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

The Addition of Alcohols to Some 1,1-Difluoroethylenes

BY PAUL TARRANT AND HENRY C. BROWN[1]

A number of ethers have been prepared by the addition of methyl, ethyl, *i*-propyl and *t*-butyl alcohols to $CF_2{=}CFCl$, $CF_2{=}CCl_2$ and $CF_2{=}CHCl$ in an effort to correlate the structures of both the alcohol and olefin with the ease of addition and the stability of the resulting saturated ether. *t*-Butyl alcohol reacted less readily than the other alcohols in the presence of a base; additions to $CF_2{=}CFCl$ were somewhat more difficult than to the other olefins. The ethers prepared from $CF_2{=}CFCl$ were more stable thermally and more resistant to the action of alkali than those from $CF_2{=}CHCl$ and $CF_2{=}CCl_2$. The orthoester of dichloroacetic acid was obtained by prolonged reaction of ethyl alcohol and $CF_2{=}CCl_2$; the orthoester of chlorofluoroacetic acid was obtained by treating $C_2H_5OCF_2CHClF$ with alcoholic alkali at 150° for 5 hours. The saturated *t*-butyl ethers were apparently the least stable thermally since only vinyl ethers, *t*-butyl fluoride, polyisobutylene and chlorofluoroacetic acid were separated when the products were processed.

The first report of the addition of alcohols to fluoroölefins was made in 1946 when a patent[2] was issued on the base-catalyzed addition of certain alcohols to $CF_2{=}CF_2$ and of ethyl alcohol to $CF_2{=}CFCl$ and $CF_2{=}CHCl$ to form ethers. In 1948, it was shown[3] that methyl alcohol added to $CF_2{=}CF_2$, $CF_2{=}CFCl$ and $CF_2{=}CCl_2$; Hurwitz and Miller[4] proposed a mechanism for the addition of anionic reagents such as amines and alcohols to these olefins. Park and co-workers[5] have reported the preparation and properties of saturated ethers from addition of several alcohols to $CF_2{=}CFCl$.

This study is concerned with the addition of methyl, ethyl, *i*-propyl and *t*-butyl alcohols to $CF_2{=}CFCl$, $CF_2{=}CCl_2$ and $CF_2{=}CHCl$. It was thought that the variation in basicity of the alcohols might affect the direction of the addition as well as the stability of the resulting ether. Although relatively wide variations in conditions during the addition reactions were employed, no products or fragments were identified that could have resulted from addition except as postulated by previous investigators.[3,4] Such a conclusion might not have been predicted from the evidence on the addition of amines to *unsym*-fluoroölefins. Although a number of amines add to $CF_2{=}CFCl$ to give both difluoro- and chlorofluoroacetamides under certain conditions,[6] a higher mole fraction of the difluoroamide is obtained when the amine contains a branched chain or is a secondary amine.[7]

TABLE I

ADDITION PRODUCTS OF ALCOHOLS TO FLUOROÖLEFINS

Product	B.p., °C.	Mm.	$n^{25}D$	d^{25}_4	Cl, % Calcd.	Obsd.	AR F
$C_2H_5OCF_2CHCl_2$	63.0	100	1.3922	1.3145	39.7	39.8	1.30
$(C_2H_5O)_3CCHCl_2$	124.0–129.0	60	1.4336	1.1306	30.8	30.8	[a]
$(CH_3)_2CHOCF_2CHCl_2$	28.0–30.2	9.0	1.3897	1.2331	36.7	36.5	1.26
$(CH_3)_3COCF{=}CCl_2$	38.0	2.9	1.4315	1.1368	37.7	37.8	1.35
$(C_2H_5O)_3CCHFCl$	67.5	10	1.4059	1.0815	16.4	16.3	0.96
$(CH_3)_3COCF{=}CFCl$	18.0	0.8	1.3989	1.0940	20.8	20.8[b]	1.9
	143	760					
$CH_3OCF_2CH_2Cl$	27.5–28.0	130	1.3560	1.2592	27.2	27.0	1.15
$(CH_3)_2CHOCF_2CH_2Cl$	53.0	121	1.3720	1.1627	22.4	22.8	0.7

[a] *MR*D (calcd.) 53.8; (obsd.) 53.3. [b] %F (calcd.) 22.3; (obsd.) 21.6.

The olefins $CF_2{=}CCl_2$ and $CF_2{=}CHCl$ were considerably more reactive than the more nearly symmetrical $CF_2{=}CFCl$. The difference in reactivity was shown particularly by their reaction with *t*-butyl alcohol; $CF_2{=}CCl_2$ yielded an addition product at atmospheric pressure and a temperature of 35–40° but $CF_2{=}CFCl$ was quite unreactive under similar conditions. When $CF_2{=}CFCl$ was refluxed for 6 hours with sodium *t*-butylate solution at atmospheric pressure, 95% of the olefin was recovered and no addition product isolated.

The addition of each of the alcohols to the olefins gave a saturated ether as the principal product with the exception of *t*-butyl alcohol. The properties of these products not previously prepared by the addition reaction are shown in Table I. Various experimental conditions were employed in order to obtain the ethers in as high yields as possible since they vary considerably in stability as discussed below.

In a number of cases rather unexpected products were found. For example, stable, high boiling compounds were formed by continued reaction of 1-ethoxy-1,1-difluoro-2,2-dichloroethane, $C_2H_5OCF_2CHCl_2$, and ethoxy-1,1,2-trifluoro-2-chloroethane, $C_2H_5OCF_2CHFCl$, with sodium ethylate in ethyl alcohol; they were found to be orthoesters. Formation of orthoesters from $CF_2{=}CCl_2$ and $CF_2{=}CHCl$ was possible at atmospheric pressure and at the reflux temperature of the alcohol. This type of compound was not encountered when alcohols were added to $CF_2{=}CFCl$; however, the orthoester was obtained from $C_2H_5OCF_2CHFCl$ at 150°.

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(1) The material in this paper is abstracted from a portion of a dissertation submitted by Henry C. Brown to the Graduate Council of the University of Florida, August, 1950, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

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

(3) W. T. Miller, Jr., E. W. Fager and P. H. Griswold, THIS JOURNAL, **70**, 431 (1948).

(4) Hurwitz and Miller, Abstracts of Papers, 114th Meeting, American Chemical Society, Washington, D. C., August, 1948, p. 41.

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

(6) Melvin Fried, Master's Thesis, University of Florida, 1949.

(7) Dale Warner, Master's Thesis University of Florida 1950.

In reactions involving $CF_2{=}CHCl$ and $CF_2{=}CCl_2$ with alcohols, the corresponding esters of chloro- and dichloroacetic acids were frequently encountered, especially when the reaction products were in contact with water for an extended period. Esters were never obtained from $CF_2{=}CFCl$ under similar conditions.

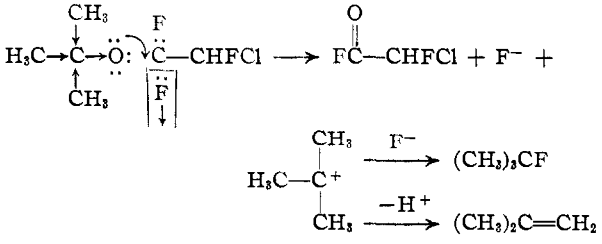
Thermal Stability of Alkyl Fluoroethers.—Ethers formed from addition of straight chain alcohols to trifluorochloroethene are relatively stable while those formed from the more reactive 1,1-difluoro-2,2-dichloroethene and 1,1-difluoro-2-chloroethene have a tendency to split off hydrogen fluoride on long standing at room temperature.

The stability of fluoroethers of the type prepared in this research is influenced greatly by substitution of methyl groups for hydrogen atoms on the alpha carbon of the alkyl group. The isopropyl ether from addition to $CF{=}CHCl$ was obtained only as a mixture of the saturated and unsaturated compounds, and the *t*-butyl ethers from additions to $CF_2{=}CFCl$ and to $CF_2{=}CCl_2$ were both unsaturated.

The *t*-butyl ethers are particularly interesting in that the saturated form is apparently not stable enough under the conditions of this work to be isolated at all.[8] In an early preparation of the addition product of *t*-butyl alcohol to trifluorochloroethene, no ether was isolated but a variety of decomposition products was obtained: isobutyl fluoride, fluorochloroacetic acid and probably a mixture of di- and triisobutylene.

Since decomposition of the isopropyl ethers had been noticed on distillation, a pure sample of $(CH_3)_2CHOCF_2CHCl_2$ was carefully decomposed by heating at atmospheric pressure. Isopropyl fluoride and dichloroacetyl fluoride were separated and identified. There was also some indication of the presence of propylene.

The products from the *t*-butyl and *i*-propyl ethers could be accounted for by assuming that the electron releasing methyl group of the alkyl radical aids in the rupture of the alkyl–oxygen bond so that the acid fluoride and a carbonium ion are formed. The carbonium ion may react with a fluoride ion or release a proton to give an olefin.



Experimental

In general, reactions of the fluoroölefins with the various alcohols were carried out in glass apparatus at atmospheric pressure by the procedure of Park, *et al.*[5] In the case of *t*-butyl alcohol, however, the use of an autoclave was necessary. The temperature at which the reactions were run was determined by the volatility of the olefin, the susceptibility of the product to dehydrofluorination and by the reactivity of the alcohol.

Addition of *t*-Butyl Alcohol to $CF_2{=}CFCl$.—Sodium *t*-butylate was prepared by refluxing the alcohol with excess sodium until the solution was saturated with the alcoholate at about 100°. While hot, 225 ml. of this solution was decanted into a stainless steel autoclave, the temperature of the autoclave lowered by cooling in Dry Ice, and 58 g. (0.5 mole) of chlorotrifluoroethylene added. The autoclave was heated with shaking for 20 hours at 100°, then cooled to $-10°$ and the contents, now acid to litmus, transferred to the distillation apparatus. To avoid decomposition, the products were not heated above 35°. At this pot temperature and atmospheric pressure, *t*-butyl fluoride, b.p. 13.5°, mol. wt. 76 (calcd.); 80 (obsd.) was separated.

Pressure in the system was then lowered gradually to 50 mm. where unreacted alcohol distilled. Since previous experiments had shown that the ether and alcohol were not separated by distillation, the material was removed, washed three times with cold water and dried over calcium chloride at about 5°. Fractionation gave 20 g. of 1-(1,1-dimethylethoxy)-2-chloro-1,2-difluoroethene whose properties are given in Table I.

The method of handling the reaction mixture affected the final products formed. In one experiment, run as above, the products were diluted with cold water, separated, washed and dried. Fractionation at atmospheric pressure gave 6 g. of *t*-butyl fluoride, b.p. 13.5–15.0°, a series of intermediate fractions and 18 g. of chlorofluoroacetic acid, b.p. 165°, n^{25}_{D} 1.4075.

The reaction of 0.5 mole of chlorotrifluoroethylene with 200 ml. of *t*-butyl alcohol or with *t*-butyl alcohol and 0.02 g. atom of sodium for 20 hours at 100° gave none of the butoxyhaloethane. There was obtained 27 g. of material boiling at 54.5–57.5°, n^{25}_{D} 1.3390. These constants indicate that this material was 1,2-dichloro-1,2,3,3,4,4-hexafluorocyclobutane.[9] In addition there was obtained a viscous material which could not be distilled at 2 mm.; this material is believed to be polyisobutylene.

The Addition of Ethyl Alcohol to $CF_2{=}CCl_2$.—The reaction was run in the usual manner at 40° by external cooling after an initial temperature rise to 70°. Fractionation of the product through a 30" column packed with Berl saddles gave an average yield of 45% of $C_2H_5OCF_2CHCl_2$ with properties listed in the table. In addition 4.5 g. of $(C_2H_5O)_3CCHCl_2$ was obtained.

When the addition reaction was carried out at a higher temperature, no ether was formed. Three moles of potassium hydroxide was added to 500 ml. of ethyl alcohol and 0.8 mole of $CF_2{=}CCl_2$ added and refluxed (liquid temperature 90°) for 6 hours. The product was washed and dried in the usual manner and 35 g. of ethyl dichloroacetate, b.p. 82.5–83.0° at 60 mm. obtained.

Addition of *i*-Propyl Alcohol to $CF_2{=}CCl_2$.—Six grams (0.26 g. atom) of sodium reacted with 600 ml. of *i*-propyl alcohol, the solution was cooled to 20° and 133 g. (1.0 mole) of $CF_2{=}CCl_2$ added dropwise. The reaction temperature was maintained at 20–25° by external cooling. The reaction mixture was poured onto crushed ice, the organic layer separated, washed with cold water and dried with calcium chloride at about 5°. Distillation was carried out at a maximum pot temperature of 50° and 152 g. of 1-(1-methylethoxy)-1,1-difluoro-2,2-dichloroethane, boiling at 28.0–30.2° at 9 mm., obtained.

Addition of *t*-Butyl Alcohol to $CF_2{=}CCl_2$.—Seventy grams (0.52 mole) of $CF_2{=}CCl_2$ and 225 ml. of a solution of sodium *t*-butylate in *t*-butyl alcohol (saturated at 100°) were heated for 20 hours at 100°. The products were distilled without further treatment and some *t*-butyl fluoride removed. The residue was washed with water and distilled at 2.9 mm.; 34.5 g. of $(CH_3)_3COCF{=}CCl_2$, with properties listed in the table, was separated.

The Addition of Methyl Alcohol to $CF_2{=}CHCl$.—The reaction was run at 57° for 4 hours by the general procedure outlined. From 132 g. of $CF_2{=}CHCl$ there was obtained 60 g. of 1-methoxy-1,1-difluoro-2-chloroethane (yield 37%).

The Addition of *i*-Propyl Alcohol to $CF_2{=}CHCl$.—The reaction was run at the reflux temperature of the alcohol for 2 hours. A crude product containing an unsaturated ether was obtained. Fifty grams of this material was treated with bromine to convert any vinyl ether to a higher boiling product. Fractionation then gave 14 g. of 1-(1-methylethoxy)-1,1-difluoro-2-chloroethane.

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(8) Since this paper was first prepared, the isolation of the *t*-butyl ether from $CF_2{=}CFCl$ has been reported. See Barr, Rapp, Pruett, Bahner, Gibson and Lafferty, THIS JOURNAL, **72**, 4480 (1950).

(9) A. L. Henne and R. P. Ruh, THIS JOURNAL, **69**, 279 (1947).

The Preparation of Orthoesters.—Small amounts of high boiling fractions were noted in the products of the reaction of ethyl alcohol to $CF_2{=}CCl_2$. In an effort to prepare larger quantities of these materials the following reactions were run.

Ethyl alcohol (325 ml.), sodium ethylate (1.5 moles) and $C_2H_5OCF_2CHCl_2$ (0.28 mole) were refluxed for 4 hours. The product was mixed with cold water and extracted with ether. Distillation gave 27.5 g. of 1,1,1-triethoxy-2,2-dichloroethane.

The orthoester of chlorofluoroacetic acid was never obtained during the addition of ethyl alcohol to $CF_2{=}CFCl$. At 150° a mixture of 1.7 moles of potassium hydroxide, 2.3 moles of ethyl alcohol and 0.41 mole of $C_2H_5OCF_2CHFCl$ in a stainless steel autoclave gave 22 g. of 1,1,1-triethoxy-2-chloro-2-fluoroethane. When 18 g. of this compound was treated with 10 ml. of sulfuric acid, there was obtained 6 g. of ethyl chlorofluoroacetate, b.p. 129–130°, $n^{25}D$ 1.3920, thus proving that the compound was the orthoester of chlorofluoroacetic acid.

Thermal Decomposition of 1-(1-Methylethoxy)-1,1-difluoro-2,2-dichloroethane.—Since the decomposition of alkoxypolyhaloethanes had been observed in a number of distillations, particularly those involving olefins containing only two fluorine atoms, a sample of the ether prepared by the addition of *i*-propyl alcohol to $CF_2{=}CCl_2$ was decomposed thermally.

About 0.25 mole (48 g.) of $(CH_3)_2CHOCF_2CCl_2$ was refluxed in a glass flask under a condenser cooled by water at 3–4°. Vapor passing through the reflux condenser was led through a 135-cm. tube containing a bed of sodium fluoride and condensed in a trap.

Fractionation of the volatile material gave 8 g. of a fraction boiling from −28 to −9° which was probably a mixture of propylene and *i*-propyl fluoride. In addition 18 g. of *i*-propyl fluoride, b.p. −9.0 to −7.0°, mol. wt. (calcd.) 62.1; (obsd.) 61.5, was obtained.

Distillation of the higher boiling material gave 16 g. of $CHCl_2COF$, b.p. 69.8, $n^{25}D$ 1.3946. Dichloroacetanilide made from this material had a melting point of 115–116°. A small amount of higher boiling material could not be distilled; this material was presumably dichloroacetic acid.

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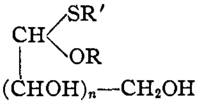
[RESEARCH LABORATORIES, AMERICAN HOME FOODS, INC.]

Mixed Acetals

BY FRANK KIPNIS,[1a] HAROLD SOLOWAY[1b] AND JOHN ORNFELT

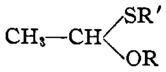
Mixed acetals containing both oxygen and sulfur loadings on the same carbon atom have been prepared by the interaction of vinyl ethers with mercaptans in the presence of acid catalysts.

Except for the acyclic carbohydrate compounds[2] (I) prepared by rather lengthy syntheses, there does not appear in the literature any mention of mixed non-cyclic acetals (II) bearing substituted oxygen and sulfur attached to the same carbon atom.[3]



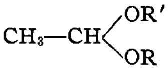
$\underset{(CHOH)_n-CH_2OH}{CH\big\langle^{SR'}_{OR}}$

I



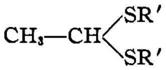
$CH_3-CH\big\langle^{SR'}_{OR}$

II



$CH_3-CH\big\langle^{OR'}_{OR}$

III



$CH_3-CH\big\langle^{SR'}_{SR'}$

IV

Since mixed acetals (II) were required for study during the course of certain researches, an investigation was conducted on the interaction of vinyl alkyl ethers with mercaptans. It had already been found[4a,b] that vinyl ethers will undergo reaction with alkanols in the presence of catalytic amounts of anhydrous acids to produce mixed O-acetals (III) in fair yields. When alcohols were replaced by mercaptans, the desired mixed O,S-acetals (II) were produced, together with symmetrical mercaptals (IV), generated, probably, by a redistribution mechanism.[5]

The new compounds are minty-odored liquids insoluble in water and soluble in most organic solvents, extremely unstable to dilute acid, generating acetaldehyde, an alcohol and a mercaptan on such treatment, and resistant to alkali. This instability to acid is similar to that shown by acetals and hemimercaptals. Treatment of the mixed O,S-acetals with ammoniacal sodium nitroprusside gives no coloration, indicating the absence of unreacted mercaptan, as well as stability to base. With sodium nitrite–hydrochloric acid, the acetals give a red color,[6] indicative of easy hydrolysis to the mercaptan and the alcohol, while an immediate pink color is given with the fuchsin–sulfur dioxide reagent, confirming hydrolysis to acetaldehyde.

Experimental

1-*n*-Butylthio-1-ethoxyethane.—To a 250-ml. 3-neck flask fitted with a sealed stirrer, reflux condenser and drying tube, thermometer and dropping funnel, was added 32 g. (0.45 mole) of *n*-butyl mercaptan, 0.2 ml. of thionyl chloride and 150 ml. of anhydrous ether. The stirrer was started and the solution was cooled to 10°. From the dropping funnel was added 32.4 g. (0.45 mole) of vinyl ethyl ether[7] at such a rate that the temperature did not rise

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[1] (a) Oxford Products, Inc., Cleveland, Ohio; (b) Sterling-Winthrop Research Institute, Rensselaer, New York.

[2] M. L. Wolfrom and D. I. Weisblat, THIS JOURNAL, **62**, 878 (1940); M. L. Wolfrom, D. I. Weisblat and A. R. Hanze, *ibid.*, **62**, 3246 (1940).

[3] W. E. Mochel, C. L. Agre and W. E. Hanford, *ibid.*, **70**, 2268 (1948), have reported the isolation of an impure compound, in addition to the ketal, from the interaction of 2,2-di-(ethylthio)-butane with methanol in the presence of hydrogen chloride. The crude material is suggested to be 2-methoxy-2-(ethylthio)-butane.

[4] (a) W. Reppe and K. Bauer, U. S. Patent 2,000,252 (May 7, 1935); German Patent 566,033 (December 8, 1932); (b) M. F. Shostakovskiĭ and N. A. Gershteĭn, *J. Gen. Chem.* (*U. S. S. R.*), **16**, 937 (1946); Gershteĭn and Shostakovskiĭ, *ibid.*, **18**, 451 (1948).

[5] During the preparation of this manuscript, a patent of J. W. Copenhaver (U. S. Patent 2,500,486, March 14, 1950) appeared, in which it was reported that interaction of methyl vinyl ether with ethyl thio-orthoformate in the presence of acid catalysts gave rise to 1-methoxy-1-ethylthio-3,3′-bis-(ethylthio)-propane.

[6] H. Rheinboldt, *Ber.*, **60**, 184 (1927).

[7] Purchased from General Aniline and Film Corp., N. Y. C., N. Y. The commercial product was washed with distilled water and then with sodium bicarbonate solution, dried over sodium hydroxide and fractionated through a 30 cm. Widmer column. Precautions were taken to eliminate traces of acid in all equipment in order to avoid polymerization.