Recrystallization of the adduct was not successful. Purification was achieved by rinsing the adduct with glyme. This gave material of m.p. 222–223° dec.

Anal. Calcd. for $C_{12}H_{10}ClN_5O$: C, 52.3; H, 3.66; Cl, 12.9; N, 25.4. Found: C, 52.3; H, 3.52; Cl, 12.8; N, 25.8.

The infrared spectrum of the azetidine confirms the fact that the CF_3S group has been removed during the reaction. There was absorption of the conjugated nitrile and the tricyanovinyl double bond as in the other azetidines. CF and SCF_3 absorptions were absent. Additional absorption due to NH and C=O was apparent. The ultraviolet absorption of the adduct in acetonitrile solution showed the presence of the tricyanovinyl group, λ_{max} 265 mμ (ε 15,300).

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Free-Radical Additions Involving Fluorine Compounds. VII.[1] The Addition of Perhaloalkanes to Vinyl Ethyl Ether and Vinyl 2,2,2-Trifluoroethyl Ether

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The addition of perhaloalkanes to some vinyl and allyl ethers were carried out satisfactorily in the presence of ultraviolet irradiation. Adducts obtained from vinyl trifluoroethyl ether showed a marked increase in thermal and hydrolytic stabilities over the vinyl ethyl ether adducts. The products, α-bromo ethers, were converted into a variety of fluorine-containing compounds.

As part of a program designed to prepare new fluorine-containing monomers, the synthesis of some unsaturated fluoro ethers has been investigated. Earlier work[1] had shown that free-radical addition of perhaloalkanes such as bromotrichloromethane, dibromodifluoromethane, and 1,2-dibromo-2-chloro-1,1,2-trifluoroethane to allyl ethers could be accomplished easily to give adducts capable of transformation to both olefinic and dienic ethers. Consequently, this reaction was extended to include addition of CCl_3Br, CF_2Br_2, and $CF_2BrCFClBr$ to some vinyl ethers. Vinyl ethyl ether and vinyl 2,2,2-trifluoroethyl ether were chosen because of their availability and also in order to compare the effect of the β-fluorine atoms on the properties of the adducts.

A number of investigators have shown the high reactivity of vinyl ethers in free-radical additions. Glickman[3] added carbon tetrachloride, carbon tetrabromide, and dibromodichloromethane to a number of vinyl ethers using peroxides or ultraviolet irradiation to give high yields of 1-halo-3-trihalopropyl ethers. Similar additions have been reported by Levas[4] and Shostakovskii.[5]

Initial attempts to carry out radical additions to vinyl ethyl ether in an autoclave using benzoyl peroxide initiator at 75° resulted, in every case, in decomposition of product as evidenced by heavy fuming and formation of black, spongy polymer. This thermal instability, characteristic of most α-haloalkyl ethers,[6] necessitated the adoption of a procedure in which materials could react at temperatures lower than the decomposition temperature of the products. Such a method was found in the use of ultraviolet irradiation as a free-radical initiator. An additional advantage of this procedure is the absence of contaminants resulting from the decomposition of the peroxide. It was subsequently found that ultraviolet-catalyzed additions to allyl ethers could be carried out in conversions comparable to those from peroxide-catalyzed reactions.[1]

The following free-radical addition reactions were carried out using ultraviolet initiation.

$$CCl_3Br + CH_2{=}CHOC_2H_5 \longrightarrow \underset{\text{I}}{CCl_3CH_2CHBrOC_2H_5} \qquad (1)$$

$$CF_2Br_2 + CH_2{=}CHOC_2H_5 \longrightarrow \underset{\text{II}}{CF_2BrCH_2CHBrOC_2H_5} \qquad (2)$$

$$CF_2BrCFClBr + CH_2{=}CHOC_2H_5 \longrightarrow \underset{\text{III}}{CF_2BrCFClCH_2CHBrOC_2H_5} \qquad (3)$$

$$CCl_3Br + CH_2{=}CHOCH_2CF_3 \longrightarrow \underset{\text{IV}}{CCl_3CH_2CHBrOCH_2CF_3} \qquad (4)$$

$$CF_2Br_2 + CH_2{=}CHOCH_2CF_3 \longrightarrow \underset{\text{V}}{CF_2BrCH_2CHBrOCH_2CF_3} \qquad (5)$$

$$CF_2BrCFClBr + CH_2{=}CHOCH_2CF_3 \longrightarrow \underset{\text{VI}}{CF_2BrCFClCH_2CHBrOCH_2CF_3} \qquad (6)$$

Adducts from vinyl ethyl ether (I, II, III) fumed heavily on exposure to moist air and decomposed rapidly with evolution of hydrogen halide between 70–85° during distillation. Consequently, only II could be satisfactorily fractionated owing to its lower boiling point, although apparent boiling points for the CCl_3Br and $CF_2BrCFClBr$ adducts (I, III) are reported (see Table I for properties of the compounds prepared). These adducts, although not isolated could be treated to give stable derivatives which will be described later. Satisfactory analysis of the α-bromoalkyl ethyl ethers was not accomplished owing to their rapid decomposition. Compounds I, II, and III were also found to be extremely reactive hydrolytically. Upon basic hydrolysis, I was found to give appreciable quantities of a highly lachrymatory material identified as dichloroacrolein, $CCl_2{=}CHCHO$. Hydrolysis of the CF_2Br_2 and $CF_2BrCFClBr$ adducts (II and III) resulted in vigorous reactions leading to the formation of extremely lachrymatory compounds which were not

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[1] Preceding paper in this series: P. Tarrant and E. C. Stump, Jr., *J. Org. Chem.*, **26**, 4646 (1961).

[2] To whom requests for reprints should be sent at Peninsular Chem-Research, Inc., P. O. Box 14318, Gainesville, Fla.

[3] S. A. Glickman, U. S. Patent 2,560,219 (1951).

[4] M. Levas, *Ann. chim.* (Paris), **7**, 697 (1952); *Chem. Abstr.*, **48**, 1243*d* (1954).

[5] M. F. Shostakovskii, A. V. Bogdanova, M. M. Zverov, and G. I. Plotnikova, *Izv. Akad. Nauk SSSR Otd. Khim. Nauk*, 1236 (1956); *Chem. Abstr.*, **51**, 5730*e* (1957).

[6] L. Summers, *Chem. Rev.*, **55**, 337 (1955).

TABLE I

PROPERTIES OF ETHERS AND ACETALS PREPARED

No.	Structure	% conversion	B.p., °C.	Pressure, mm.	$n^{23}D$	d^{23}
I	$CCl_3CH_2CHBrOC_2H_5$		51	0.7	1.4835	1.395
II	$CF_2BrCH_2CHBrOC_2H_5$	83	53.5	5	1.4490	1.734
III	$CF_2BrCFClCH_2CHBrOC_2H_5$		71	1	*a*	*a*
IV	$CCl_3CH_2CHBrOCH_2CF_3$	91	45	0.4	1.4488	1.739
V	$CF_2BrCH_2CHBrOCH_2CF_3$	72	29	1.5	1.4052	1.901
VI	$CF_2BrCFClCH_2CHBrOCH_2CF_3$	72	55	0.5	1.4188	1.935
VII	$CCl_3CH_2CH_2OC_2H_5$	40[b]	67	7.5	1.4615	1.305
VIII	$CF_2BrCH_2CH_2OC_2H_5$	21[b]	36	20	1.4026	1.410
IX	$CF_2BrCFClCH_2CH_2OC_2H_5$	33[b]	42	3	1.4185	1.526
X	$CCl_3CH_2CH_2OCH_2CF_3$	21[c]	54	6	1.4119	1.460
XI	$CF_2BrCH_2CH_2OCH_2CF_3$	24[c]	56	40	1.3604	1.613
XII	$CF_2BrCFClCH_2CH_2OCH_2CF_3$	21[c]	43	2.5	1.3840	1.705
XIII	$CF_2{=}CHCH_2OC_2H_5$	36	67	760	1.3548	1.007
XIV	$CF_2{=}CFCH_2CH_2OC_2H_5$	35	96	760	1.3555	1.069
XV	$CF_2{=}CHCH_2OCH_2CF_3$	45	81	760	1.3207	1.299
XVI	$CF_2{=}CFCH_2CH_2OCH_2CF_3$	42	103	760	1.3302	1.307
XVII	$CF_2BrCH_2CH(OC_2H_5)_2$	75	64	14	1.4057	1.325
XVIII	$CF_2BrCFClCH_2CH(OC_2H_5)_2$	38	52	0.5	1.4190	1.440
XIX	$CF_2BrCH_2CH(OCH_2CF_3)_2$	21	78	20	1.3512	1.670
XX	$CF_2BrCFClCH_2CH(OCH_2CF_3)_2$	67	50	0.5	1.3745	1.754
XXI	$CF_2BrCH_2CH(CH_3)OC_2H_5$	19[b]	55	41	1.4020	1.335
XXII	$CF_2{=}CHCH(CH_3)OC_2H_5$	45	76	760	1.3588	0.969
XXIII	$(CH_3)_2C(OCH_2CF_3)_2$	10	120–126	760	1.3270	1.261

[a] Pure sample not isolated. [b] Based on vinyl ethyl ether. [c] Based on vinyl 2,2,2-trifluoroethyl ether.

TABLE II

ANALYSES OF COMPOUNDS PREPARED

	MRD		% C		% H		% halogen		Mol. wt.[a]	
No.	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
I	*b*								270.4	
II	42.46	43.61[b]	21.30	23.26	2.86	3.52	56.70[c]	54.95	281.9	
III	*b*								348.6	
IV	49.30	50.02	18.50	18.58	1.56	1.63	81.09[e]	81.80	324.4	
V	42.46	43.10	17.87	17.87	1.50	1.77	47.58[c]	47.25	335.9	
VI	51.95	52.41	17.90	18.06	1.25	1.55			402.6	
VII	41.53	40.50	31.34	31.54	4.74	4.88	55.54[d]	55.45	191.5	
VIII	34.71	35.10	29.58	29.64	4.47	4.58	39.46[c]	39.60	203.0	205
IX	44.18	44.48	26.74	26.77	3.37	3.43	134.7[e]	133.0	269.5	
X	41.53	42.10	24.47	24.52	2.46	2.45	43.33[d]	43.33	245.5	
XI	34.71	35.20	23.36	23.50	2.35	2.45	31.09[c]	30.83	257.0	250
XII	44.18	44.51	22.28	22.41	1.87	1.98	161.8[e]	163.5	323.5	
XIII	26.47	26.56	49.18	49.18	6.63	6.58			122.1	130
XIV	31.08	31.41	46.77	46.51	5.89	5.99			154.1	154
XV	26.47	27.05	34.10	34.25	2.86	3.14			176.1	175
XVI	31.08	32.50	34.58	34.63	2.73	2.91			208.1	208
XVII	45.58	45.13	33.99	37.30	5.30	5.64	32.34[c]	30.57	247.1	
XVIII	55.06	54.95	30.63	31.01	4.18	4.43			313.6	
XIX	45.58	46.08	23.68	23.81	1.97	2.25			355.1	
XX	55.06	54.92	22.80	23.06	1.67	1.88			421.5	
XXI	39.32	39.50	33.20	33.48	5.11	5.27	36.82[c]	37.15	217.1	
XXII	31.08	30.97	52.93	52.93	7.40	7.53			136.2	
XXIII	37.81	38.50	35.01	35.21	4.20	4.36			240.2	

[a] By freezing point depression in benzene. [b] Sample decomposes. [c] % bromine. [d] % chlorine. Silver equivalent.

identified, partially owing to their tendency to polymerize to viscous liquids. Similar results were observed by Durrell[7] in handling the adducts of CF_2Br_2 and $CF_2BrCFClBr$ and vinyl acetate.

Adducts obtained from the addition of perhaloalkanes to vinyl 2,2,2-trifluoroethyl ether (IV, V, VI) exhibited a marked increase in thermal and hydrolytic stabilities over those of the vinyl ethyl ether adducts. They showed little tendency to hydrolyze in moist air, could be stored several months without decomposition, and gave good analytical results (see Table II for analyses of compounds prepared). The thermal stability of these compounds was so greatly enhanced that a 62-g. sample of V was recovered unchanged after passing through a hot tube at 220°.

The reactivity of the bromine atom in alkyl α-bromoalkyl ethers may be attributed to the possibility of resonance involving an oxonium form. Physical evidence supporting this has been presented by Brey and

$$R\overset{+}{C}H—\underset{\cdot\cdot}{\overset{\cdot\cdot}{O}}—R' \longleftrightarrow RCH{=}\underset{\cdot\cdot}{\overset{+}{O}}—R'$$

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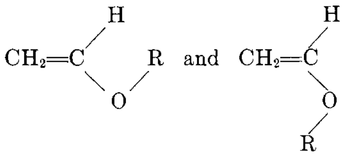
[7] W. Durrell, WADC Technical Report 58-589 (May, 1959); W. Durrell, A. M. Lovelace, and R. L. Adamczak, *J. Org. Chem.*, **25**, 1662 (1960).

Tarrant[8] who noted a doublet in the infrared spectra of vinyl alkyl ethers arising from the existence of rotational isomers. To explain the presence of rotational isomers, Batuev[9] postulated a resonance structure for vinyl ethers, $\bar{C}H_2-CH=\overset{+}{O}-R$, for which rotation of the alkyl group about the carbon–oxygen bond would be hindered; this resulted in these following isomers.



However, when R′ is a CF_3CH_2- group, the negative (electron-withdrawing) inductive effect of the three fluorine atoms is evidently strong enough to inhibit drastically the ability of the oxygen atom to denote its unshared electrons in the formation of the oxonium structure. Brey and Tarrant found only a single carbon–carbon double bond stretching region in vinyl α,α-difluoro ethers. This result was attributed to the strong inductive effect of the α-fluorine atoms which prevented resonance of the oxygen electrons with the double bond. However, the inductive effect of fluorine in the β-position, insulated from the oxygen atom by a methylene group, is not sufficient to overcome the resonance completely, as evidenced by the appearance of doublet in the carbon–carbon double bond stretching region in the spectra of all vinyl β-fluoro ethers examined.

The comparative unreactivity of the α-bromoalkyl 2,2,2-trifluoroethyl ethers reported here is unusual in that this effect is transmitted through the methylene group. Thus, this appears to be a case in which the resonance interactions are not inhibited enough to change the physical (*i.e.*, infrared absorption) properties but are inhibited sufficiently to cause a marked change in chemical reactivity.

In contrast to the additions of perhaloalkanes to allyl ethers, it was found that additions to vinyl ethers resulted in high conversions (72–91%) to the 1:1 adducts. Moreover, very little telomerization occurred, evidenced by the very small amount of high boiling material remaining after distillation of the reaction products, even though smaller ratios of perhaloalkane to ether were used.

Attempts to dehydrobrominate the α-bromo compounds (I–VI) to give α,β-unsaturated ethers using pyridine or aqueous base were not successful. Reaction of II with pyridine resulted only in the formation of higher boiling material. Reactions with aqueous base resulted in rupture of the carbon–oxygen bond, as previously mentioned, apparently to give an unsaturated aldehyde. Attempts to prepare an acetate (to be followed by pyrolysis to the α,β-unsaturated ether) from II by reaction with sodium acetate were also unsuccessful, resulting in decomposition involving the elimination of hydrogen fluoride.

A suitable method for converting the α-bromo ethers to unsaturated fluoro ethers was found in the reduction of the α-bromo atom with lithium aluminum hydride

$$CF_2BrCH_2CHBrOR \xrightarrow{LiAlH_4} \underset{\text{VIII and XI}}{CF_2BrCH_2CH_2OR} \tag{7}$$

$$CF_2BrCFClCH_2CHBrOR \xrightarrow{LiAlH_4} \underset{\text{IX and XII}}{CF_2BrCFClCH_2CH_2OR} \tag{8}$$

$$(\text{where } R = C_2H_5 \text{ and } CH_2CF_3)$$

(eq. 7 and 8), followed by dehydrohalogenation or dehalogenation of the products.

Although the reduction of I resulted in the formation of several impurities as determined by gas chromatography, the desired $CCl_3CH_2CH_2OC_2H_5$ was shown to be a product of the reaction by its conversion to $C_2H_5O_2CCH_2CH_2OC_2H_5$ with ethanolic potassium hydroxide.

The unsaturated fluoro ether derivatives were prepared as shown in eq. 9 and 10.

$$CF_2BrCH_2CH_2OR \xrightarrow[\text{mineral oil}]{KOH} \underset{\text{XIII and XV}}{CF_2{=}CHCH_2OR} \tag{9}$$

$$CF_2BrCFClCH_2CH_2OR \xrightarrow[\text{alcohol}]{\text{zinc}} \underset{\text{XIV and XVI}}{CF_2{=}CFCH_2CH_2OR} \tag{10}$$

$$(\text{where } R = C_2H_5 \text{ and } CH_2CF_3)$$

Characteristic infrared carbon–carbon double bond stretching absorption peaks were observed in the 5.72–5.73-μ region for the compounds (XIII, XV, XXII) containing the $CF_2{=}CH-$ group and in the 5.53–5.54-μ region for compounds (XIV, XVI) containing the $CF_2{=}CF-$ group.

The α-bromo ethers were also found to react with alcohols to give acetals as illustrated in eq. 11 and 12. Preparation of the mixed acetals was not attempted.

$$CF_2BrCH_2CHBrOC_2H_5 + C_2H_5OH \longrightarrow \underset{\text{XVII}}{CF_2BrCH_2CH(OC_2H_5)_2} + HBr \tag{11}$$

$$CF_2BrCH_2CHBrOCH_2CF_3 + CF_3CH_2OH \longrightarrow \underset{\text{XIX}}{CF_2BrCH_2CH(OCH_2CF_3)_2} + HBr \tag{12}$$

An attempt to pyrolyze XVII to $CF_2BrCH{=}CH-OC_2H_5$ by passing it over anhydrous monosodium phosphate[10] at 300° gave only unchanged starting material. Attempts to obtain the unsaturated ether by passage of XVII through a glass-packed hot tube at 400° were also unsuccessful.

The relative unreactivity of the α-bromoalkyl 2,2,2-trifluoroethyl ethers was again demonstrated in the reaction of methylmagnesium bromide with II and V. The ethyl ether (II) reacted vigorously to give the methyl-substituted compound (XXI) as shown in eq. 13 but the 2,2,2-trifluoroethyl ether (V) did not react

$$CF_2BrCH_2CHBrOC_2H_5 + CH_3MgBr \longrightarrow \underset{\text{XXI}}{CF_2BrCH_2CH(CH_3)OC_2H_5} + MgBr_2 \tag{13}$$

under the same conditions to give the desired methyl-substituted ether.

Finally, in attempting the synthesis of 1-methylvinyl 2,2,2-trifluoroethyl ether by the base-catalyzed reaction of trifluoroethanol with methylacetylene, the new acetal $(CH_3)_2C(OCH_2CF_3)_2$ (XXIII) was obtained in low yield. This product could be accounted for by

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(8) M. L. Brey and P. Tarrant, *J. Am. Chem. Soc.*, **79**, 6533 (1957).

(9) M. I. Batuev, E. N. Prilezhaeva, and M. F. Shostakovskii, *Bull. acad. ci. URSS Classe sci. chim.*, 123 (1947); *Chem. Abstr.*, **42**, 4463i (1948).

(10) I. N. Nazorov, S. M. Makin, B. K. Kruptsov, and V. A. Miranov, *J. Gen. Chem. USSR* (Eng. Transl.), **29**, 116 (1959).

the reaction of the desired methylvinyl ether with trifluoroethanol as shown in eq. 14.

$$CH_2{=}C(CH_3)OCH_2CF_3 + CF_3CH_2OH \xrightarrow{KOH} \underset{\text{XXIII}}{(CH_3)_2C(OCH_2CF_3)} \quad (14)$$

Experimental[11,12]

Materials.—Vinyl ethyl ether was obtained from Union Carbide Chemicals Co., bromotrichloromethane from Dow Chemical Co., dibromodifluoromethane from E. I. du Pont de Nemours and Co., 1,2-dibromo-2-chloro-1,1,2-trifluoroethane from Peninsular ChemResearch, Inc., and trifluoroethanol from Pennsalt Chemicals Corp. A typical preparation of vinyl 2,2,2-trifluoroethyl ether is described elsewhere in this section.

Description of Apparatus.—A Pyrex tube fitted with a Vycor 7910 immersion well[13] was used to carry out the addition reactions. The volume of the outer Pyrex tube with immersion well in place was 750 ml. A vent at the top of the outer tube allowed for pressure changes. The Vycor immersion well with standard taper 60/50 joint was double walled, with inlet and outlet tube to provide for air or water cooling. A type 60B A-36 quartz mercury arc lamp[13] with 2.9-in. arc length was suspended in the immersion well to provide ultraviolet irradiation. A type 7620 ballasting control[13] was used with the lamp. Stirring was provided by a magnetic stirring bar.

Addition of Bromotrichloromethane to Vinyl Ethyl Ether.—A solution of 475 g. (2.4 moles) of bromotrichloromethane and 158 g. (2.2 moles) of vinyl ethyl ether was placed in the reaction vessel described above and irradiated at 0° with stirring for 12 hr. The unchanged material was stripped from the solution at reduced pressure and the remainder was fractionated to give a cut, b.p. 51° (0.7 mm.). Although this sample decomposed too rapidly to allow analysis and proper determination of its physical properties, it was assigned the structure $CCl_3CH_2CHBrOC_2H_5$ (I) on the basis of its reduction with lithium aluminum hydride to $CCl_3CH_2CH_2OC_2H_5$ and hydrolysis to $CCl_2{=}CHCHO$.

Addition of Dibromodifluoromethane to Vinyl Ethyl Ether.—A solution of 720 g. (3.45 moles) of dibromodifluoromethane and 144 g. (2.0 moles) of vinyl ethyl ether was treated as described above for 10.5 hr. The products were processed as described above to give 362 g. (83% conversion[14]) of $CF_2BrCH_2CHBrOC_2H_5$ (II). Decomposition of the compound by elimination of hydrogen bromide would account for the high carbon–hydrogen and low bromine analysis noted in Table II. Assignment of structure was based on reduction of the compound to $CF_2BrCH_2CH_2OC_2H_5$.

Addition of 1,2-Dibromo-2-chloro-1,1,2-trifluoroethane to Vinyl Ethyl Ether.—A solution of 600 g. (2.17 moles) of $CF_2BrCFClBr$ and 144 g. (2.0 moles) of vinyl ethyl ether was treated as before for 12 hr. The products were processed as described above. A few grams of product (apparent b.p. 71° at 1 mm.) was collected when the material in the distilling flask began to decompose at 85°. The structure $CF_2BrCFClCH_2CHBrOC_2H_5$ (III) was assigned to this compound on the basis of its reduction to $CF_2BrCFClCH_2CH_2OC_2H_5$.

Addition of Bromotrichloromethane, Dibromodifluoromethane, and 1,2-Dibromo-2-chloro-1,1,2-trifluoroethane to Vinyl 2,2,2-Trifluoroethyl Ether.—A solution of 397 g. (2.0 moles) of bromotrichloromethane and 200 g. (1.59 moles) of $CH_2{=}CHOCH_2CF_3$ was irradiated at 0° for 11 hr. as previously described. Unchanged material was stripped under reduced pressure and the remainder was fractionally distilled to give 470 g. (91% conversion) of $CCl_3CH_2CHBrOCH_2CF_3$ (IV).

A solution of 560 g. (2.68 moles) of dibromodifluoromethane and 126 g. (1.0 mole) of $CH_2{=}CHOCH_2CF_3$ was treated for 13 hr. and worked up as previously described. On fractionation, 241 g. (72% conversion) of $CF_2BrCH_2CHBrOCH_2CF_3$ (V) was obtained.

A solution of 700 g. (2.54 moles) of $CF_2BrCFClBr$ and 200 g. (1.59 moles) of $CH_2{=}CHOCH_2CF_2$ was irradiated for 13 hr. and worked up as before. Fractional distillation provided 457 g. (72% conversion) of $CF_2BrCFClCH_2CHBrOCH_2CF_3$ (VI).

Reaction of I with Lithium Aluminum Hydride.—A solution of 24 g. (0.63 mole) of lithium aluminum hydride in 350 ml. of anhydrous ethyl ether was added to crude $CCl_3CH_2CHBrOC_2H_5$ (I) remaining after stripping unchanged material from the addition of excess CCl_3Br to vinyl ethyl ether (2.0 moles) by the method previously described. The ether was not isolated before action with lithium aluminum hydride owing to its tendency to decompose during distillation. The reaction was carried out at 0° and was necessarily slow owing to the extremely vigorous reaction. After the addition of lithium aluminum hydride, the mixture was stirred an additional 1.5 hr. at room temperature, followed by the addition of 200 ml. of water. The mixture was extracted with ethyl ether, separated, and dried over anhydrous calcium chloride. Low boiling material was stripped, and the remainder was fractionated to give 208 g. of material, boiling range 55–64° (15 mm.). A gas chromatogram showed that this sample consisted of three components with the higher boiling material richer in the major component. An infrared absorption peak at 6.22 μ indicated an unsaturated impurity. The sample was washed with water, separated, dried, and refractionated with a 65-cm. column packed with protruded nickel packing to give chromatographically pure $CCl_3CH_2CH_2OC_2H_5$ (VII).

An assignment of structure was based on conversion of the compound to ethyl β-ethoxypropionate by ethanolic potassium hydroxide.

In a similar manner II, III, IV, V, and VI were reduced to the corresponding α,α-dihydro ethers.

Dehydrobromination of VIII.—A slurry of 9.5 g. (0.15 mole) of powdered potassium hydroxide and 50 ml. of mineral oil was heated to 100° and 23 g. (0.113 mole) of $CF_2BrCH_2CH_2OC_2H_5$ was added dropwise with vigorous stirring. The reaction products were stripped at reduced pressure into a cold trap. The crude material then was dried over calcium chloride and fractionated to give 4.5 g. (36% conversion) of $CF_2{=}CHCH_2OC_2H_5$ (XIII). An infrared spectrum of this compound showed a very strong absorption peak in the carbon–carbon double bond region at 5.73 μ.

Dehydrobromination of XI.—A slurry of 9.5 g. (0.152 mole) of powdered potassium hydroxide in 50 ml. of mineral oil was heated to 100°, and 32 g. (0.125 mole) of $CF_2BrCH_2CH_2OCH_2CF_3$ was added dropwise with vigorous stirring. The material was handled as before to give 25 g. of crude material which was dried and distilled over a 20° boiling range. An analytical sample of $CF_2{=}CHCH_2OCH_2CF_3$ (XV) was obtained using preparative scale gas chromatography. An infrared spectrum showed a strong, sharp absorption peak assigned to the $CF_2{=}CH-$ group at 5.72 μ. Conversion was 45%. In a similar manner XXI, $CF_2BrCH_2CH(CH_3)OC_2H_5$, was converted to $CF_2{=}CHCH(CH_3)OC_2H_5$ (XXII), which exhibited the band at 5.74 μ characteristic of the $CF_2{=}CH-$ group.

Dehalogenation of IX.—A mixture of 19.5 g. (0.30 mole) of powdered zinc, 0.5 g. of zinc chloride, and 100 ml. of absolute ethanol was heated to reflux and 60 g. (0.223 mole) of $CF_2BrCFClCH_2CH_2OC_2H_5$ was added with stirring over a 1-hr. period. The mixture was stirred at reflux an additional 2 hr., and the liquid was decanted, washed with water, and separated. The wash water was extracted with ethyl ether which was combined with the organic layer, dried, and fractionated to give 17 g. of material, b.p. 72–76°, and 4.5 g. of material, b.p. 78°. A vapor phase chromatogram revealed that the former contained 50% ethyl ether and 50% $CF_2{=}CFCH_2CH_2OC_2H_5$ (XIV), while the latter fraction consisted of approximately 90% $CF_2{=}CFCH_2CH_2OC_2H_5$. The high boiling fraction was purified by passing through a preparative scale gas chromatography column to give a chromatographically pure analytical sample, whose properties are given in the tables. An infrared spectrum of XIV exhibited a strong, sharp absorption peak at 5.54 μ, characteristic of the $CF_2{=}CF-$ group.[15,16] Conversion was 35%.

In a similar manner XII, $CF_2BrCFClCH_2CH_2OCH_2CF_3$, was dehalogenated to XVI, $CF_2{=}CFCH_2CH_2OCH_2CF_3$. An infrared spectrum exhibited a distinctive $CF_2{=}CF-$ absorption peak at 5.53 μ.

Reaction of II with Ethanol.—Absolute ethanol (300 ml.) was placed in a 1-l. three-necked flask fitted with stirrer, condenser, and dropping funnel. To the stirred ethanol was added 175 g. (0.62 mole) of $CF_2BrCH_2CHBrOC_2H_5$. Addition required 1 hr. and was accompanied by evolution of heat. The solution was

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(11) Analyses by Galbraith Laboratories, Knoxville, Tenn.

(12) In most cases, no attempt was made to optimize conversions.

(13) Obtained from Englehard Hanovia, Inc., Newark, N. J.

(14) Conversion is defined as the moles of product divided by the moles theoretically obtainable.

(15) M. R. Lilyquist, Ph.D. dissertation, University of Florida, 1955.

(16) R. N. Haszeldine, *J. Chem. Soc.*, 4423 (1952).

stirred an additional 1.5 hr. at room temperature, washed thoroughly with water, and the crude product (150 g.) was separated, dried over Drierite, and fractionated to give 122 g. of material with boiling range 61–67° (14 mm.). An analytical sample was shown by a vapor phase chromatogram to contain one major and three minor components. The major component has been assigned the structure $CF_2BrCH_2CH(OC_2H_5)_2$ (XVII) on the basis of n.m.r. spectra for hydrogen and fluorine.

An infrared spectrum showed two strong, broad absorption peaks in the 9.0–9.5-μ region and no absorption in the carbonyl or carbon–carbon double bond regions. Conversion was approximately 75%.

In a similar manner III, $CF_2BrCFClCH_2CHBrOC_2H_5$, reacted with ethanol to give XVIII, $CF_2BrCFClCH_2CH(OC_2H_5)_2$. N.m.r. spectra for hydrogen and fluorine were consistent with the assigned structure.

Reaction of V with Trifluoroethanol.—Trifluoroethanol (100 ml.) and 58 g. (0.17 mole) of $CF_2BrCH_2CHBrOCH_2CF_3$ were combined and stirred at room temperature with slow evolution of heat for 16 hr. and at 75° for 6 hr. White fumes were evolved and the flask was etched, indicating elimination of hydrogen fluoride. After work-up and fractionation of the crude material, a center cut showed both carbonyl and carbon–carbon double bond absorption in its infrared spectrum.

The desired acetal was successfully prepared in the following manner. Trifluoroethanol (200 ml.) and 84 g. (0.25 mole) of the subject ether were combined and stirred for 48 hr. at room temperature. During this period, the flask was swept with nitrogen and was backed by a cold trap. The solution was washed with water, and the crude material (64 g.) was dried over Drierite and fractionated to give 17.5 g. (21% conversion) of $CF_2BrCH_2CH(OCH_2CF_3)_2$ (XIX).

An infrared spectrum showed a strong, broad peak from 8.9-9.3 μ. No carbonyl or carbon–carbon double bond absorption was observed.

Trifluoroethanol also reacted with VI, $CF_2BrCFClCH_2CHBrOCH_2CF_3$, to give the corresponding acetal XX.

Reaction of II with Methylmagnesium Bromide.—$CF_2BrCH_2CHBrOC_2H_5$ was prepared from 2.84 moles of vinyl ethyl ether and excess CF_2Br_2 and was used without distillation. The crude ether was placed in a three-necked flask fitted with an addition funnel, stirrer, and condenser and was cooled to 0°. Two moles of methylmagnesium bromide in ethyl ether was then added dropwise over a 1-hr. period. The reaction was very vigorous and necessitated continued cooling. After addition was complete, the mixture was stirred for 1 hr. at 0° and for 4 hr. at room temperature. The mixture was filtered, and the organic layer was separated, dried, and fractionated to give 80 g. (19% conversion based on the vinyl ethyl ether) of $CF_2BrCH_2CH(CH_3)OC_2H_5$ (XXI). An infrared spectrum showed no carbonyl or carbon–carbon double bond absorption.

Reaction of Trifluoroethanol with Methylacetylene.—An autoclave was charged with 200 g. (2.0 moles) of trifluoroethanol, 80 g. (2.0 moles) of methylacetylene, and 10 g. of potassium hydroxide and was heated at 225° for 18 hr. Unchanged methylacetylene (65 g.) was bled into a trap, and the remainder was fractionated to give 17 g. of material, b.p. 57–72°. A vapor phase chromatogram showed that this fraction consisted of three components, the major one being trifluoroethanol. The material was washed thoroughly with water, and the organic layer was separated, dried, and fractionated to give 1 g. of material, identified as $(CH_3)_2C(OCH_2CF_3)_2$.

N.m.r. spectra of hydrogen and fluorine were consistent with the proposed structure. Conversion, based on chromatographic analysis of the 57–72° cut, was approximately 10%.

Reaction of $CCl_3CH_2CH_2OC_2H_5$ with Ethanolic Potassium Hydroxide.—A solution of 80 g. (1.2 moles) of potassium hydroxide in 200 ml. of 95% ethanol was heated to reflux followed by the dropwise addition of 70 g. (0.37 mole) of $CCl_3CH_2CH_2OC_2H_5$. The mixture was stirred at reflux for 20 hr., decanted, and washed with water. The insoluble organic layer was separated, dried, and fractionated to give a single product, b.p. 66° (17 mm.); $n^{23}\mathrm{D}$ 1.4059; d^{23} 0.960; $\mathrm{MR_D}$ calcd. for $C_2H_5OOCCH_2CH_2OC_2H_5$, 37.82; $\mathrm{MR_D}$ found, 37.48. Physical constants reported for ethyl β-ethoxy propionate are b.p. 67° (17 mm.), $n^{25}\mathrm{D}$ 1.4070, d^{25} 0.949.

An infrared spectrogram was identical with that of an authentic sample.

Preparation of Vinyl 2,2,2-Trifluoroethyl Ether.—A solution of 50 g. of potassium hydroxide in 300 g. (3.0 moles) of trifluoroethanol was sealed in a 1.4-l. stainless steel autoclave, which was then charged with acetylene to a pressure of 300 p.s.i.g. The autoclave was heated with rocking at 135° for 5 hr. and at 150° for 5 hr. Distillation of the product mixture gave the desired ether, b.p. 40–42°, in approximately 90% conversion.

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Fluoro Compounds. II.[1] Reactions and Nuclear Magnetic Resonance Studies of Some Fluorobromo Esters

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Fluorobromination of several α,β-unsaturated esters has been carried out using hydrofluoric acid and N-bromoacetamide. In each case the fluorine atom appeared on the β-carbon and was more easily lost than the α-bromine substituent in reaction with potassium phthalimide. Proton and fluorine nuclear magnetic resonance studies were made on several fluorobromo compounds. The fluorobromo compound derived from dialkyl maleate has been assigned the *threo* configuration; the corresponding fumarate derivative has been assigned the *erythro* configuration. At higher temperatures these two fluorobromo derivatives undergo interconversion. Electron paramagnetic resonance data and deuterium-exchange experiments do not indicate either a free radical or a carbanion intermediate for this interconversion.

In recent years there has been considerable interest in fluorinated compounds, particularly as potential antimetabolites. Some time ago we undertook a project on the synthesis of α-fluoro-β-alanine,[2,3] fluoroaspartic acid, and other fluoroamino acids. A possible intermediate in the synthesis of α-fluoro-β-alanine appeared to be β-bromo-α-fluoropropionic ester. Henne and Fox[4] tentatively assigned such a structure for the product obtained from ethyl dibromopropionate by halogen

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[1] Part I: A. K. Bose, K. G. Das, and T. M. Jacob, *Chem. Ind.* (London), 452 (1963).

[2] Recently isolated as a metabolic product of 5-fluorouracil: C. Heidelberger and K. L. Mukherjee, *J. Biol. Chem.*, **235**, 433 (1960).

[3] Synthesized by E. D. Bergmann and S. Cohen, *J. Chem. Soc.*, 4669 (1961).

[4] A. L. Henne and C. J. Fox, *J. Am. Chem. Soc.*, **76**, 479 (1954)