57, 64 c.p.s., and 52, 59, 66 c.p.s., $J_1 = J_2 = 7.0$ c.p.s., weight $\sim$3.3), *t*-butyl (two peaks, 78 and 80 c.p.s.), =CH— (four peaks, 339, 346, 353, 360 c.p.s., due to two nearly superimposed triplets, $J = 7.0$ c.p.s., weight $\sim$1.0), CH_2 (split quintet 113–147, $J =$ 7.0 c.p.s., weight $\sim$2.2).

Anal. Calcd. for $C_8H_{15}ClS$: C, 53.76; H, 8.46. Found: C, 53.39; H, 8.43.

These data are consistent with the assigned structure *cis-trans* 1-*t*-butylmercapto-1-chlorobutene (VII). The butene VII (0.8 g.) was oxidized to the sulfone (0.3 g., oil), *cis,trans*-1-*t*-butylsulfonyl-1-chlorobutene-1, which showed ν^{neat} C=C (1590–1605 cm.$^{-1}$), no CH=CH_2 (absence of absorption near 985 and 1830 cm.$^{-1}$); n.m.r. spectrum[9] (20% in CCl_4): CH_3 (two triplets, 53, 61, 68 c.p.s. and 56, 67, 71 c.p.s.), *t*-butyl (split singlet, 79 c.p.s.), =CH− (five peaks, probably two triplets at 367, 375, 383 c.p.s. and 383, 391, and 399 c.p.s., weight $\sim$1.0), CH_2 (multiplet 117–165 c.p.s., weight $\sim$1.8).

Anal. Calcd. for $C_8H_{15}ClO_2S$: C, 45.49; H, 7.18. Found: C, 45.60; H, 7.04.

4-Phenylmercaptobutene-1 (XXII).—This sulfide (b.p. 72–74° at 1.4 mm., $n^{25}\text{D}$ 1.5621) was prepared (86% yield) from 1-bromobutene-3[24] and thiophenol as described[22] for the preparation of allyl *t*-butyl sulfide. This sulfide (XXII) showed ν^{neat} C=C (1635 cm.$^{-1}$), −CH=CH_2 (905, 983, and 1840 cm.$^{-1}$).

Anal. Calcd. for $C_{10}H_{12}S$: C, 73.11; H, 7.37. Found: C, 73.30; H, 7.61.

1,1-Dichloro-2-(2-phenylmercaptoethyl)cyclopropane (XXIII).—The reaction of XXII (16.4 g., 0.10 mole) with ethyl trichloroacetate (28.7 g., 0.15 mole) and commercial sodium methoxide (8.7 g., 0.16 mole), as described for olefins Ia–c, gave recovered sulfide XXII (8.3 g., 50%), the cyclopropane XXIII (impure, b.p. 110–130° at 0.1–0.6 mm., $n^{26}\text{D}$ 1.5771, 4.2 g., 17% yield), and residual tar (5.6 g.).

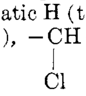
The cyclopropane XIII, after redistillation (b.p. 85–87° at 0.01 mm., $n^{26}\text{D}$ 1.5754) showed weak absorption at ν^{neat} 1635, 910, and 985 cm.$^{-1}$ assigned to olefin impurity. The cyclopropane XXIII (1.7 g., 0.006 mole) was characterized by conversion to 1,1-dichloro-2-(2-phenylsulfonylethyl)cyclopropane by oxidation with hydrogen peroxide in acetic acid. The crude oily sulfone was crystallized by cooling its solution in ethanol to Dry Ice temperature. The solid sulfone was then recrystallized from ethanol–petroleum ether (30–60°) and melted at 64.5–65.5° (0.7 g., 36% yield from XXIII).

1,1-Dichloro-2-(2-phenylsulfonylethyl)cyclopropane showed absence of olefin in its infrared and n.m.r. spectra. The n.m.r. spectrum[9] (20% in $DCCl_3$) showed aromatic H (complex, 438–453 c.p.s., weight $\sim$4.9), SCH_2 (complex, 177–197 c.p.s., weight $\sim$2.0), other H (complex, 57–126 c.p.s., weight $\sim$5.2).

Anal. Calcd. for $C_{11}H_{12}Cl_2O_2S$: C, 47.32; H, 4.33. Found: C, 47.40; H, 4.48.

The reaction XXII with dichlorocarbene precursors was carried out as described above; however, the reaction time was increased to 66 hr. Essentially identical results were obtained.

Reaction of *n*-Butyl Phenyl Sulfide with Dichlorocarbene.—The reaction of ethyl trichloroacetate (38.0 g., 0.20 mole), commercial sodium methoxide (10.8 g., 0.20 mole), and *n*-butyl phenyl sulfide (20.0 g., 0.12 mole) in olefin-free petroleum ether (90 ml., b.p. 30–60°) was carried out as described for Ia. Distillation of the residue gave recovered *n*-butyl phenyl sulfide (15.0 g., 75%). A small amount of higher boiling material (2.1 g., $n^{26}\text{D}$ 1.5596) was obtained which was not obtained pure by fractionation (b.p. 75–80° at 0.05 mm., $n^{22}\text{D}$ 1.5656). This product (2.1 g.) was oxidized with hydrogen peroxide in acetic acid and the crude sulfone was dissolved in ethanol and cooled in Dry Ice–acetone. The crude solid sulfone (0.6 g., m.p. 85–91°) was recrystallized from alcohol–petroleum ether (b.p. 30–60°); the product melted at 100–102°.

The sulfone showed $\nu^{CCl_4-CS_2}$ $-SO_2-$ (1335–1345 and 1155 cm.$^{-1}$); n.m.r. spectrum[9] (20% in $DCCl_3$): CH_3 (triplet, 47, 53, and 60 c.p.s., $J = 6.7$ c.p.s., weight $\sim$3.2), aromatic H (two split peaks, 419–429 and 429–457 c.p.s., weight $\sim$5.1),  $-\underset{\underset{\text{Cl}}{|}}{\text{CH}}-$ (four peaks of equal intensity, probably two doublets, 218, 220, 224, and 227 c.p.s., weight $\sim$1.0), CH_2 (multiplet, 75–111 c.p.s., weight $\sim$2.1), CH_2 (multiplet, 111–147 c.p.s., weight $\sim$2.0).

Anal. Calcd. for $C_{11}H_{13}Cl_3O_2S$: C, 41.85; H, 4.15; Cl, 33.70; S, 10.16. Found: C, 41.80; H, 4.12; Cl, 33.63; S, 10.07.

This product has not been identified but is tentatively assigned the structure 1-phenylsulfonyl-1,1,2 trichloropentane (XXIV).

The reaction of cyclohexene (8.2 g., 0.10 mole), ethyl trichloroacetate (24.8 g., 0.13 mole), commercal sodium methoxide (7.2 g., 0.13 mole), and *n*-butyl phenyl sulfide (0–0.10 mole) was carried out as described for Ia. The results are described in Table I. Impure **7,7-dichloronorcarane** was collected, $\sim$b.p. 85–88° at 20 mm., $n^{24}\text{D}$ 1.4992, and showed ester carbonyl in the infrared spectrum. The material was purified by washing with two portions of concentrated sulfuric acid and with two portions of water.

The **carbon tetrachloride** and **recovered cyclohexene** were collected with solvent petroleum ether by stripping the volatile components (rotatory evaporator) from the dried reaction mixture. Known amounts of tetrachloroethylene (absent in the mixture) were added, and the carbon tetrachloride and cyclohexene were analyzed by vapor phase chromatography (column, silicone grease set at 67°, carrier He, flow $\sim$15 p.s.i.).

Acknowledgment.—The authors would like to thank Professor Dr. H. Wynberg, Department of Chemistry, the University of Groningen, The Netherlands, for helpful discussions relative to this investigation.

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[24] R. P. Linstead and H. N. Rydon, *J. Chem. Soc.*, 1995 (1934).

The Radiation-Induced Addition Reaction of Ethers to Chlorofluoroolefins

HIROSHIGE MURAMATSU, KAN INUKAI, AND TERUO UEDA

Government Industrial Research Institute, Nagoya Kita-ku, Nagoya, Japan

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The radiation-induced addition reactions of tetrahydrofuran, dioxane, and diethyl ether to chlorofluoroolefins such as 1,2,2-trichloro-2-fluoroethylene, 1,2-dichloro-1,2-difluoroethylene, and 1,1-dichloro-2,2-difluoroethylene were carried out. While the addition of tetrahydrofuran and dioxane gave mainly 1:1 adducts in appreciable yields, diethyl ether added to the olefins to give a 1:1 adduct and a 1:2 adduct in a molar ratio of about 1:1. The structures of the adducts were determined by proton n.m.r. spectroscopy.

Among the various methods[1] of preparing fluorine-containing ethers, the addition of alcohols to fluoroolefins by an ionic mechanism using sodium alkoxides was most extensively studied. On the other hand, little attention has been paid to the free-radical addition of ethers to fluoroolefins, and the only report[2] available was on the peroxide-induced addition of certain cyclic ethers to CF_2=CF_2 to give 1:1 adducts and telomers.

This study is concerned with the addition of tetrahydrofuran, 1,4-dioxane, and diethyl ether to CFCl=CCl_2, CFCl=CFCl, and CF_2=CCl_2 by γ-ray irradia-

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[1] For a review of the syntheses of fluorine-containing ethers, see A. M Lovelace, D. A. Rausch, and W. Postelnek, "Aliphatic Fluorine Compounds," Reinhold Publishing Corp., New York, N. Y., 1958, p. 155.

[2] W. E. Hanford, U. S. Patent 2,433,844 (1948).

TABLE 1

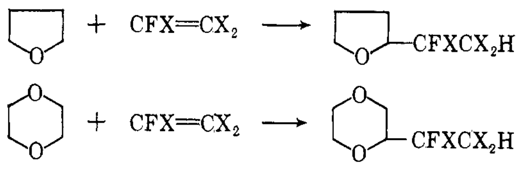
IRRADIATION CONDITIONS

Ethers	Molar ratio of ether to olefin	Irradiation time, hr.	Total dosage, r. × 10^6	Yield,[a] % 1:1 adduct	Yield,[a] % 1:2 adduct
		$CFCl{=}CCl_2$			
Tetrahydrofuran	2.33	312	23	89	
Dioxane	2.31	313	23	23	
Diethyl ether	2.37	312	23	16	26
		$CFCl{=}CFCl$			
Tetrahydrofuran	2.28	309	23	84	
Dioxane	2.28	309	23	27	
Diethyl ether	1.96	309	23	28	30
		$CF_2{=}CCl_2$			
Tetrahydrofuran	2.31	389	24	65	4
Dioxane	2.30	389	24	5	3
Diethyl ether	2.14	359	22	15	14

[a] Based on the amount of olefin added.

tion. The reactants were irradiated in a glass tube at a rate of 0.6–0.7 × 10^5 r./hr. for a period of 2 weeks at room temperature. The irradiation conditions of each run are listed in Table I with yields based on the amount of olefin added.

While the γ-irradiation-induced addition of the cyclic ethers, tetrahydrofuran and dioxane, to chlorofluoroolefins gave mainly 1:1 adducts in appreciable yields, the addition of diethyl ether produced 1:1 adducts and 1:2 adducts in a molar ratio of about 1:1. The over-all reactions are represented by the equations



$$CH_3CH_2OCH_2CH_3 + CFX{=}CX_2 \longrightarrow CH_3CH_2OCH(CFXCX_2H)CH_3 + CH_3CH(CFXCX_2H)OCH(CFXCX_2H)CH_3$$

where X is F or Cl. Further, in the addition of these ethers to 1,1-dichloro-2,2-difluoroethylene, telomers were formed with 1:1 adducts as in the additions of aldehydes[3] and alcohols.[4]

The directions of attack of acyl and α-hydroxyalkyl radicals to the asymmetric chlorofluoroolefins in the addition of aldehydes and alcohols were determined earlier by the reactions

$$\left.\begin{array}{l} CF_2{=}CCl_2 + CH_3CHO \longrightarrow CHCl_2CF_2COCH_3 \\ CF_2{=}CCl_2 + CH_3OH \longrightarrow CHCl_2CF_2CH_2OH \end{array}\right] \xrightarrow[\text{2. aq. NaOH}]{\text{1. } K_2Cr_2O_7}$$

$$CHCl_2CF_2COONa \xrightarrow{\Delta} CHCl{=}CF_2 + NaCl + CO_2$$

and were found to be the $=CF_2$ side by the identification of the olefin formed.[3,4] The ether adducts obtained in the present work, however, were so stable that such chemical methods were not practical for the determination of their structure.

The structures of 1:1 adducts and 1:2 adducts were determined by their proton n.m.r. spectra. Some examples of spectra at 60 Mc. of the 1:2 adducts of diethyl ether and 1:1 adducts of tetrahydrofuran are shown in Fig. 1 and 2, respectively. Since only a single multiplet appears in the methyl region of the spectrum of the 1:2 adduct in Fig. 1, the chlorofluoroethyl groups must attach themselves in such a way as to preserve the symmetry of the molecule, and thus each α-hydrogen must have one of these groups attached. The large doubling of the methyl pattern is due to coupling with the remaining α-hydrogen, and the smaller doubling is probably the result of coupling with the fluorine two carbons removed.

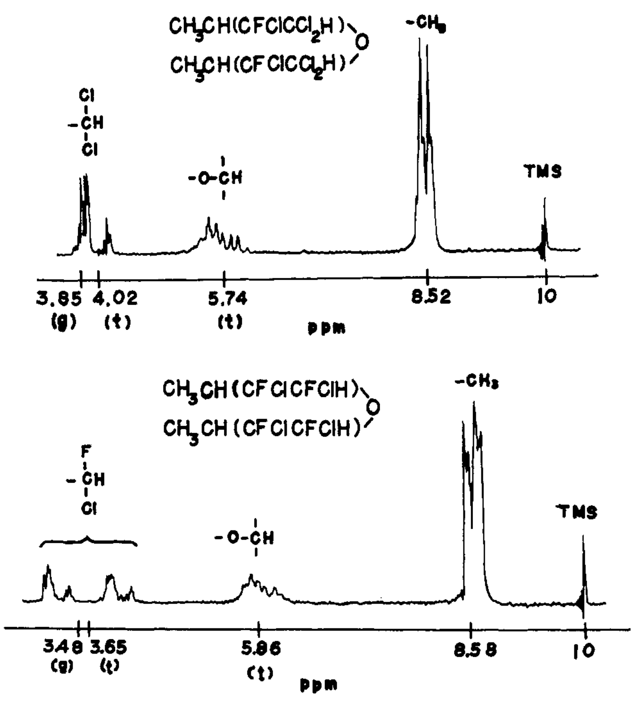


Fig. 1.—N.m.r. spectra (60 Mc.) of bis(1-methyl-2,3,3-trichloro-2-fluoropropyl) ether and bis(1-methyl-2,3-dichloro-2,3-difluoropropyl) ether in carbon tetrachloride (25%) using tetramethylsilane as internal standard at 10 (τ-scale).

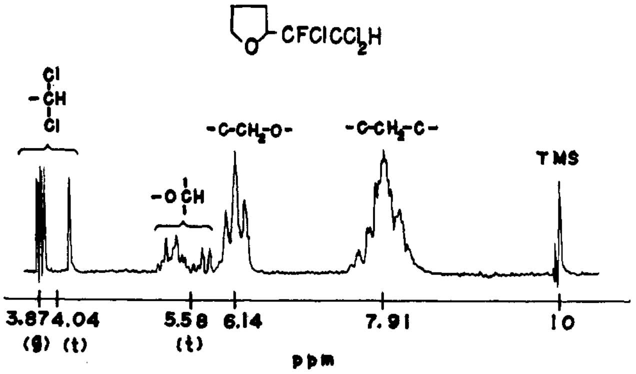


Fig. 2.—N.m.r. spectrum (60 Mc.) of 2-(1,2,2-trichloro-1-fluoroethyl)tetrahydrofuran in carbon tetrachloride (25%) using tetramethylsilane as internal standard at 10 (τ-scale).

The pattern of absorptions of protons on chlorofluoroethyl groups of $CH_3CH(CFClCHCl_2)OCH(CFClCHCl_2)CH_3$ is consistent with the presence of four partially overlapping doublets. They may be assigned to the *gauche* and *trans* form of vicinal H and F. Gutowsky and co-workers[5] reported the coupling constants of 1.00 ± 0.02 c.p.s. for J_g^{HF} and 18.2 ± 0.08 c.p.s. for J_t^{HF} of $CFCl_2CHCl_2$, and Abraham and Bernstein[6] ob-

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(3) H. Muramatsu and K. Inukai, *J. Org. Chem.*, **27**, 1572 (1962); *Kogyo Kagaku Zashi*, **65**, 1992 (1962).

(4) H. Muramatsu, *J. Org. Chem.*, **27**, 2325 (1962).

(5) H. S. Gutowsky, G. G. Belford, and P. E. McMahon, *J. Chem. Phys.*, **36**, 3353 (1962).

(6) R. J. Abraham and H. J. Bernstein, *Can. J. Chem.*, **39**, 39 (1961).

TABLE II

CHLOROFLUORO ETHERS (1:1 ADDUCTS)

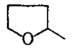
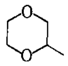
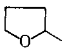
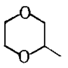
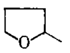
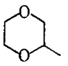
R	B.p., °C.	mm.	$n^{20}D$	d^{20}_4	MR		Fluorine, %		Chlorine, %	
					Calcd.	Found	Calcd.	Found	Calcd.	Found
$CHCl_2CFClR$										
	102–104	21	1.4739	1.412	44.03	44.06	8.58	8.49	48.04	46.85
	130–132	30	1.4762	1.467	45.68	45.67	8.00	8.05	44.80	43.91
$CH_3CH_2O\underset{\mid}{C}HCH_3$	78–79	17	1.4482	1.318	46.23	45.40	8.50	8.39	47.60	47.49
$CHFClCFClR$										
	117–118	80	1.4416	1.393	39.25	38.91	18.54	17.94	34.60	33.54
	124–125	60	1.4439	1.451	40.89	40.45	17.20	17.20	32.09	32.29
$CH_3CH_2O\underset{\mid}{C}HCH_3$	91–93	79	1.4132	1.279	41.45	40.38	18.36	18.42	34.26	33.86
$CHCl_2CF_2R$										
	117–118	80	1.4412	1.372	39.25	39.47	18.54	18.08	34.60	34.06
	123–124	56	1.4434	1.476	40.89	39.73	17.20	17.69	32.09	32.61
$CH_3CH_2O\underset{\mid}{C}HCH_3$	97–99	80	1.4110	1.262	41.45	40.72	18.36	18.38	34.26	34.22

TABLE III

CHLOROFLUORO ETHERS (1:2 ADDUCTS)

Compound	B.p., °C.	mm.	$n^{20}D$	d^{20}_4	MR		Fluorine, %		Chlorine, %	
					Calcd.	Found	Calcd.	Found	Calcd.	Found
$CH_3CH(CFClCCl_2H)OCH(CFClCCl_2H)CH_3$	135–138	6	1.4842	1.539	70.15	69.36	10.19	10.02	57.05	56.30
$CH_3CH(CFClCFClH)OCH(CFClCFClH)CH_3$	133–134	20	1.4390	1.490	60.58	60.04	22.35	22.31	41.71	41.46
$CH_3CH(CF_2CCl_2H)OCH(CF_2CCl_2H)CH_3$	135–136	21	1.4393	1.502	60.58	59.59	22.35	22.27	41.71	41.75

tained 1.03 c.p.s. for J_{g}^{HF} and 18.08 c.p.s. for J_{t}^{HF} of the same chlorofluoroethane. Based on these values, we may assign each doublet to the *gauche* and *trans* form and get 2 c.p.s. for J_{g}^{HF} and 16 c.p.s. for J_{t}^{HF}. Although the presence of the *gauche* and *trans* form was exhibited in the resonance absorption of the proton on the α-carbons of the ether, the *trans* form is predominant and 18 c.p.s. was obtained for J_{t}^{HF}.

It is known[7] that J_{gem}^{HF} is severalfold larger than J_{vic}^{HF}. For example, Gutowsky, *et al.*,[5] obtained 49.1 ± 0.2 c.p.s. for J_{gem}^{HF} of $CHFClCHCl_2$. Since only the adduct from $CFCl{=}CFCl$, $CH_3CH(CFClCHFCl)OCH(CFClCHFCl)CH_3$, shows a large value of J^{HF}, 48 c.p.s., in our spectrum of a proton on chlorofluoroethyl group, this coupling may be due to the interaction between geminal H and F. This fact indicates accordingly that, in the adducts from $CFCl{=}CCl_2$ and $CF_2{=}CCl_2$, H and F in haloethyl groups are vicinal to each other; *i.e.*, in the addition to asymmetrical olefins, the α-ethereal radicals formed attack the $=CFX$ side where X is F or Cl.

From the positions and areas of the absorptions in the spectra of adducts of tetrahydrofuran, we assigned the various absorptions as written in Fig. 2. The analysis of the positions and J^{HF} of peaks indicates that the chlorofluoroethyl group is on the α-carbon, and the direction of the attack of the α-ethereal radical of tetrahydrofuran is the same as in the addition of diethyl ether, and almost equal amounts of the *gauche* and *trans* form exist between the vicinal H and F on the chlorofluoroethyl group at room temperature.

Wallace and Gritter[8] found that, in the peroxide-induced free-radical addition of four-, five-, and six-membered cyclic ethers to 1-octene, ketones in addition to ethers were produced as the major products. They suggested that the intermediate α-ethereal radicals undergo decyclization. Matsuda, *et al.*,[9] however, reported that ketones were not formed in the radiation-induced addition reaction of cyclic ethers to tetrachloroethylene and they obtained α-trichlorovinyl cyclic ethers with α-tetrachloroethyl cyclic ethers. In our experiments, both the corresponding ketones, $CH_3(CH_2)_2COCFXCX_2H$ and α-chlorofluorovinyl tetrahydrofuran, were not isolated in the addition reaction of tetrahydrofuran.

In the additions of diethyl ether, however, several grams of the corresponding ketones, $CH_3COCFXCX_2H$, were obtained. These ketones were identified by comparing their retention times in the vapor phase chromatograms with those of the authentic samples which were prepared in the addition of the acetaldehyde to $CFX{=}CX_2$.[3] The structures of ketones were also confirmed by the use of mixture melting points of 2,4-dinitrophenylhydrazones of the ketones and those of authentic samples.

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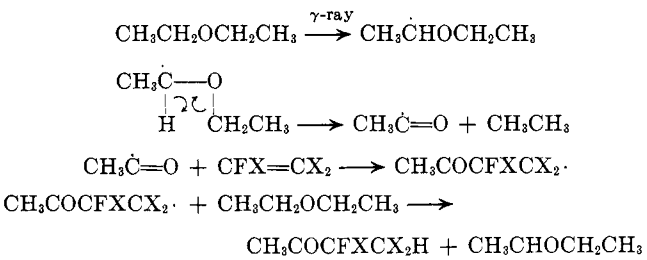
[7] H. S. Gutowsky, C. H. Holm, A. Saika, and G. A. Williams, *J. Am. Chem. Soc.*, **79**, 4596 (1957).

[8] T. J. Wallace and R. J. Gritter, *J. Org. Chem.*, **26**, 5256 (1961); **27**, 3067 (1962).

[9] T. Matsuda, K. Yumoto, and K. Iseda, Abstract, Symposium on Isotopes of the 4th Meeting, Tokyo, Japan, 1963.

The mechanism of the formation of these ketones may be as shown.



$$CH_3CH_2OCH_2CH_3 \xrightarrow{\gamma\text{-ray}} CH_3\dot{C}HOCH_2CH_3$$

$$\begin{array}{ll} CH_3C & \text{—}O \\ | & | \\ H & CH_2CH_3 \end{array} \longrightarrow CH_3\dot{C}{=}O + CH_3CH_3$$

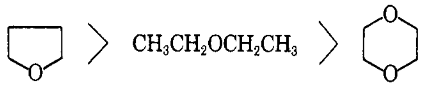
$$CH_3\dot{C}{=}O + CFX{=}CX_2 \longrightarrow CH_3COCFXCX_2\cdot$$

$$CH_3COCFXCX_2\cdot + CH_3CH_2OCH_2CH_3 \longrightarrow CH_3COCFXCX_2H + CH_3\dot{C}HOCH_2CH_3$$

Since crotonaldehyde was not isolated, another possible mechanism which proceeds through the formation of acetaldehyde would not occur appreciably.[10]

In the additions of dioxane, infrared examination of foreruns collected during product isolation revealed the presence of trace amounts of carbonyl-containing compounds, which were isolated as their 2,4-dinitrophenylhydrazones. Qualitative analyses showed the presence of fluorine and chlorine in them. Therefore, it seemed that similar radical cleavage occurred in these addition reactions. Further attempt to elucidate the structures of the compounds was not undertaken.

The physical properties and analyses of 1:1 adducts, the new fluorine-containing ethers, are shown in Table II. Table III shows those of the 1:2 adducts of diethyl ether to chlorofluoroolefins. The trends in apparent reactivity of ethers and chlorofluoroolefins observed in the addition reaction are the following.



$$CFCl{=}CCl_2 \fallingdotseq CFCl{=}CFCl > CF_2{=}CCl_2$$

Experimental[11]

Materials.—The chlorofluoroolefins used were prepared by the dechlorination of the corresponding chlorofluoroethanes with zinc dust in ethanol or 1-butanol according to the method of Henne, *et al.*[12] All of the ethers used were purified by conventional methods.

Irradiation by γ-Ray.—A mixture of chlorofluoroolefin and ether in a molar ratio of about 1:2 was added to a Pyrex tube, 20 × 5 cm. (*ca.* 300 ml.). The reaction tube was then sealed and irradiated by γ-ray from Co^{60} for a period of 2 weeks at a dose rate of 0.6–0.7 × 10^6 r./hr.

Addition Reactions of Ethers to 1,1,2-Trichloro-2-fluoroethylene.—A mixture of 95.5 g. (0.64 mole) of 1,1,2-trichloro-2-fluoroethylene and 112.5 g. (1.52 moles) of diethyl ether was sealed in a glass tube and irradiated at room temperature to a total dosage of 2.3 × 10^7 r. for a period of 312 hr. Distillation of the unchanged olefin and ether gave 22.4 g. (0.10 mole, 16% yield) of 1-methyl-2-fluoro-2,3,3-trichloropropyl ethyl ether, b.p. 75–79° (17 mm.), 30.5 g. (0.082 mole, 26% yield) of bis(1-methyl-2-fluoro-2,3,3-trichloropropyl) ether, b.p. 135–138° (6 mm.), and *ca.* 6 g. of residue.

During product isolation by distillation, 7 g. of the forefraction, b.p. 60–72° (28 mm.), was obtained. The infrared spectrum and vapor phase chromatogram showed that it was a mixture of 1,1,2-trichloro-2-fluorobutanone-3 and 1-methyl-2-fluoro-2,3,3-trichloropropyl ethyl ether. To *ca.* 3 g. of the fraction in ethanol (3 ml.), *ca.* 5 ml. of 2,4-dinitrophenylhydrazine reagent[13] was added. Yellow-orange crystals (0.4 g.) precipitated and they did not show the depression of melting point when mixed with the hydrazone of the authentic sample which was prepared by the free radical-induced addition of acetaldehyde to 1,1,2-trichloro-2-fluoroethylene.[3]

The addition reactions of tetrahydrofuran and dioxane to 1,1,2-trichloro-2-fluoroethylene were carried out under similar conditions.

Addition Reactions of Ethers to 1,2-Dichloro-1,2-difluoroethylene.—In a glass tube were sealed 113 g. (0.85 mole) of 1,2-dichloro-1,2-difluoroethylene and 171 g. (1.94 moles) of dioxane. The content of the tube were irradiated to a total dosage of 2.3 × 10^7 r. for 309 hr. Distillation of the reaction mixture under reduced pressure yielded 50 g. (0.23 mole, 27% yield) of 2-(1,2-dichloro-1,2-difluoroethyl)dioxane, b.p. 123–126° (60 mm.), and 14 g. of residue.

Using the same procedure, other ethers were added to 1,2-dichloro-1,2-difluoroethylene.

Addition Reactions of Ethers to 1,1-Dichloro-2,2-difluoroethylene.—A mixture of 131 g. (0.99 mole) of 1,1-dichloro-2,2-difluoroethylene and 164 g. (2.27 moles) of tetrahydrofuran was irradiated to a total dosage of 2.4 × 10^7 r. for 389 hr. Distillation of the irradiation products under reduced pressure gave 131 g. (0.64 mole, 65% yield) of 2-(1,1-difluoro-2,2-dichloroethyl)-tetrahydrofuran, b.p. 115–119° (80 mm.), 14 g. (0.40 mole, 4% yield) of crude 1:2 adduct, b.p. 110–113° (8 mm.), and 29 g. of a residue which seemed to be higher telomers.

Table II and III summarize the physical properties and analyses of the 1:1 adducts and 1:2 adducts prepared by the addition of ethers to chlorofluoroolefins.

Proton N.m.r. Spectra.—Spectra were obtained for 25% solution in carbon tetrachloride, using a Nihondenshi JNM-3 Type high resolution spectrometer operating at a frequency of 60 Mc. Tetramethylsilane was used as an internal reference.

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(10) In the irradiation- and peroxide-induced addition reactions of acetaldehyde to chlorofluoroolefins, an appreciable amount of crotonaldehyde was produced with the 1:1 adducts; see ref. 3.

(11) All temperature readings are uncorrected.

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