORPORATION]

The Synthesis and Polymerization of Organosilanes Containing Vinyl and Hydrogen Joined to the Same Silicon Atom

By JAMES W. CURRY¹

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Certain organosilanes containing vinyl and hydrogen joined to the same silicon atom were prepared and then polymerized to polysilylenes at atmospheric pressure, using platinum, suspended on finely divided carbon, as the catalyst. In addition to the polymeric products, there were isolated in all cases lesser amounts of lower molecular weight materials, which were identified as the first authentic examples of the 1,4-disilacyclohexane ring system.

The continuing interest in organosilicon polymers, wherein the occurrence of alternating silicon atoms and difunctional organic groups² is a distinguishing structural feature of the polymer chain, led us to consider the possibility of synthesizing certain of these materials, namely, the polysilylenes, in which the recurring silicon atoms are connected through ethylenic bridges. The general procedure, as visualized at the outset, involved the polymerization of compounds containing the vinyl group and the Si-H function within the same molecule through addition of Si-H to the carbon-carbon double bond of an adjacent molecule.

Dimethylvinylchlorosilane, diethylvinylchlorosilane, diphenylvinylchlorosilane and methylphen-

ylvinylchlorosilane were used as starting materials for the preparation of the organosilicon monomers. The chloro compounds were reduced with lithium aluminum hydride³ in the usual way to afford silanes containing vinyl and hydrogen joined to the same silicon atom.⁴ The monomers thus prepared were heated at atmospheric pressure, in the absence of solvent, with a catalyst consisting of 0.06% by weight of platinum suspended on finely divided carbon.^{5,6} Polymerization took place in all cases.

(3) A. E. Finholt, A. C. Bond, Jr., K. E. Wilzbach and H. I. Schlesinger, *THIS JOURNAL*, **69**, 2692 (1947).

(4) S. Tannenbaum, S. Kaye and G. F. Lewenz, *ibid.*, **75**, 3753 (1953).

(5) G. H. Wagner (to Union Carbide and Carbon Corp.), U. S. Patent 2,637,738, May 5, 1953.

(6) Earlier, Wagner had reported the polymerization of vinylchlorosilane under conditions of high temperature and pressure, using other types of platinum catalysts. The product was a liquid polymeric material containing no Si-H. See G. H. Wagner (to Union Carbide and Carbon Corp.), U. S. Patent 2,632,013, March 17, 1953.

(1) Department of Physical Sciences, University of California, Santa Barbara College, Goleta, Calif.

(2) For a discussion of polymers of this general type, see E. G. Rochow, "An Introduction to the Chemistry of the Silicones," 2nd Edition, New York, N. Y., John Wiley and Sons, Inc., 1951, pp. 62-66.