TABLE X

EQUILIBRIUM COMPOSITIONS OF HALOETHYLBENZENES

	% isomeric haloethylbenzene		
	ortho	*meta*	*para*
Fluoroethylbenzenes	36	52	12
Chloroethylbenzenes	28	52	20
Bromoethylbenzenes	24	56	20

TABLE XI

EQUILIBRIUM COMPOSITIONS OF HALOTOLUENES[a]

	% isomeric halotoluenes		
	ortho	*meta*	*para*
Fluorotoluenes	31	56	13
Chlorotoluenes	31	44	25
Bromotoluenes	38	44	18

tendency can be observed. There is evidence of only a slight steric *ortho* effect in the case of the haloethylbenzenes, with the bromoethylbenzenes showing the lowest and the fluoroethylbenzenes the highest amount of *ortho* isomer in equilibrium.

A kinetic evaluation of the isomerization data of the haloethylbenzenes in the present work was not possible, as the reactions are not homogeneous and σ-complex formation may tend to deactivate the catalyst to varying degrees.

Experimental

Materials.—The haloethylbenzenes used, with the exception of the fluoroethylbenzenes, were samples obtained from The Dow Chemical Co., Midland, Mich. Their purity determined by gas chromatography and infrared analysis is shown in the tables. Anhydrous aluminum chloride was reagent grade by Fisher Scientific Co. The fluoroethylbenzenes were prepared by the Schiemann reaction of the corresponding aminoethylbenzenes.

TABLE XII

RETENTION TIMES OF HALOETHYLBENZENES, HALOBENZENES, AND ETHYLBENZENE

Compd.	Column temp., °C.	Retention time, min.	He carrier gas pressure, p.s.i.
Fluorobenzene	40	14	10
o-Fluoroethylbenzene	40	48	10
m-Fluoroethylbenzene	40	53	10
p-Fluoroethylbenzene	40	53.7	10
Chlorobenzene	90	9.8	15
o-Chloroethylbenzene	90	21.8	15
m-Chloroethylbenzene	90	24.2	15
p-Chloroethylbenzene	90	25.0	15
Ethylbenzene	100	6	20
Bromobenzene	100	9	20
o-Bromoethylbenzene	100	21	20
m-Bromoethylbenzene	100	23	20
p-Bromoethylbenzene	100	25	20

General Process of Isomerization.—Reactions were carried out in stoppered flasks with magnetic stirring at $\sim 25°$. Two-tenths mole of aluminum chloride/mole of haloethylbenzene was used and 1 ml. of water was added as a promoter. Samples were drawn periodically, the reaction was stopped with water, and the organic material was extracted with ether. The dried ether extracts were analyzed by gas–liquid chromatography.

Results given in tables are normalized % of *ortho, meta,* and *para* isomer.

Gas–Liquid Chromatographic Analysis.—Gas–liquid chromatographic analyses were carried out on a Perkin-Elmer Model 226 vapor fractometer equipped with a 150-ft. polypropyleneglycol-coated capillary column and hydrogen flame ionization detector. Column conditions are given together with characteristic retention times in Table XII. Peak areas were directly determined by the use of a high speed electronic Infotronics Model CRS-1 integrator.

The Radiation-Induced Addition Reaction of Ethers to 1,2-Dichlorotetrafluorocyclobutene and 1,2-Dichlorohexafluorocyclopentene

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The addition reactions of tetrahydrofuran, dioxane, and diethyl ether to 1,2-dichlorotetrafluorocyclobutene and 1,2-dichlorohexafluorocyclopentene were carried out under γ-ray irradiation. Though the addition of tetrahydrofuran to 1,2-dichlorotetrafluorocyclobutene gave only the 1:1 adduct in a excellent yield, the addition of dioxane yielded mainly the dehydrochlorinated 1:1 adduct, 2-(2-chlorotetrafluoro-1-cyclobutenyl)-dioxane, along with the 1:1 adduct. In the case of diethyl ether, both the dehydrochlorinated 1:1 and 1:2 adducts, α-(2-chlorotetrafluoro-1-cyclobutenyl)diethyl ether and α-(1,2-dichlorotetrafluorocyclobutyl)-α'-(2-chlorotetrafluoro-1-cyclobutenyl)diethyl ether, were formed along with the 1:1 and 1:2 adducts. In the addition of the ethers to 1,2-dichlorohexafluorocyclobutene, only the corresponding dehydrochlorinated 1:1 adducts were obtained.

The nucleophilic additions of alcohols to fluorine-containing cyclobutene[1] and cyclopentene[2] in the presence of base to give ethers with polyfluorocycloalkyl groups have been investigated by several workers. So far as we know, no report on the synthesis of ethers containing polyfluorocycloalkyl groups by free-radical reaction has appeared in the literature.

This paper presents the addition reaction of ethers, such as tetrahydrofuran, dioxane, and diethyl ether, to 1,2-dichlorotetrafluorocyclobutene and 1,2-dichlorohexafluorocyclopentene under γ-ray irradiation. A mixture of the halocyclobutene or halocyclopentene and the ether in a molar ratio of 1:3 was irradiated in a glass tube at a rate of 0.59×10^5 r./hr. for a period of 4 weeks at room temperature (total dosage $4.2\text{–}4.3 \times 10^7$ r.).

A previous paper[3] on the γ-ray induced addition of ethers to chlorofluoroethylene reported that only the

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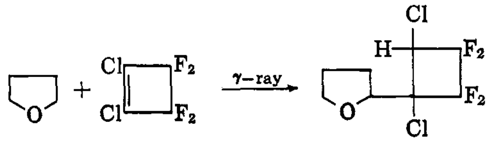
(1) J. D. Park, M. L. Sharrah, and J. R. Lacher, *J. Am. Chem. Soc.*, **71**, 2337 (1949); J. T. Barr, K. E. Rapp, R. L. Pruett, C. T. Bahner, J. D. Gibson, and R. H. Lafferty, Jr., *ibid.*, **72**, 4480 (1950); J. D. Park, C. M. Snow, and J. R. Lacher, *ibid.*, **73**, 2342 (1951).

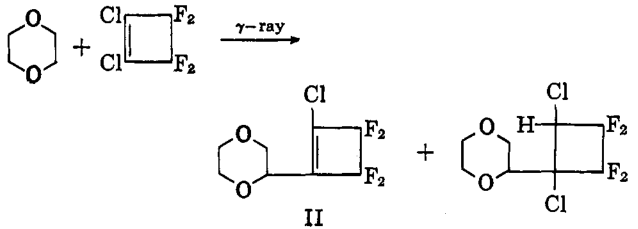
(2) R. A. Shepard, H. Lessoff, J. D. Domijan, D. B. Hilton, and T. F. Finnegan, *J. Org. Chem.*, **23**, 2011 (1958).

(3) H. Muramatsu, K. Inukai, and T. Ueda, *ibid.*, **29**, 2220 (1964).

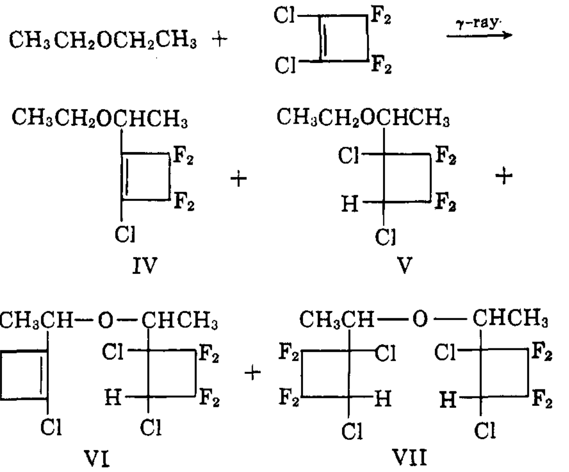
1:1 adducts were produced in appreciably good yields in the case of tetrahydrofuran and dioxane, and that the addition of diethyl ether gave the 1:2 adducts with the symmetrical structure in addition to the 1:1 adducts. The free-radical addition of the ethers to dichlorotetrafluorocyclobutene and dichlorohexafluorocyclopentene was found to give the dehydrochlorinated adducts along with the 1:1 adduct, although the molar ratio of both products varied markedly with the structure of substrates. Thus, the addition of tetrahydrofuran yielded exclusively the 1:1 adduct, 2-(1,2-dichlorotetrafluorocyclobutyl)tetrahydrofuran (I). On the other hand, the unsaturated product, 2-(2-chlorotetrafluorocyclobutenyl)dioxane (II), was predominant over the 1:1 adduct (III) in the addition of dioxane. In the case of diethyl ether, α-(2-chlorotetrafluoro-1-cyclobutenyl)diethyl ether (IV), α-(1,2-dichlorotetrafluorocyclobutyl)diethyl ether (V), α-(1,2-dichlorotetrafluorocyclobutyl)-α′-(2-chlorotetrafluoro-1-cyclobutenyl)diethyl ether (VI), and α,α′-bis(1,2-dichlorotetrafluorocyclobutyl)diethyl ether (VII) were obtained in a molar ratio of 1.2:2.1:1.0:0.8. The addition reactions of the ethers to 1,2-dichlorohexafluorocyclopentene gave the corresponding unsaturated 1:1 adducts, VIII, IX, and X, which contained 2-chlorohexafluoro-1-cyclopentenyl groups on the α-carbon.



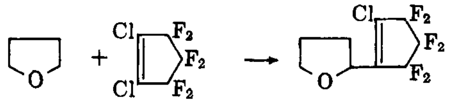
I



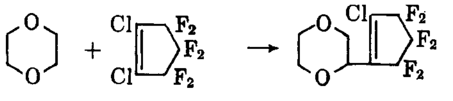
II III



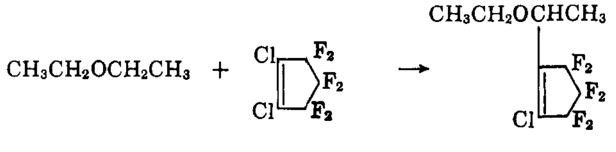
IV V VI VII



VIII



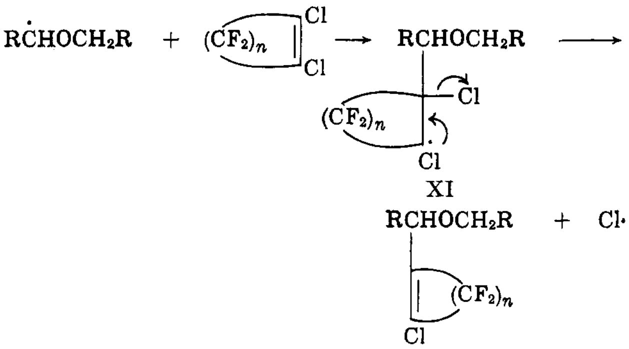
IX



X

The mechanism for the formation of the unsaturated products, such as II, IV, VI, VIII, IX, and X, may be explained by the radical dechlorination of the intermediate radical XI. The intermediate radical XI will give the 1:1 adduct by the abstraction of a hydrogen atom from the substrate. The difference of the ratio of the 1:1 adduct and the dehydrochlorinated 1:1 adduct XII with the structure of the ethers may arise from the ease in removal of hydrogen atom from the ethers. With more reactive ethers such as tetrahydrofuran,[4] the abstraction of hydrogen by the intermediate radical XI to form the 1:1 adduct might occur predominantly. No radical dechlorination was observed in the addition of tetrahydrofuran to the halocyclobutene where the 1:1 adduct was formed in a high yield (81%). On the other hand, if the abstraction of hydrogen from the substrate is difficult owing to the electronic or steric effect, the radical dechlorination to give XII would predominate. Actually, in the addition of dioxane where the yield was poor, the dehydrochlorinated adduct (30% yield) predominated over the saturated adduct (4% yield). It is interesting that even the reactive tetrahydrofuran gave the unsaturated 1:1 adduct in the addition reaction to 1,2-dichlorohexafluorocyclopentene. It would be due partly to the steric effect of the halocyclopentyl group that only the unsaturated 1:1 adducts were formed in the addition to the halocyclopentene.

$$RCH_2OCH_2R \xrightarrow{\gamma\text{-ray}} RCHOCH_2R + H\cdot$$



XII

$R = CH_3$- or -CH_2-; $n = 2$ or 3

The structures of 1:1 adducts and 1:2 adducts were determined by their proton n.m.r. spectra.[5] Although

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[4] In the addition reactions of ethers to chlorofluoroethylenes, the trend in apparent reactivity of ethers was found to be the following order: tetrahydrofuran > diethyl ether > dioxane. See ref. 3.

[5] Spectra were obtained for 25% solution in carbon tetrachloride, using a Nihondenshi JNM-3 high resolution spectrometer operating at a frequency of 60 Mc. Tetramethylsilane was used as an internal reference. The interpretation of the spectra was done as reported in the paper of ref. 3.

TABLE I

ETHERS CONTAINING POLYFLUOROCYCLOBUTYL AND POLYFLUOROCYCLOBUTENYL GROUP

				MRD		Fluorine, %		Chlorine, %	
Compd.	B.p., °C. (mm.)	$n^{20}D$	d^{20}_4	Calcd.	Found	Calcd.	Found	Calcd.	Found
			Derivatives of Tetrahydrofuran						
I	115–116 (40)	1.4317	1.487	46.44	46.54	28.5	28.9	26.6	26.7
XIII	104–105 (65)	1.4151	1.381	41.11	41.84	33.0	33.1	15.4	15.2
XIV	99–100 (65)	1.3990	1.302	36.24	36.44	38.8	38.4		
			Derivatives of Dioxane						
II	99–100 (31)	1.4240	1.449	42.75	43.42	30.8	30.5	14.4	14.7
III	102–105 (14)	1.4380	1.518	48.08	48.95	26.9	26.7	25.1	21.4
			Derivatives of Diethyl Ether						
IV	78–79 (75)	1.3878	1.246	43.31	44.04	32.7	32.0	15.2	15.2
V	94–95 (39)	1.4090	1.385	48.64	48.02	28.3	29.2	26.4	25.6
VI	93–95 (7)	1.4173	1.509	69.63	71.30	35.6	35.5	24.9	23.0
VII	122–124[a] (7)					32.8	33.0	30.6	29.4
XV	76–77 (75)	1.3725	1.177	38.44	38.33	38.4	38.2		
XVI	111–112 (18)	1.3880	1.382	54.57	55.01	47.2	45.5		
XVII	107–109[b] (23)					38.9	39.4	18.1	18.2

[a] M.p. 99–100°. [b] M.p. 41–42°.

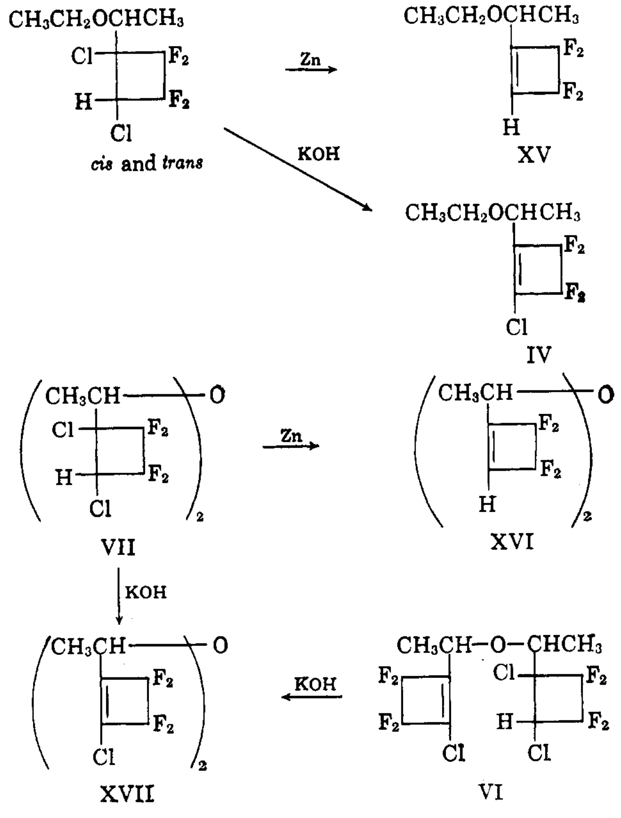
TABLE II

ETHERS CONTAINING CHLOROHEXAFLUOROCYCLOPENTENYL GROUP

				MRD		Fluorine, %		Chlorine, %	
Compd.	B.p., °C. (mm.)	$n^{20}D$	d^{20}_4	Calcd.	Found	Calcd.	Found	Calcd.	Found
VIII	108–109 (50)	1.4090	1.494	45.89	46.43	40.6	40.4	12.6	12.7
IX	102–103 (27)	1.4131	1.537	47.53	48.14	38.4	38.0	12.0	11.9
X	81.5–82 (62)	1.3810	1.352	48.09	48.53	40.3	40.3	12.6	12.5

the vapor phase gas chromatograms of the some of 1:1 adducts showed the presence of *cis* and *trans* forms in the halogenated cyclobutyl group, an attempt to assign each peak to the two forms was not undertaken.

In order to obtain an additional proof of the assigned structures of the products, dehydrohalogenation and dehalogenation of the 1:1 adduct of the halocyclobutene were carried out using ethanolic potassium hydroxide and zinc dust in ethanol, respectively.



Treatment of I and III with potassium hydroxide in ethanol gave 2-(2-chlorotetrafluoro-1-cyclobutenyl)-tetrahydrofuran (XIII) and II, and dechlorination of I with zinc yielded 2-(tetrafluoro-1-cyclobutenyl)tetrahydrofuran (XIV). In the same way, the reactions of the preceding scheme proceeded with the 1:1 adduct and 1:2 adducts of diethyl ether.

The physical properties and analyses of the adducts, the new fluorine-containing ethers, are shown in Tables I and II.

Experimental[6]

Materials.—1,2-Dichlorotetrafluorocyclobutene and 1,2-dichlorohexafluorocyclopentene obtained from Peninsular Chemical Research, Inc., were found to be pure by their gas chromatograms and were used without further purification.

Addition of Tetrahydrofuran to 1,2-Dichlorotetrafluorocyclobutene.—A mixture of 108 g. (1.50 moles) of tetrahydrofuran and 97.5 g. (0.50 mole) of dichlorotetrafluorocyclobutene was sealed in a glass tube and placed in the Co^{60} irradiation room for a period of 709 hr. to receive γ-irradiation at a rate of 0.59 × 10^{6} r./hr. (total dosage 4.2 × 10^{7} r.). After recovery of unchanged tetrahydrofuran (66 g.), distillation of the irradiation products gave 108 g. (0.41 mole, 81 % yield[7]) of 2-(1,2-dichlorotetrafluorocyclobutyl)tetrahydrofuran, b.p. 110–117° (43 mm.), and 26.5 g. of a tarry residue. Though the gas chromatogram[8] of the 2-(halocyclobutyl)tetrahydrofuran obtained showed two peaks (retention time 6.1 and 7.3 min.), both the peaks disappeared completely on treatment with zinc dust in ethanol to give 2-(tetrafluorocyclobutenyl)tetrahydrofuran, and one new peak (retention time 2.7 min.) appeared. The 1:1 adduct seems, therefore, to consist of two geometrical isomers (in a ratio of 1:10). An attempt to separate the isomers by fractional distillation was unsuccessful.

Addition of Dioxane to 1,2-Dichlorotetrafluorocyclobutene.—A mixture of 144.5 g. (1.64 moles) of dioxane and 108 g. (0.56

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[6] All temperature readings are uncorrected.

[7] Throughout this manuscript, the yields in the addition reactions were based on the amounts of the halocyclobutene and halocyclopentene.

[8] A Hitachi-GC-2 was employed using helium as the carrier gas at a flow rate of 42 ml./min. and a column temperature of 153°; a 2-m. column packed with 25% silicone DC-550 was used.

mole) of the halocyclobutene was irradiated under similar conditions. In opening the glass tube, white fumes were evolved, which were identified as hydrogen chloride. Distillation of the products gave 41.5 g. (0.17 mole, 30% yield) of 2-(2-chlorotetrafluoro-1-cyclobutenyl)dioxane, b.p. 97–100° (31 mm.); 6 g. (0.021 mole, 4% yield) of 2-(1,2-dichlorotetrafluorocyclobutyl)-dioxane, b.p. 108–115° (12 mm.); and 11 g. of a tarry residue. The infrared spectrum of the first product exhibited a C=C absorption band at 6.02 μ.

Addition of Diethyl Ether to 1,2-Dichlorotetrafluorocyclobutene.—A mixture of 126.3 g. (1.70 moles) of diethyl ether and 109.5 g. (0.56 mole) of dichlorotetrafluorocyclobutene was irradiated as described above. The unchanged reactants were distilled off and the residue was fractionated to give 18.9 g. (0.08 mole, 14% yield) of α-(2-chlorotetrafluoro-1-cyclobutenyl)diethyl ether, b.p. 78–80° (75 mm.), a C=C absorption band at 6.07 μ; 39.6 g. (0.15 mole, 26%, yield) of α-(1,2-dichlorotetrafluorocyclobutyl)diethyl ether, b.p. 93–95° (39 mm.); 29.7 g. (0.07 mole, 25% yield) of α-(1,2-dichlorotetrafluorocyclobutyl)-α′-(2-chlorotetrafluoro-1-cyclobutenyl)diethyl ether, b.p. 119–122° (10 mm.), a C=C band at 6.06 μ; 25.1 g. (0.05 mole, 19% yield) of α,α′-bis(1,2-dichlorotetrafluorocyclobutyl)diethyl ether, b.p. 118–120° (4 mm.), m.p. 99–100°; and 13 g. of a residue.

The physical properties and analyses of the ethers containing the halocyclobutyl or halocyclobutenyl group are shown in Table I.

Addition of Ethers to 1,2-Dichlorohexafluorocyclopentene.—In a glass tube were sealed 105 g. (0.43 mole) of 1,2-dichlorohexafluorocyclopentene and 98.6 g. (1.37 moles) of tetrahydrofuran. The content of the tube were irradiated to a total dosage 4.3 × 10^7 r. for 730 hr. Distillation of the products under reduced pressure, after recovery of the unchanged ether (83 g.) and halocyclopentene (18 g.), gave 73.2 g. (0.26 mole, 61% yield) of 2-(2-chlorohexafluoro-1-cyclopentenyl)tetrahydrofuran, b.p. 99–108° (48 mm.); 6.2 g. of an unidentified product, b.p. 117–121° (21 mm.); and 10 g. of a tarry residue. The infrared spectrum of the 2-(halocyclopentenyl)tetrahydrofuran exhibited a sharp C=C absorption band at 6.075 μ.

Using the same procedure, dioxane and diethyl ether were added to 1,2-dichlorohexafluorocyclopentene to give the corresponding dehydrochlorinated 1:1 adduct with 2-chlorohexafluorocyclopentenyl group in the yields of 28 and 65%, respectively. Both the products showed the C=C band at 6.06 (the adduct of dioxane) and 6.095 μ (the adduct of diethyl ether) in their infrared spectra.

Table II summarizes the physical properties and analyses of the dehydrochlorinated 1:1 adducts prepared by the addition reaction of ethers to 1,2-dichlorohexafluorocyclopentene.

Dechlorination of 2-(1,2-Dichlorotetrafluorocyclobutyl)tetrahydrofuran.—To 11 g. (0.17 mole) of zinc dust in 45 ml. of ethanol was added dropwise 29.5 g. (0.11 mole) of the halocyclobutyltetrahydrofuran for 15 min. The mixture was refluxed for 2.5 hr. and filtered. Dilute hydrochloric acid was added to the filtrate. The organic layer was separated and dried. Distillation gave 20.4 g. (0.104 mole, 95% yield) of 2-(3,3,4,4-tetrafluoro-1-cyclobutenyl)tetrahydrofuran, b.p. 99–103° (65 mm.), and 1 g. of a residue. The infrared spectrum of the tetrafluorocyclobutenyl)tetrahydrofuran showed a C=C band at 6.13 μ.

Using the above procedure, α-(3,3,4,4-tetrafluoro-1-cyclobutenyl)diethyl ether (62% yield) and α,α′-bis(3,3,4,4-tetrafluoro-1-cyclobutenyl)diethyl ether (87% yield) were obtained by the dechlorination of the 1:1 and 1:2 adduct of diethyl ether to dichlorotetrafluorocyclobutene. Both the (tetrafluorocyclobutenyl)- and bis(tetrafluorocyclobutenyl)diethyl ether obtained showed the C=C band at 6.13 μ.

Dehydrochlorination of 2-(1,2-Dichlorotetrafluorocyclobutyl)-tetrahydrofuran.—In a 200-ml. flask with a stirrer and reflux condenser was placed 44.7 g. (0.17 mole) of the halocyclobutyltetrahydrofuran. A solution of 12 g. (0.21 mole) of potassium hydroxide in 50 ml. of absolute ethanol was added dropwise for 10 min. and the mixture was kept stirring for an additional 30 min. at room temperature. The reaction mixture was filtered to remove the potassium chloride, and water was added to the filtrate. The organic layer was separated, dried, and distilled to give 32.7 g. (0.14 mole, 85% yield) of 2-(2-chlorotetrafluoro-1-cyclobutenyl)tetrahydrofuran, b.p. 102–105° (65 mm.), and about 3 g. of a residue. The infrared spectrum of the halocyclobutenyltetrahydrofuran exhibited a C=C band at 6.06 μ.

In a similar manner, α-(1,2-dichlorotetrafluorocyclobutyl) diethyl ether was treated with an ethanolic potassium hydroxide to give α-(2-chlorotetrafluoro-1-cyclobutenyl)diethyl ether (72% yield), which was identical with the dehydrochlorinated 1:1 adduct obtained in the addition reaction of diethyl ether to 1,2-dichlorotetrafluorocyclobutene.

Dehydrochlorination of α-(1,2-Dichlorotetrafluorocyclobutyl)-α′-(2-chlorotetrafluoro-1-cyclobutenyl)diethyl Ether.—The α-(halocyclobutyl)-α′-(halocyclobutenyl)diethyl ether (20.4 g., 0.048 mole) was treated with ethanolic potassium hydroxide as described above to give 11.5 g. of crude α,α′-bis(2-chlorotetrafluoro-1-cyclobutenyl)diethyl ether, b.p. 107–109° (23 mm.), which was shown by its gas chromatogram to contain an impurity. Purification by fractional distillation was unsuccessful and the pure product, plate-shaped crystals, m.p. 41–42°, was obtained using a preparative gas chromatograph.

The dehydrochlorination of the α,α′-bis(halocyclobutyl)diethyl ether gave the same compound, which was confirmed by the retention time of its gas chromatogram and by the infrared spectrum which showed a C=C band at 6.06 μ.

Acknowledgment.—The authors wish to thank Dr. Toshio Goto of the University of Nagoya for proton n.m.r. spectrometric analyses.