[CONTRIBUTION FROM THE CHEMICAL CORPS, CHEMICAL RESEARCH DIVISION, CHEMICAL WARFARE LABORATORIES]

The Addition of Alcohols to Octafluoroisobutene[1]

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The addition of several alcohols to octafluoroisobutene $(CF_3)_2C=CF_2$ (I), in neutral or slightly acidic media afforded as the main reaction products the corresponding saturated ethers of the type $(CF_3)_2CHCF_2OR$ (II). The aliphatic alcohols employed, with the exception of methanol, yielded in addition to the II considerable amounts of vinyl ethers of the type $(CF_3)_2C=CFOR$ (III). The ratio of II to III in the reaction mixture was found to be dependent on the nature of the reacting alcohol. Allyl alcohol and ethylene chlorohydrin gave similarly the corresponding saturated ethers II but no III; instead bis-(trifluoromethyl)-ketene acetals, $(CF_3)_2C=C(OR)_2$ (IV), were obtained as by-products. A possible mechanism accounting for the different types of reaction products is discussed.

Introduction

The preparation of tetrafluoroethyl and chlorotrifluoroethyl alkyl ethers by the base-catalyzed addition of alcohols to tetrafluoroethylene and chlorotrifluoroethylene, respectively, was first reported by Hanford and Rigby.[3] The general applicability of this addition reaction to other polyfluorinated olefins was demonstrated later by various investigators.[4] However, the only alcohol additions which have been successful under neutral or weakly acidic conditions were the additions to perfluoroacrylonitrile[5] and the addition of ethanol to octafluoroisobutene.[6]

The work reported in this paper was undertaken to study further the uncatalyzed addition of alcohols to octafluoroisobutene (I) in order to determine its scope.

Discussion of Results

The uncatalyzed addition to octafluoroisobutene of the aliphatic unsubstituted and substituted alcohols employed in our investigation yielded in all cases the saturated ethers $(CF_3)_2CHCF_2OR$ (II) as the main products. The reactions with the alcohols were, in general, carried out by passing the olefin through a gas-dispersion disk into the appropriate alcohol. Addition reactions were performed in this manner successfully with methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-chloroethanol, 2-fluoroethanol and allyl alcohol. However, 2,2,2-trifluoroethanol, 2-mercaptoethanol and phenol were unreactive in the absence of a basic catalyst. The unsubstituted aliphatic alcohols, with the exception of methanol, afforded, along with the saturated addition products II, unsaturated ethers of the type $(CF_3)_2C=CFOR$ (III), with yields increasing in the order: $C_2H_5 < n\text{-}C_3H_7 < \text{iso-}C_3H_7 < n\text{-}C_4H_9$. Olefinic by-products were also obtained in low yields in the addition of allyl alcohol and 2-chloroethanol to I. These unsaturated reaction products were not of the type obtained from the unsubstituted, saturated aliphatic alcohols but were identified by elemental and infrared analysis and by their nuclear magnetic resonance (NMR) spectra as bis-(trifluoromethyl)-ketene acetals of the type $(CF_3)_2C=C(OR)_2$ (IV). *t*-Butanol underwent reaction with I under the conditions of the general addition procedure, but the principal product was the ester $t\text{-}C_4H_9O_2CCH(CF_3)_2$.

The physical properties and analytical data of the various addition products are listed in Table I. The average calculated atomic refraction of fluorine for the saturated ethers II was 1.17 as compared with 1.28 for the corresponding olefinic ethers III. In general, the boiling points of the unsaturated ethers III were approximately 30° higher than those of the corresponding saturated compounds II. A similar difference of +17.5° at 628–630 mm. pressure between the boiling points of the analogous products $CF_3CCl=CFOC_2H_5$ and $CF_3CClHCF_2OC_2H_5$, obtained by the base-catalyzed reaction of ethanol with $CF_3CCl=CClF$ and $CF_3CCl=CF_2$, respectively, has been reported by Park, *et al.*[7]

The nature of the reacting alcohol was found to have a significant effect on (1) the rate of the addition and (2) the yield of the olefinic ethers. The relative rate of the addition appeared to decrease with increasing acidity of the alcohol reactant or reaction mixture. Allyl alcohol, 2-chloroethanol and 2-fluoroethanol were the least reactive of the alcohols that underwent addition. On the basis of the percentage conversion of I, 1-butanol appeared to be the least reactive of the saturated alcohols. Methanol and ethanol exhibited the highest reactivity and were followed by the somewhat less reactive propanols. The difference in the conversion of I observed with 1- and 2-propanol, which proceeded to an extent of 77 and 80%, respectively, is too small to allow a differentiation between the two isomers with regard to their reactivity in this addition reaction. However, the conversion of I may not be a useful criterion of the reactivity of an alcohol, since it was observed that in some of the runs with progressing reaction, hydrogen fluoride was formed in a side reaction in amounts sufficient to cause a strongly acidic reaction of the mixture and thus prevent further reaction of the alcohol. The reaction of *t*-butanol with I was initially rapid but ceased soon, probably because of the liberation of hydrogen fluoride.

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[1] Presented at the 130th Meeting of the American Chemical Society in Atlantic City, N. J., September 17–21, 1956.

[2] To whom inquiries about this paper should be directed.

[3] W. E. Hanford and G. W. Rigby, U. S. Patent 2,409,274 (1946).

[4] Excellent summaries and a complete bibliography on this work are given in J. H. Simons, "Fluorine Chemistry," Vol. II, Academic Press, Inc., New York, N. Y., by P. Tarrant, pp. 232–235, and J. H. Simons and T. J. Price, pp. 236–238.

[5] J. D. LaZerte, R. J. Koshar, W. H. Pearlson, T. D. Park, D. A. Rausch and J. R. Lacher, Abstracts of Papers, 126th Meeting of the American Chemical Society, New York, N. Y., September, 1954, p. 26M.

[6] T. J. Brice, J. D. LaZerte, L. J. Hals and W. H. Pearlson, THIS JOURNAL, **75**, 2698 (1953).

[7] J. D. Park, W. M. Sweeny, S. Hopwood and J. R. Lacher, 124th Meeting of the American Chemical Society, Chicago, Ill., September, 1953.

TABLE I

PHYSICAL DATA AND ANALYSES OF REACTION PRODUCTS FROM ALCOHOLS AND OCTAFLUOROISOBUTENE

Product	Boiling point[a] °C.	Boiling point[a] Mm.	n^{25}_D	d^{25}_4	MR_D Calcd.[b]	MR_D Found[c]	AR_F Obsd.[d]	Carbon, % Calcd.	Carbon, % Found	Fluorine, % Calcd.	Fluorine, % Found	Hydrogen, % Calcd.	Hydrogen, % Found
$(CF_3)_2CHCF_2OCH_3$[e]	68.5	760	1.2809	1.4931	26.93	27.35	1.15	25.9	25.5	65.5	64.8	..	..
$(CF_3)_2CHCF_2OC_2H_5$[f]	82.0	760	1.2909	1.3982	31.55	32.01	1.16	29.3	29.0	61.8	61.2	..	..
$(CF_3)_2CHCF_2OCH_2CH_2CH_3$	101.5	760	1.3047	1.3463	36.17	36.67	1.16	32.3	32.2	58.5	57.5	3.1	3.1
$(CF_3)_2CHCF_2OCH(CH_3)_2$	43.5	113	1.3005	1.323	36.17	36.75	1.17	32.3	32.4	58.5	56.6	..	..
$(CF_3)_2CHCF_2O(CH_2)_3CH_3$	53.5	65	1.3172	1.3037	40.79	41.35	1.17	35.0	35.3	55.5	53.7	..	..
$(CF_3)_2CHCF_2OCH_2CH_2F$	64.0	100	1.3018	1.540	31.55	32.24	1.18	27.3	27.7	64.8	62.3	1.9	2.0
$(CF_3)_2CHCF_2OCH_2CH_2Cl$	74.0	100	1.3292	1.5364	36.42	37.07	1.18	25.7	25.8	54.3	52.3	1.8	1.9
$(CF_3)_2CHCF_2OCH_2CH{:}CH_2$	100.0	760	1.3135	1.3893	35.70	36.14	1.16	32.5	32.6	58.0	58.5	2.3	2.3
$(CF_3)_2C{=}CFOCH_3$	101.5	760	1.3139	1.4973	26.46	27.62	1.28	28.3	28.4	62.7	62.5	1.4	1.7
$(CF_3)_2C{=}CFOC_2H_5$	114.0	760	1.3234	1.3995	31.08	32.36	1.28	31.9	31.9	58.8	57.6	2.2	2.1
$(CF_3)_2C{=}CFOCH_2CH_2CH_3$	129.8	760	1.3345	1.339	35.70	37.02	1.29	35.0	35.1	55.5	54.7	2.9	3.3
$(CF_3)_2C{=}CFOCH(CH_3)_2$	45.0	50	1.3302	1.322	35.70	37.04	1.29	35.0	35.1	55.5	53.2	..	..
$(CF_3)_2C{=}CFO(CH_2)_3CH_3$	75.0	53	1.3449	1.2933	40.32	41.71	1.29	37.8	37.8	52.4	51.2	..	..
$(CF_3)_2C{=}C(OCH_2CH_2Cl)_2$[g]	99.0	3.5	1.4110	....	...	...	..	29.9	29.7	35.6	35.9	2.5	2.4
$(CF_3)_2C{=}C(OCH_2CH{=}CH_2)_2$	75.5	35	1.3727	1.270	50.25	49.46	0.97	43.5	43.5	41.3	38.7	3.6	3.4

[a] All boiling points are uncorrected. [b] MR_D is the molecular refraction obtained by adding the accepted values for the refraction of C, H, O, Cl, F (1.1) and the double bond increment. [c] MR_D is the molecular refraction calculated by the Lorentz–Lorenz equation. [d] AR_F denotes the observed atomic refraction for F. [e] The infrared absorption spectrum is listed in ref. 5, p. 480. [f] Previously prepared by Brice, *et al.*, ref. 7. [g] Calcd.: Cl, 22.1. Found: Cl, 21.3.

The percentage conversion of I with various alcohols and the yields of the resulting II and III are listed in Table II. It appears from the results that with increasing molecular weight of the alcohol an increase in the yield of the unsaturated ether III could be noted and that the only secondary alcohol employed favored the formation of the vinyl ether as compared with the primary isomer.

TABLE II

REACTION OF ALCOHOLS WITH OCTAFLUOROISOBUTENE.[a] PERCENTAGE CONVERSION OF OLEFIN[b] AND PERCENTAGE YIELDS[c] OF $(CF_3)_2CHCF_2OR$ (II) AND $(CF_3)_2C{=}CFOR$ (III)

Alcohol used	Conversion, %	Yield of II, %	Yield of III, %
CH_3OH	95	70	0
C_2H_5OH	95	59	6
$CH_3CH_2CH_2OH$	77	43	14
$(CH_3)_2CHOH$	80	35	26
$CH_3(CH_2)_3OH$	70	52	27
$CH_2{=}CHCH_2OH$	60	56	0
$ClCH_2CH_2OH$	70	51	0
FCH_2CH_2OH	65	60	..

[a] The olefin was passed at an approximate flow rate of 0.1 mole per hour into the appropriate alcohol; a mole ratio of about 4:1 alcohol to olefin was used. [b] The weight difference between crude or purified olefin passed through the alcohol and the condensate collected in the attached cold trap was taken as the amount of olefin converted. [c] Percentage yield of purified products based on the I absorbed by the alcohol.

An entirely different behavior was exhibited by allyl alcohol and 2-chloroethanol which both yielded, in addition to the expected saturated ether II, the ketene acetals $(CF_3)_2C{=}C(OR)_2$ (IV) but none of the unsaturated mono-adducts III.

The product from the reaction of t-butanol with I contained t-$C_4H_9O_2CCH(CF_3)_2$ as the predominant component. This ester might have been formed by the decomposition of the regular addition product t-$C_4H_9OCF_3CH(CF_3)_2$ to form $(CF_3)_2CHCOF$ which then reacted with t-butanol, or by the hydrolysis of the fluorine in the α-positions of either II or III with water during the isolation of the product. The formation of acid fluorides or derivatives by the decomposition of t butyl polyfluoroalkyl ethers has been reported by Tarrant and Brown.[8]

The hydrogen attached to the tertiary carbon of the saturated adducts II was found to be very labile. Good yields of the unsaturated ethers $(CF_3)_2C{=}CFOCH_3$ and $(CF_3)_2C{=}CFOC_3H_7$-n were obtained from $CH_3OCF_2CH(CF_3)_2$ and n-C_3H_7-$OCF_2CH(CF_3)_2$, respectively, by refluxing the saturated ethers at 100° with 15% aqueous potassium hydroxide. In dilute alcoholic alkali at room temperature, both the saturated and the unsaturated ethers decomposed extensively to give an almost quantitative yield of fluoride ion on the basis of the cleavage of all C–F bonds present. In neutral or acidic media the saturated ethers were completely stable, even at higher temperatures. Thus, the ethanol-adduct, $(CF_3)_2CHCF_2OC_2H_5$, was recovered unchanged when refluxed at 100° with water or with 50% aqueous sulfuric acid.

All of the saturated ethers were found to decompose slowly when stored at room temperature in ordinary glass vials. Attack of the glass was also observed when the adducts were kept in Pyrex bottles. The fractionation of the 2-propanol adduct, $(CF_3)_2CHCF_2OCH(CH_3)_2$, which had been stored at room temperature for six months, gave a 10% yield of $(CF_3)_2C{=}CFOCH(CH_3)_2$.

The various products formed in the reaction of I with alcohols in neutral media can best be explained by postulating a mechanism which involves in its first step the nucleophilic attack of an alkoxide ion on the terminal carbon atom of the olefin. The resulting carbanion is then stabilized by the addition of a proton[9] with the formation of the saturated ether or by the elimination of a fluoride ion[10,11] yielding the vinyl ether. A similar nucleophilic attack on the vinyl ether by an alkoxide ion followed by a fluoride elimination leads to the ketene acetals. This secondary concurrent addition-elimination cycle appears to be only possible in

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(8) P. Tarrant and H. C. Brown, THIS JOURNAL, **73**, 1781 (1951).

(9) Wm. T. Miller, E. W. Fager and P. H. Griswold, *ibid.*, **70**, 431 (1948).

(10) J. R. Lacher, "Conference on Fluorides and Fluorocarbons," Office of Naval Research, 1949.

(11) J. D. Park, M. L. Sharrah and J. R. Lacher, THIS JOURNAL, **71**, 2337 (1949).

cases where the normal electron-donating property of the alkyl group has been reduced sufficiently by proper substitution to permit the necessary polarization of the double bond of the vinyl ether. The formation of the ketene acetal was observed only with chloroethanol and allyl alcohol. In these cases, only the saturated ethers and the ketene acetals were formed but none of the corresponding vinyl ethers. The stabilization of the intermediate carbanion $[(CF_3)_2\ddot{C}CF_2OR]^-$ by elimination of a fluoride ion appears to be facilitated by increasing the electron-releasing properties of the alkoxide group on the carbon atom bearing the fluorine atom to be eliminated as an ion. Increasing the size of the alkyl group, as well as branching, results in an increasingly higher yield of the corresponding vinyl ethers.

That the vinyl ethers are not formed in the reaction of excess alcohols with I as secondary products from the saturated adducts seems to be demonstrated by the fact that no reaction occurred when $(CF_3)_2CHCF_2OC_2H_5$ or $(CF_3)_2CHCF_2O(CH_2)_3CH_3$ were refluxed several hours with ethanol and 1-butanol, respectively, and that the unsaturated ethers were not obtained upon redistillation of freshly prepared saturated ethers. The ratio of $(CF_3)_2CHCF_2O(CH_2)_3CH_3$ to $(CF_3)_2C{=}CFO(CH_2)_3CH_3$ obtained in the reaction of 1-butanol with I, carried out in a polyethylene container using an inlet tube of the same material, showed that the glass of the reactor was without noticeable effect on the course of the reaction.

While in the reactions of I with alkanols, allyl alcohol and chloroethanol substantial amounts of the olefinic products III and IV, respectively, accompany the formation of the principal product II, the reaction of 2-fluoroethanol and I gave only minute amounts of a crude, unsaturated product along with a yield of 60% $(CF_3)_2CHCF_2OCH_2CH_2F$. The amount of the crude olefinic product was too small to allow an identification. On the basis of the results obtained in the reaction of chloroethanol with I, a substantial yield of the corresponding acetal IV might be expected from the analogous addition of 2-fluoroethanol to I. The apparent anomaly observed in the reaction with fluoroethanol, however, could very well be the result of the rapidly occurring change of the fluoroethanol–olefin reaction mixture from a neutral to a lower *p*H value. The addition of 2-chloroethanol to I was found to be suppressed completely, if the alcohol was not neutralized carefully before treatment with the olefin.[12]

Identification of Adducts.—The vinyl ethers, $(CF_3)_2C{=}CFOR$, showed unsaturation to neutral permanganate and reacted readily with bromine in the dark to give the corresponding dibromides. The dibromide $(CF_3)_2CBrCBrFOC_2H_5$ was prepared in this manner by the addition of bromine to $(CF_3)_2C{=}CFOC_2H_5$.

The structure of the vinyl ethers III having the alkoxy group attached to the terminal carbon was confirmed by the infrared spectra of these compounds.[13] Infrared absorption bands for the C–H and C–F stretching vibrations occurred at 3.36–3.40 μ and 7.4–10.0 μ, respectively, for the unsaturated, as well as the saturated ethers. The spectra of the III showed strong absorption at 5.90 μ in the carbon–carbon double bond region. The acetals IV exhibited an absorption for the double bond at *ca.* 6.1 μ. The IV also showed absorption at *ca.* 5.65 μ which may have been caused by an ester impurity.

Further confirmation of the proposed structures was derived from NMR measurements on $(CF_3)_2CHCF_2OCH_3$, $(CF_3)_2C{=}CFOCH_3$ and $(CF_3)_2C{=}CFOCH(CH_3)_2$.[14] The saturated ether exhibited peaks of the expected intensities for fluorine in the CF_3 and CF_2 regions. The assignment of the structure $(CF_3)_2CHCF_2OR$ to the saturated ethers is based further on their ready dehydrofluorination with dilute aqueous alkali to the corresponding vinyl ethers which could not have been formed in this fashion from the isomeric structure $(CF_3)_2C(OR)CHF_2$. The dehydrohalogenation of the II also confirms the proposed structure III of the vinyl ethers. The resonance bands for the β-hydrogen atom of the II were very complex due to spin–spin interaction with the adjacent fluorine atoms.

The unsymmetrical, olefinic di-adducts from I and allyl alcohol or 2-chloroethanol showed resonance for fluorine only in the CF_3 region as expected. Although a symmetrical structure of the type $CF_3(RO)C{=}C(OR)CF_3$ cannot be excluded on account of the NMR spectrum, it seems rather unlikely that under the conditions of the formation of the IV a migration of one CF_3 group takes place.

Experimental

Materials.—Impure octafluoroisobutene was generously supplied by E. I. du Pont de Nemours & Co., Polychemicals Department, Wilmington, Del.[15] Mass spectrometer analysis by du Pont indicated that the gas mixture contained 51 mole % of I, 27 mole % of octafluorocyclobutane, 11.3 mole % of hexafluoropropene and 1.5 mole % of hexfluorocyclobutene; the remainder of the material consisted of saturated fluorocarbons. The removal of the other olefins from the crude I was accomplished by selective bromination.[6] Analysis of the purified material by infrared spectrometry showed that the crude I was accompanied by approximately 55% of octafluorocyclobutane and other saturated fluorocarbons; no other olefins appeared to be present. This mixture was used in most of the experiments without further purification.

The pure I used in some of the runs was obtained by rectifying the crude gaseous mixture (previously brominated) in a low-temperature column and further purifying the distilled I by the acetamide-catalyzed bromination as described by Brice, *et al.*,[6] through its dibromide. Debromination of the resulting solid dibromide, b.p. 96°, m.p. 46°, with zinc in diethyl ether yielded the pure I.

The alcohols used were commercial grade materials and were purified by fractional distillation.

General Procedure.—The alcohol additions were performed in a manner similar to that described[6] for the addition of ethanol to I. In general, the pure octafluoroisobutene or the crude gaseous mixture containing about 45 mole % I was passed through a 24-in. Pyrex bubbler containing a 3-mole excess of the appropriate alcohol. The bubbler was equipped with a coarse glass dispersion disk and a water-cooled reflux condenser. The exit gases were condensed in

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(12) Commercial C.P. grade ethylene chlorohydrin, stored in brown bottles, showed always a strong acidic reaction. Even after neutralization and rectification the freshly distilled material reacted acidic.

(13) E. Halpern and J. Goldenson, *J. Phys. Chem.* **60**, 1372 (1956).

(14) The nuclear magnetic resonance spectra were determined and interpreted by Drs. Norbert Muller and G. Svatos, Physical Branch, Chemical Research Division, Chemical Warfare Labs. The authors wish to express their gratitude for this valuable help.

(15) For this generous gift the authors wish to express their appreciation to Dr. D. E. Kvalnes who made this material available to them.

an attached trap cooled with Dry Ice and acetone. All of the addition reactions were started at room temperature; with an average flow rate of 0.1 mole of I per hour, the temperature of the reaction mixture did not exceed 40°.

After completion of the addition, the system was purged with nitrogen to remove any residual I. The weight increase of the reactor charge was taken as the amount of I reacted neglecting any determination of the part which might still have remained in solution after purging with nitrogen. To remove the excess alcohol, the reaction mixture was washed several times with water. The crude water-insoluble addition product was then separated, dried with Drierite or calcium chloride and distilled.

Using this procedure, the addition of methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-fluoroethanol and allyl alcohol proceeded successfully. The physical constants and analytical data of the reaction products are listed in Table I. A comparison of the yields of saturated addition products and vinyl ethers is found in Table II. 2,2,2-Trifluoroethanol, 2-mercaptoethanol and phenol could not be added under these conditions to octafluoroisobutene.

Addition of 2-Chloroethanol.—Initial attempts to add commercial grade or freshly distilled 2-chloroethanol to I under the same conditions as employed for the other alcohols were unsuccessful. The addition was finally accomplished by exactly neutralizing the alcohol with triethylamine.

2-Chloroethanol (64 g., 0.8 mole) was neutralized with 1.5 g. (0.01 mole) of triethylamine and placed into the Pyrex bubbler. Crude I (133 g.) (other olefins previously removed) containing 60 g. (0.3 mole) of the desired olefin was then passed slowly through the charge. The reaction mixture was worked up in the same fashion as described for the general procedure to yield 54.7 g. of crude, water-insoluble product. Fractionation of 50 g. of the product gave 29.5 g. of $(CF_3)_2CHCF_2OCH_2CH_2Cl$, b.p. 73.5–74.0° (160 mm.), and 5.0 g. of higher boiling distillate, b.p. 94° (1.7 mm.), $n^{25}D$ 1.4110. The analysis and the infrared spectrum of the latter product agreed with the ketene acetal structure, $(CF_3)_2C=C(OCH_2CH_2Cl)_2$; this material was also prepared by the base-catalyzed reaction of chloroethanol with I.

Base-catalyzed Addition of 2-Chloroethanol.[16]—Octafluoroisobutene (40 g., 0.2 mole) (purified through its dibromide) was passed in the usual fashion through a mixture of 81 g. (1.0 mole) of ethylene chlorohydrin and 10 g. (0.1 mole) of triethylamine at such a rate that complete absorption of the olefin occurred. The temperature of the reaction mixture did not exceed 40° during the addition of the I. After the usual bubbling with nitrogen, the contents of the bubbler were drowned in excess water to give an insoluble, heavy layer. Distillation of this material yielded 20 g. of unreacted 2-chloroethanol and 17.4 g. of $(CF_3)_2C=C(OCH_2CH_2Cl)_2$, b.p. 99.0–99.5° (3.5 mm.), $n^{26}D$ 1.4110. The infrared spectrum of the ketene acetal showed an absorption band at 6.1 μ (C=C).

Addition of Allyl Alcohol.—This reaction was carried out according to the general procedure. The crude gas mixture (115 g.), containing 52 g. (0.26 mole) of I, was passed into 68.4 g. (1.2 moles) of allyl alcohol in the Pyrex bubbler. From the reaction mixture was isolated 52 g. of crude, insoluble addition product. Fractionation of a 45-g. portion of this material at atmospheric pressure yielded 25 g. of $(CF_3)_2CHCF_2OCH_2CH=CH_2$, b.p. 100°, $n^{25}D$ 1.3135, and 6 g. of a product, b.p. 79° (40 mm.), $n^{25}D$ 1.3727. The analytical data and physical properties of the higher boiling product indicated that it was mainly the unsaturated diadduct, $(CF_3)_2C=C(OCH_2CH=CH_2)_2$. Its infrared spectrum showed an absorption band at 6.1 μ which is attributed to the C=C double bond. The spectrum also showed a weak absorption at 5.65 μ which was probably due to an ester impurity.

Reaction of Saturated Ethers with Aqueous Potassium Hydroxide.—$(CF_3)_2CHCF_2OCH_3$ (35 g., 0.15 mole) and 100 cc. of 15% aqueous potassium hydroxide were refluxed at 100° for a period of 20 hr. The organic phase was then separated and taken up in diethyl ether and the ethereal solution washed several times with water and dried with anhydrous magnesium sulfate. Removal of the ether by atmospheric distillation left 26.9 g. of a water-insoluble product. Fractional distillation of this liquid residue yielded 7.0 g. (0.03 mole) of unreacted starting material and 15.0 g. (0.07 mole) of $(CF_3)_2C=CFOCH_3$, b.p. 101.5–101.8°, 47% yield.

The infrared spectrum of the unsaturated reaction product showed the presence of a strong absorption band at 5.90 μ (C=C). Absorption in the same region was observed for all vinyl ethers III obtained by the reaction of I with various alkanols.

A mixture of 33 g. (0.13 mole) of $(CF_3)_2CHCF_2O(CH_2)_2CH_3$ and 150 cc. of 15% aqueous potassium hydroxide, refluxed vigorously for a period of 25 hr., yielded similarly 18.0 g. (0.08 mole) of $(CF_3)_2C=CFO(CH_2)_2CH_3$, b.p. 129–130°, $n^{25}D$ 1.3345. The physical properties and infrared spectrum were identical with those of the unsaturated adduct obtained by the addition of 1-propanol to I.

Bromine Addition to $(CF_3)_2C=CFOC_2H_5$.—To 12 g. (0.08 mole) of bromine in a 100-cc. round-bottomed flask equipped with a reflux condenser was added slowly from a dropping funnel 16 g. (0.07 mole) of $(CF_3)_2C=CFOC_2H_5$ at room temperature at such a rate that only a minimum amount of bromine vapors escaped through the condenser. During the addition of the vinyl ether, the reaction flask was immersed in a bath of water at room temperature and frequently shaken to avoid local overheating of the reaction mixture. The red-orange liquid reaction mixture was then poured into a large excess of dilute aqueous potassium hydroxide in a separatory funnel and the two-phase mixture shaken to remove the unreacted bromide. The resulting heavy, pale yellow layer of 23 g. of the crude bromine addition product was separated, dried with anhydrous magnesium sulfate, filtered and fractionated. A cut of 10.2 g. of pure dibromide, $(CF_3)_2CBrCBrFOC_2H_5$, $n^{25}D$ 1.3906, was obtained at 75.5° and 35 mm. pressure.

Anal. Calcd. for $C_6H_5F_7Br_2O$: C, 18.67; F, 34.46; Br, 41.41. Found: C, 18.9; F, 33.9; Br, 41.2.

Stability of $(CF_3)_2CHCF_2O(CH_2)_3CH_3$ in 1-Butanol.—A mixture of 24.9 g. (0.09 mole) of $(CF_3)_2CHCF_2O(CH_2)_3CH_3$ and 40 g. of 1-butanol was refluxed for 10 hr. in a 250-cc. Pyrex flask. The reaction mixture was cooled, washed several times with water and dried over anhydrous magnesium sulfate. After removal of the butanol at atmospheric pressure, rectification of the residual liquid gave 21.5 g. of unchanged starting material. The aqueous washings from the crude reaction mixture reacted neutral indicating the absence of a solvolytic reaction. The infrared spectrum of the distillate showed the recovered product to be free of the corresponding vinyl ether.

Stability of $(CF_3)_2CHCF_2OC_2H_5$ and $(CF_3)_2C=CFOC_2H_5$ in Alcoholic Sodium Hydroxide.[17]—The stabilities of $(CF_3)_2CHCF_2OC_2H_5$ and $(CF_3)_2C=CFOC_2H_5$ toward alcoholic alkali at room temperature were examined using an alcoholic solution of sodium hydroxide.

Freshly cut metallic sodium (2.3 g.) was dissolved in 40–50 cc. of absolute ethanol. The resulting clear, colorless solution was then treated with 3.2 cc. of distilled water and diluted in a volumetric flask to 100 cc. with absolute ethanol. To the resulting alcoholic alkali containing 4% of sodium hydroxide was added 0.1461 g. of $(CF_3)_2CHCF_2OC_2H_5$ and the mixture allowed to stand at room temperature (24°). Aliquots of the mixture were titrated at various intervals for fluoride ion by the standard thorium nitrate method using sodium alizarin sulfonate as the indicator. No further increase of the fluoride concentration was noted after 30 hr. The amount of fluoride ion formed was 84.3 mg. corresponding to 93.4% cleavage of all C–F bonds of the adduct.

A similar decomposition of 0.1935 g. of $(CF_3)_2C=CFOC_2H_5$ yielded, over a period of 19 hr. at 24°, 104.8 mg. of fluoride ion corresponding to 92.1% decomposition of the vinyl ether.

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