boxy-3-nitrophenylphosphonic acid, which was purified by dissolution in ether, treatment of this solution with charcoal, and evaporation of the clarified solution.

3-Carboxy-5-nitrophenylphosphonic acid. A solution of 50 g. of *m*-carboxyphenylphosphonic acid in 270 ml. of anhydrous nitric acid (Baker and Adamson) was gently heated for about 3 hr. until approximately two thirds of the nitric acid was distilled. On cooling the reaction mixture to −25°, crystals were obtained which were washed with 8 ml. of cold water and then dried *in vacuo* at 100°.

4-Carboxy-2-nitrophenylphosphonic acid. *p*-Carboxyphenylphosphonic acid (40.4 g.) was nitrated with 200 ml. of anhydrous nitric acid by the procedure described above for the *meta* isomer. On cooling the reaction mixture, 39.6 g. (80%) of nitrated material, m.p. 191–200°, was obtained.

Anal. Calcd. for $C_7H_6NO_7P$: Neut. equiv., 82.4. Found: Neut. equiv., 83.5.

This material was dissolved in a mixture of 65 ml. of absolute ethanol and 65 ml. of carbon tetrachloride, and the solvents slowly removed by distillation. The residue, which consisted of crude isomeric carbethoxynitrophenylphosphonic acids, was dissolved in 200 ml. of 10% aqueous ammonia and mixed with 640 ml. of $0.27M$ magnesium chloride solution. The resulting solution was boiled for at least 30 min. in order to precipitate the magnesium salt of the 3,4 isomer. The precipitate, after being washed with hot water and dried *in vacuo*, weighed 10.7 g. The filtrate from the magnesium salt was made alkaline (pH > 10) with 30 ml. of 20% sodium hydroxide solution, filtered and then aerated to remove ammonia. The resulting solution was stirred for 30 min. with 350 g. of Dowex-50 (which changed the pH of the solution to 0.6) and then passed through a Dowex-50 column. The residue obtained by evaporating this solution to dryness was recrystallized from $9N$ hydrochloric acid to yield pure 4-carboxy-2-nitrophenylphosphonic acid. Obviously, the ester was cleaved to the free carboxy group during the course of the separation procedure. Mixed melting point of the pure acid with authentic 4-carboxy-3-nitrophenylphosphonic acid (the preparation of which is described above) was 191–198° with decomposition.

2-Carboxy-3-nitrophenylphosphonic acid. 6-Nitroanthranilic acid[15] (35 g.) was converted to the corresponding diazonium fluoborate in 73% yield. The dried salt was suspended in ethyl acetate and treated with phosphorus trichloride and cuprous bromide in the usual manner.[8a] After the steam distillation, the residual liquid in the distilling flask was filtered from tarry material, all of which was alkali-insoluble, and the filtrate was evaporated to 125 ml. The crystalline solid obtained on cooling was dissolved in aqueous potassium hydroxide (30%), and the pH adjusted to 7.6. The resulting solution was treated with charcoal and then acidified to Congo Red. The precipitate obtained was dried and extracted with ether in a Soxhlet apparatus in order to remove unphosphonated organic acids. The ether insoluble residue was dissolved in warm water and passed through a Dowex-50 column in the hydrogen ion form. The effluent was taken to dryness, and the solid recrystallized from $6N$ hydrochloric acid to yield pure 2-carboxy-3-nitrophenylphosphonic acid. A second crop was obtained by evaporating the original filtrate from 125 ml. to 15 ml. The solid thus obtained was purified in the same manner as the main crop.

Bis(2-carboxy-5-nitrophenyl)phosphinic acid. Bis(5-nitro-2-tolyl)phosphinic acid (16.8 g.), dissolved in a mixture of 75 ml. of pyridine and 75 ml. of water, was oxidized with 125 g. of potassium permanganate. After steam distillation, the reaction mixture was filtered, decolorized with charcoal, and then added slowly, with good stirring, to 150 ml. of $6N$ hydrochloric acid. The phosphinic acid, which separated on cooling, was removed by filtration and recrystallized from 90% aqueous acetone.

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(15) R. Kahn, *Ber.*, **35**, 3857 (1902); see also M. T. Bogert and V. J. Chambers, *J. Am. Chem. Soc.*, **27**, 649 (1905).

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF COLORADO]

Stepwise Chlorination of 1,1,2-Trifluoro-2-chloroethyl *n*-Propyl Ether[1]

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The stepwise photochemical chlorination of 1,1,2-trifluoro-2-chloroethyl *n*-propyl ether was carried out and the products were isolated and identified.

Previous papers,[2–4] described the methods for the preparation of several fluoroalkyl ethers and of their chlorinated derivatives.

The present paper reports a study of the stepwise photochemical chlorination of 1,1,2-trifluoro-2-chloroethyl *n*-propyl ether in the liquid phase.

The determination of the ratios of the monochlorinated product shows the following weight ratios of the isomers.

$$\text{II:III:IV} = 1.6:1.0:1.5$$

It is interesting to note that the chlorination[5] of I or of II, III, and IV individually did not yield a separable entity of the α,α-dichloro isomer (X)

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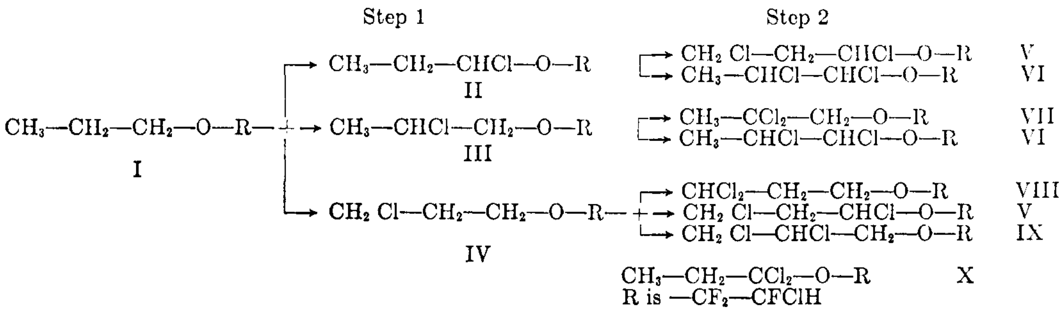
(1) This paper represents parts of a thesis submitted by G. Pavlov to the Graduate School, University of Colorado, in partial fulfillment of the requirements for the Ph.D. degree, June 1958, and parts from the Master's thesis of F. M. Hammock, submitted to the Graduate School, University of Colorado, August 1959, whose current address is U. S. Air Force Academy, Colorado Springs, Colo.

(2) J. D. Park, D. K. Vail, K. R. Lea, and J. R. Lacher, *J. Am. Chem. Soc.*, **70**, 1550–52 (1948).

(3) J. D. Park, D. M. Griffin, and J. R. Lacher, *J. Am. Chem. Soc.*, **74**, 2292 (1952).

(4) J. D. Park, Buck Stricklin, and J. R. Lacher, *J. Am. Chem. Soc.*, **76**, 1387 (1954).

(5) J. D. Park, D. R. Wolf, M. Shahab, and J. R. Lacher, *J. Org. Chem.*, **23**, 1474 (1958).



although the other five of the six possible dichloro isomers were isolated and identified.

The proofs of structure of the various mono- and dichlorinated ethers were arrived at either by a method of unequivocal synthesis or by a process of elimination. As indicated by our previous studies,[3,4] the directive effect was such that the replacement of the hydrogen atoms took place preferentially in the unfluorinated portion of the ether.

The tendency of chlorine to attack the hydrogen atoms in the alkyl groups in preference to the β-hydrogen atom in the fluorochloro moiety is not surprising and has been plausibly explained in previous papers[3,6] insofar as chlorination of 1,1,2,2-tetrafluoroethyl ethyl ether and of 1,1,2-trifluoro-2-chloroethyl ethyl ether are concerned. It is surprising, however, that the chlorination of 1,1,2-trifluoro-2-chloroethyl *n*-propyl ether does not yield any α,α-dichloro ether. No logical explanation for this behavior seems evident at this time.

Compounds III and IV were synthesized from $CH_3—CHOH—CH_2—O—R$ and $CH_2(OH)—(CH_2)_2—O—R$, respectively, and the structure of II arrived at by a process of elimination. All these fractions were subjected to gas chromatography and infrared analysis.

Compound IX was prepared by the addition of chlorine to the β,γ-unsaturated ether ($CH_2{=}CH—CH_2—O—R$) obtained from allyl alcohol and trifluorochloroethylene. Compound VI was obtained from the dehydrochlorination of II, followed by chlorination of the resulting olefin.

Compound VII was obtained from the chlorination of III. Since the resulting dichloride was neither VI nor IX (both of which are known), it was assigned the only remaining plausible dichloride structure VII ($CH_3—CCl_2—CH_2—O—R$).

The chlorination of II yielded a dichloride which was not VI, but could be either X or V. This was designated as being V on the following bases: The dehydrochlorination of VI resulted in the formation of $CH_3—CH{=}CCl—O—R$, whose structure was confirmed by ozonolysis.

If II produced X upon chlorination, X upon dehydrochlorination would result in the formation of $CH_3—CH{=}CCl—O—R$ (XI) as the only possible product which would be identical with that obtained from the dehydrochlorination of VI. This was not the case; hence, it was deduced that V was the only possible structure that could be assigned since it was not VI, which is known.

The chlorination of IV resulted in 70% conversion to VIII, 20% conversion to V, and 10% to IX.

The structure of VIII was deduced from its infrared spectrum, which is different from that of V and IX (both known).

The dehydrochlorination of IX resulted in the formation of $CH_2Cl—CH{=}CH—O—R$ (XII) with the elimination of the acidic *alpha* hydrogen atom. This was confirmed by ozonolysis with the resultant identification of $CH_2Cl—CHO$.

The dehydrochlorination of V resulted in the formation of $CH_2{=}CH—CHCl—O—R$ (XIII) as the major product. The dehydrochlorination of IX resulted in the isolation of XII whose spectrum was identical with the product obtained in the dehydrochlorination of $CH_2Cl—CHClCH_2—O—R$ (IX) (from the addition of $CH_2{=}CH—CH_2—O—R$ and chlorine).

The preparation and identification of the trichloro derivatives increase in complexity due to the large number of isomers possible. Two of these isomers were prepared.

1′,2′,3′-Trichloro-*n*-propyl 1,1,2-trifluoro-2-chloroethyl ether, XIV, was synthesized by the addition of chlorine to XII or XIII.

The chlorination of IX did not give XIV. The third chlorine substitution therefore, prefers the *beta* or the *gamma* position in preference to the *alpha* position.

An attempt to prepare XIII by the reaction of *N*-chlorosuccinimide on 1,1,2-trifluoro-2-chloroethyl allyl ether was not successful.

The yields in the dehydrochlorination of II were found to be very low, due most probably to the difficulty with which the *alpha* chlorine atom takes part in elimination reactions.

The acidity of the *alpha* hydrogen is confirmed by the ease of dehydrohalogenation of VI to $CH_3—CH{=}CCl—O—R$ (XI). This latter product upon ozonolysis yielded acetaldehyde.

EXPERIMENTAL

1,1,2-Trifluoro-2-chloroethyl n-propyl ether. This ether (I) was prepared by the base-catalyzed reaction of *n*-propyl

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(6) A. L. Henne, J. B. Hinkamp, and W. J. Zimmerschield, *J. Am. Chem. Soc.*, **67**, 1906 (1945).

TABLE I. PHYSICAL PROPERTIES OF SOME FLUOROCHLORO ETHERS

	Compound[a]	B.P.	Mm.	n_D^{25}	d_4^{25}	MR[b]	MR[c]	Carbon, %		Hydrogen, %		Chlorine, %		Fluorine, %	
								Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
II	$CH_3-CH_2-CHCl-O-R$	37-39	8	1.3880	1.352	36.67	36.50	28.41	28.45	3.32	3.48			27.01	27.25
		53.5°	18												
III	$CH_3-CHCl-CH_2-O-R$	69–70	34	1.3875	1.366	36.67	36.56	28.41	28.52	3.32	3.52	33.60	33.51		
IV	$CH_2Cl-CH_2-CH_2-O-R$	64.5	13.8	1.3935	1.375	36.67	36.67	28.41	28.45	3.32	3.61	33.60	33.82		
V	$CH_2Cl-CH_2-CHCl-O-R$	74–75	10	1.4170	1.477	41.32	41.78	24.44	24.79	2.44	2.74	43.38	43.48		
VI	$CH_3-CHCl-CHCl-O-R$	63–45	10	1.4082	1.440	41.32	41.67	24.44	24.69	2.41	2.63	43.38	43.48		
VII	$CH_3-CCl_2-CH_2-O-R$	90	11	1.4061	1.466	41.32	41.32	24.44	24.53	2.44	2.57	43.38	43.33		
VIII	$CHCl_2-CH_2-CH_2-O-R$	83–85	14	1.4136	1.487	41.32	41.38	24.44	24.68	2.44	2.61	43.38	43.32		
IX	$CH_2Cl-CHCl-CH_2-O-R$	83-84	14	1.4188	1.497	41.32	41.39	24.44	24.47					23.22	22.27
X	$CH_3-CCl_2-CH_2-O-R$	...	...	...	...	...	...	...	...	...	...	...	...		
XI	$CH_3-CH=CCl-O-R$	57–59	40	1.3925	1.380	36.44	36.13	28 67	28.70	2.39	2.58	33.87	33.67		
XII	$CH_2Cl-CH=CH-O-R$	91–92	155	1.3978	1.396	36.44	36.12	28.67	29.2	2.39	2.61	33.87	34.02		
XIII	$CH_2=CH-CHCl-O-R$	85–87	100	1.3989	1.387	36.44	36.38	28.67	29.0	2.39	2.64	33.87	33.78		
XIV	$CH_2Cl-CHCl-CHCl-O-R$	74–75	5	1.4296	1.565	45.83	46.17	21.41	21.58	1.79	2.0	50.75	50.50		
XV	$CH_3-CH=CH-O-R$	32–33	51	1.3674	1.251	31.33	31.33	34.40	34.63					32.65	32.82
XVI	$CH_2=CH=CH_2-O-R$	58	121	1.3681	1.251	31.33	31.42	34.40	34.73					32.65	32.73
XVII	$CH_3-CH(OCOC_6H_5)-CH_2-O-R$	135–137	8	1.4736^{20}	1.31^{20}	62.66	62.77	48.60	48.79	4.27	4.21	12.01	12.24		
XVIII	$CH_3-CHOH-CH_2-O-R$	59	3	1.3912^{20}	1.354^{20}	33.58	33.78	31.00	30.9	4.15	4.02	18.50	18.68		

[a] R = $-CF_2-CHFCl$. [b] Molecular Refractions calculated by adding the customary increments of the pertinent elements $AR_F^{1.1}$. [c] Molecular refractions calculated by the Lorentz-Lorentz equation.

alcohol with $CF_2=CFCl$ according to the method of Park *et al.*[2]

Chlorination of I. Into a reaction vessel equipped with a bubbler and illuminated with two 300-watt incandescent lamps was placed 239 g. of I (1.35 moles) and for a period of 6 hr., chlorine was bubbled through the ether.The chloroether was removed, washed, and dried. Distillation yielded three fractions identified as II, III, and IV.

In order to assure that chlorination had not taken place in the fluoroalkyl portion of the ether ($R-O-CF_2CFClH$), small portions of the chlorinated ethers II, III, and IV were subjected to cleavage with aluminum trichloride according to the procedure of Park *et al.*[4] In each case, *N*-phenyl-α-chloro-α-fluoroacetamide (m.p. 86–87°) was isolated indicating that chlorination had taken place in the hydrocarbon portion of the ether and not in the fluoroalkyl portion of the ether.

Identification of II. About 21 g. (0.1 mole) of II and 5 ml. of absolute methanol were placed in a 500-ml. three-neck flask and subjected to the action of methanolic potassium hydroxide. Separation and distillation of the reaction product yielded 6 g. of XV. The infrared spectrum of the chromatographed sample was identical with that obtained from the dechlorination of VI and different from that of XVI obtained either from the dechlorination of IX or from the addition of allyl alcohol to trifluorochloroethylene.

Chlorination of II. Chlorine (14 g., 0.39 mole) in the presence of actinic light was bubbled through 128 g. of the α-monochloroether (0.61 mole). Hydrogen chloride was evolved. The resulting dichlorinated compounds were separated, washed with water until neutral to litmus, dried, and distilled. Compounds V and VI were obtained in the ratio of 1.5 to 1.

Chlorination of III. Chlorine (2.96 g., 0.02 mole) was bubbled through a solution of 5 g. of the β-chloroether (0.02 mole) and 6 g. of carbon tetrachloride in the presence of incandescent light. After washing and drying, the neutral compound was subjected directly to gas chromatography for separation. The main product CH_3-CCl_2-CH_2-O-R was separated from CH_3-CHCl-CHCl-O-R and found to be in the ratio of 4 to 1.

Chlorination of IV. Chlorine (7 g., 0.1 mole) was bubbled through the γ-monochloro ether (21 g., 0.1 mole). The product was washed, dried, and separated by means of gas chromatography. This indicated three products: V, VIII, and IX.

Chlorination of IX. Compound IX (62.5 g., 0.254 mole) was subjected to the action of chlorine (14 g., 0.195 mole). The resulting compound washed with water, dried, and distilled, yielded 20 g. of $C_3H_4Cl_3$-O-CF_2-CHFCl. The infrared spectrogram was different from that of XIV. It was therefore assumed that this compound was either the β,β,γ- or β,γ,γ-trichloro isomer.

Cleavage of the above trichlorinated compound with aluminum chloride showed the absence of any chlorine replacement of the hydrogen atom in the fluoroalkyl portion of the ether. This was substantiated by the formation of *N*-phenyl-α-chloro-α-fluoroacetamide, m.p. 86–87°, according to a previously described procedure.[4]

Dehydrochlorination of VI *to* XI. Into a three-neck 100-ml. flask equipped with a stirrer, dropping funnel, and reflux condenser was placed 18.5 g. (0.075 mole) of VI. To this was added 10 g. of potassium hydroxide dissolved in 40 ml. of absolute methanol under reflux conditions. The reaction products were washed with water until neutral and distilled. Eight grams of XI was obtained.

The proof of structure was obtained by means of ozonolysis with the isolation of the 2,4-dinitrophenylhydrazine derivative of acetaldehyde, m.p. 167–169° which showed no depression in a mixed melting point with an authentic sample. From this, the compound was deduced to be $CH_3-CH=CCl-O-CF_2-CHFCl$.

Dehydrochlorination of IX *to* XII. The β,γ-dichloro ether (80 g., 0.33 mole) was mixed with 15 ml. of absolute methanol and placed in an apparatus as outlined in the chlorination of I. Forty-one grams of potassium hydroxide (0.73 mole) dissolved in 160 ml. of absolute methanol was added slowly to the refluxing ether and continued refluxing for 1 hr. The product was washed with water until neutral to litmus and distilled. The structure, CH_2Cl—CH=CH—O—CF_2—CHFCl was proven by ozonolysis[3] in which chloroacetic acid was isolated as a 2,4-dinitrophenylhydrazone, m.p. 149–150°; mixed melting with an authentic sample showed no depression.

Dehydrochlorination of V *to* XIII. About 27 g. (0.11 mole) of the α,γ-dichloro ether and 12 g. (0.21 mole) of potassium hydroxide dissolved in 40 ml. of absolute methanol were refluxed for 3 hr., then cooled, washed with water until neutral, and distilled. Comparison of the physical properties and infrared spectrograms of this compound with that of XII showed them to be different. Hence, by elimination, structure XIII (CH_2=CH—CHCl—O—R) is assigned to the product obtained by dehydrochlorination of V.

Dechlorination of VI *to* XV. Into a 150-ml. three-neck flask equipped with a stirrer, reflux condenser, and a dropping funnel was placed 3.8 g. (0.06 mole) of powdered zinc mixed with 25 ml. of reagent grade 1-pentanol. The stirred mixture was brought to reflux and 11.5 g. (0.05 mole) of the α,β-dichloro ether was added slowly. It was necessary to apply heat throughout the reaction.

The reaction mixture was filtered, washed with water, dried, and distilled at reduced pressure. Ozonolysis of the material and conversion of the volatile aldehyde to 2,4-dinitrophenylhydrazone[4] gave an orange solid. The recrystallization from hot ethanol–ethyl acetate gave a solid whose m.p. was 168°. Mixed melting point determination with authentic 2,4-dinitrophenylhydrazone showed no depression. On the above basis, the unsaturated ether was assigned structure XV, (CH_3—CH=CH—O—CF_2—CHFCl).

1,1,2-Trifluoro-2-chloroethyl allyl ether. The base-catalyzed addition of allyl alcohol to trifluorochloroethylene was carried out in an apparatus essentially as described above for the chlorination of I. The olefin (230 g., 1.97 moles) was bubbled through the allyl alcohol (112 g., 2 moles) into which potassium hydroxide had been dissolved (35 g., 0.62 mole). The reaction was exothermic and took about 6 hr. for completion. The product was washed with water until neutral to litmus, dried, and distilled at reduced pressure. The position of the double bond was shown to be in the terminal position by ozonolysis. The infrared spectrogram was compared to the one for XV and found to be different. On this basis the structure was ascertained to be CH_2=CH—CH_2—O—CF_2—CHFCl (XVI).

Preparation of 1,1,2-trifluoro-2-chloroethyl-2'-hydroxyl n-propyl ether. The 1,2-propanediol (230 g., 3 moles) together with 85 g. of potassium hydroxide (1.5 moles) was placed in a 500-ml. Parr hydrogenation bomb. Trifluorochloroethylene (350 g., 3 moles) was then charged into the bomb and rocked at room temperature for 12 hr. The product was washed with water until neutral to litmus and dried. The crude product (200 g.) was placed in a 1-l. flask equipped with a reflux condenser together with 150 g. of benzoyl chloride (1.09 moles) and 120 ml. of pyridine. At first the reaction was exothermic, but later required heating for 3 hr. This product was washed with water followed by a 10% hydroxide solution wash, then washed with water until neutral to litmus, dried, and distilled at reduced pressure. The desired ether-ester product (XVII) weighed 110 g. Saponification was carried out at reflux with 110 g. of the ester (0.37 mole) and 46 g. of potassium hydroxide (0.82 mole) dissolved in 330 ml. of 95% ethanol. The reaction was exothermic. The product was added to 320 ml. of water and extracted with ether. The solvent was removed on a steam bath. Thirty grams of the desired ether-alcohol, CH_3CHOH—CH_2—O—CF_2—CHFCl (XVIII), was collected.

Synthesis of 1,1,2-trifluoro-2-chloroethyl-2'-chloro n-propyl ether. The ether-alcohol XVIII (27 g., 0.14 mole) was added dropwise to 44 g. of phosphorus pentachloride (0.14 mole + 50% excess) in a 100-ml. flask equipped with a stirrer, dropping funnel, and reflux condenser attached to a trap and water bubbler. The reaction was exothermic as hydrogen chloride was removed. The product was poured into water, then washed with 10% sodium bicarbonate solution until neutral to litmus, then dried and distilled. Physical properties and infrared spectrograms of 40 g. of product (CH_3—CHCl—CH_2—O—R) were obtained and found to be identical with that of III.

Preparation of 1,1,2-trifluorochloro ethyl-3'-hydroxy n-propyl ether. This compound was prepared according to the method of Park, *et al.*[7] The fraction boiling at 129° (3 mm.) was collected as the desired benzoate, n_D^{25} 1.4886, d^{25} 1.363. (Lit.[6] d_4^{20} 1.313).

The benzoate was saponified with ethanolic potassium hydroxide as described in the literature.[6]

Fractionation yielded a center cut of 20 g. of the desired alcohol-ether b.p. 58–59° (3 mm.), n_D^{25} 1.3826, d_4^{25} 1.354). The infrared spectrum of this compound was identical with that of the literature.[6]

Preparation of 1,1,2-trifluoro-2-chloro ethyl-3'-chloro n-propyl ether. About 33 g. of CH_2—(OH)—CH_2—CH_2—O—CF_2—CHFCl (0.17 mole) was added slowly to 53.5 g. of phosphorus pentachloride (0.17 mole + 50% excess). The reaction was quite exothermic. The product was then washed with sodium bicarbonate until neutral to litmus, dried, and distilled. This compound, CH_2ClCH_2—CH_2—O—R was identical with IV in all respects.

Chlorination of XV. Chlorine (9.5 g., 0.13 mole) was passed through 22.5 g., of XV (0.13 mole) for 2 hr. The reaction vessel was wrapped with aluminum foil to minimize the effect of light. It was necessary to cool the exothermic reaction. The reaction resulted in a 93% yield of the desired product, VI (CH_3—CHCl—CHCl—O—R).

Chlorination of 1,1,2-trifluoro-2-chloroethylallyl ether. Chlorine was passed through 147 g. of 1,1,2-trifluoro-2-chloroethyl allyl ether (0.84 mole). The resulting product was identical with IX.

Chlorination of XII *to* XIV. Chlorine was slowly passed through 23 g. of the olefin XII (0.11 mole). After 7.5 g. of chlorine (0.10 mole) was absorbed, the distilled product CH_2Cl—CHCl—CHCl—O—R was found to be identical with XIV.

Attempted preparation of 1,1,2-trifluoro-2-chloroethyl 1'-chloroallyl ether (XIII). The olefin XVI (63 g.) was allowed to react with 30 g. of *N*-chlorosuccinimide in 65 g. of carbon tetrachloride at reflux temperature for 30 hr. No allylic chlorination product was isolable.

Acknowledgment. We wish to express our appreciation to the Minnesota Mining and Manufacturing Co., St. Paul, Minn.; and to The Monsanto Chemical Co., St. Louis, Mo., for their support of this work.

BOULDER, COLO.

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(7) J. D. Park, J. Abramo, and J. R. Lacher, *J. Org. Chem.*, **23**, 1394 (1958).