

picrate of 2-ethyl-3-methylindole. The yields of all these fractions were too small for further investigation.

Summary

The non-catalytic hydrogenolysis of carbazole for different lengths of time at 450° and at cold hydrogen pressures of about 1900 p.s.i. has shown the following:

1. The carbazole is quite resistant to reaction and is only decomposed to the extent of 48% under the most severe conditions.
2. The primary reaction is, in all probability, the formation of unidentifiable reactive fragments

which polymerize into undistillable ether-soluble products.

3. The heterocyclic nitrogen is quite resistant to removal since 5% is the maximum amount found in the reaction gases.

4. The nitrogen in the gaseous products increases slowly with an increase in the time of hydrogenolysis and appears initially as ammonia.

5. Benzene, aniline, methane and ethane are minor products of the hydrogenolysis.

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Reactions of Polyfluoro Olefins. III.¹ Preparation of Polyfluoro Ethers²

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Saturated polyfluoroalkyl ethers have been prepared by the base-catalyzed addition of alcohols to polyfluoro olefins.^{3,4,5} Saturated and unsaturated aryl polyfluoroalkyl ethers have been prepared by the action of alkali metal aryl-oxides on polychloropolyfluoroethanes and propane.⁶ Park, Sharrah and Lacher⁷ have obtained 1,2-dialkoxy-3,3,4,4-tetrafluorocyclobutenes by what they regard as a metathetical reaction of metal alkoxides and hexafluorocyclobutene.

This paper describes the preparation of several of these previously reported polyfluoro ethers and several unreported ones, and a study of the mechanism of the reaction between hexafluorocyclobutene and alcohols.

Chlorotrifluoroethyl ethers were prepared by the method of Park, *et al.*⁵ The yields and physical constants are shown in Table I. Analytical results for all new compounds are given in Table III. Samples were prepared for analysis and for the determination of physical properties by careful fractionation.

The finding of Park, Sharrah and Lacher⁷ that only the dialkoxy cyclobutenes were formed by the reaction of alcohols and hexafluorocyclobutene in the presence of potassium hydroxide in the bubble tube has been substantiated. However, when potassium hydroxide was the catalyst for the reaction in a closed system a large proportion of the product was the monoalkoxy butene,

even in the presence of a large excess of alcohol. Benzyltrimethylammonium hydroxide catalyst gave predominantly the monoether in either the bubble tube or a closed system. In contrast to the instability during storage which was reported⁷ and found for the dialkoxy butenes, these monoalkoxy compounds were relatively stable. The reaction of phenolic compounds with hexafluorocyclobutene in ether solution, using tertiary amines as catalysts, gave only the mono-alkoxy butenes.

Because of their failure to obtain saturated ethers from the reaction of metal alkoxides and hexafluorocyclobutene, Park and associates⁷ have proposed a vinylic substitution mechanism for this reaction, supported by an extrapolation from thermodynamic data which they had obtained. It has been proposed,^{1,8} however, that the reactions of thiols and amines with hexafluorocyclobutene proceed by an addition mechanism analogous to the reactions of other polyfluoro olefins. A saturated bis-(butylthio)-pentafluorocyclobutane of the structure to be expected from an addition mechanism has been reported. The more stable unsaturated products were thought to have been formed by the loss of hydrogen fluoride from the saturated addition products.

During this work the presence of hydrogen fluoride was noted many times during the purification of the products, and an effort was made to isolate a corresponding saturated mono- or dialkoxy substituted cyclobutane. In every case decomposition occurred before the material could be obtained in a pure state. Quantities of hydrogen fluoride were formed by this spontaneous decomposition of the products within a few hours after their formation. It was found repeatedly,

(1) The previous paper in this series is: Pruett, Barr, Rapp, Bahner, Gibson and Lafferty, *THIS JOURNAL*, **72**, 3646 (1950).

(2) This document is based on work performed for the Atomic Energy Commission by Carbide and Carbon Chemicals Division, Union Carbide and Carbon Corporation.

(3) Hanford and Rigby, U. S. Patent 2,409,274 (1946); *cf.* E. I. du Pont de Nemours and Company, British Patent 583,874 (1947).

(4) Miller, Fager and Griswold, *THIS JOURNAL*, **70**, 431 (1948).

(5) Park, Vail, Lea and Lacher, *ibid.*, **70**, 1550 (1948).

(6) McBee and Bolt, *Ind. Eng. Chem.*, **39**, 412 (1947).

(7) Park, Sharrah and Lacher, *THIS JOURNAL*, **71**, 2337 (1949).

(8) Rapp, Pruett, Barr, Bahner, Gibson and Lafferty, *ibid.*, **72**, 3642 (1950).

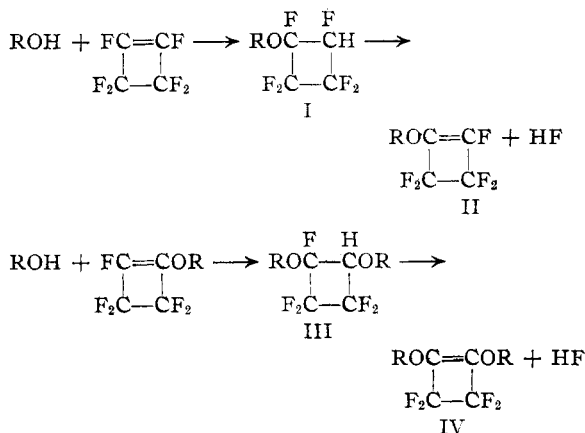
TABLE I
 ALKYL CHLOROTRIFLUOROETHYL ETHERS

Compound	Catalyst, Base	Wt. % ^a	Yield, ^b %	Boiling point, °C.	Mm.	<i>n</i> _D ²⁰	<i>d</i> ₄ ²⁵
CH ₃ OCF ₂ CHClF ^c	NaOCH ₃	6.1	68	68.7	725	1.3315	
C ₂ H ₅ OCF ₂ CHClF ^d	KOH	2.8	47	87.2	725	1.3425	
CH ₂ =CHCH ₂ OCF ₂ CHClF	KOH	8.0	45 ^e	109.2	750	1.3694	1.250
<i>t</i> -C ₄ H ₉ OCF ₂ CHClF	KOC ₄ H ₉	20.1	93	19-20 ^f	50	1.3653	1.1516

^a Weight per cent. of the alcohol-catalyst mixture. ^b Based on the alcohol. ^c Previously prepared by Miller, *et al.*, ref. 4. ^d Previously prepared by Park, *et al.*, ref. 5. ^e Yield lowered by the formation of an azeotrope with unremoved alcohol, b. p. 92°. ^f Melting point -80°.

however, that more moles of polyfluoro ethers were formed than there were moles of base present during the reaction of alcohols with hexafluorocyclobutene. This fact requires that either substitution took place after all the available base had been neutralized, or that the reaction was one of addition, and that subsequent loss of hydrogen fluoride neutralized the catalyst and stopped the reaction. The latter explanation seems far more plausible in view of the fact that no reactions of polyfluoro olefins with hydroxyl groups under neutral or acidic conditions have been reported.

With this in mind, and in view of the fact that it has been shown that alcohols and polyfluoroethylenes react by addition,⁹ it is proposed that the reaction of alcohols and hexafluorocyclobutene is also one of addition, analogous to the action of thiols and amines with this olefin, according to the scheme of reactions



The new type compound II has been isolated and characterized.¹⁰ The elimination of hydrogen fluoride to form the more stable compounds type II and IV is spontaneous at room temperature, and results in the neutralization of the basic catalysts used, stopping further reaction. It is possible to produce predominantly either compound type II or IV by proper choice of catalyst and reaction conditions.

(9) Hurwitz and Miller, "Reactions of Chlorofluoro Olefins with Anionic Reagents," Abstracts of Papers, 114th Meeting of American Chemical Society, Washington, D. C., August 1948, p. 4L.

(10) Proof of structure of the new compounds described will be presented in paper IV of this series, which will deal with the chemical properties of these anionic addition compounds.

 TABLE II
 MONOARYLOXY AND MONO- AND DIALKOXY POLYFLUORO-
 CYCLOBUTENES

Compound	Melting point, °C.	Boiling point, °C.	Mm.	<i>n</i> _D ²⁰	<i>d</i> ₄ ²⁰
CH ₃ OC ₄ F ₈	-42	39.0	114	1.3300	1.426 ²³
(CH ₃ O) ₂ C ₄ F ₈ ^a	-0.5 to 0.0	87.0	747		
		47.4	15	1.3714	1.330 ²³
C ₂ H ₅ OC ₄ F ₈		29.5	36	1.3400	1.3233 ²⁰
		103.2	745		
(C ₂ H ₅ O) ₂ C ₄ F ₈ ^a		61.6	11.5	1.3796	
C ₂ H ₅ OC ₄ F ₈		38-40	0.5 to	1.4294	1.368 ²⁵
			0.6		
2-C ₁₀ H ₇ OC ₄ F ₈	46-47				

^a Previously prepared by Park, *et al.*, ref. 7.

 TABLE III
 ANALYSES OF REACTION PRODUCTS^a

Compound	Carbon, %		Hydrogen, %	
	Calcd.	Found	Calcd.	Found
CH ₂ =CHCH ₂ OCF ₂ CHClF ^b	34.40	33.73	3.47	3.21
<i>t</i> -C ₄ H ₉ OCF ₂ CHClF	37.81	38.23	5.29	5.26
CH ₃ OC ₄ F ₈	34.50	34.01	1.74	2.06
C ₂ H ₅ OC ₄ F ₈	38.31	38.20	2.68	2.64
C ₆ H ₅ OC ₄ F ₈	50.86	50.46	2.13	2.20
2-C ₁₀ H ₇ OC ₄ F ₈	58.75	58.93	2.47	2.59

^a Analyses were performed by Clark Microanalytical Laboratories, Urbana, Illinois, Miss Frances Ball and Mr. R. R. Rickard of the Microchemical Group of the Analytical Research Section and Mr. R. E. Millsbaugh of the Special Analyses Group of the Works Laboratory. ^b Calcd.: Cl, 20.31. Found: Cl, 20.61.

The properties of the butenyl ethers prepared are given in Table II. The alkyl ethers were purified by careful refractionation, and the 1-(2-naphthoxy)-2,3,3,4,4-pentafluorocyclobutene by repeated crystallization from dilute methanol.

There is some disagreement between the constant found here for the dialkoxytetrafluorocyclobutenes, and those reported by Park, *et al.*,⁷ notably in the melting point and *n*_D²⁰ of the dimethoxy compound, which were reported as -5.3° and 1.3690, respectively, and which were found to be -0.5 to 0.0° and 1.3714.

Experimental

Apparatus and Materials.—All reactions were carried out in either a bubble tube similar to that described by Park, Vail, Lea and Lacher⁵ or pressure vessel as previously described.^{1,8}

The chlorotrifluoroethylene was obtained from the K-25 Fluoroethene Plant. Hexafluorocyclobutene was prepared by the method of Rapp and associates.⁸ The methyl alcohol was a product of Carbide and Carbon Chemicals Division, the ethyl alcohol was obtained from Publicker Industries, and the *t*-butyl and allyl alcohols from

Eastman Kodak Company. Phenol was obtained from General Chemicals Company and 2-naphthol from The Coleman and Bell Company.

Chlorotrifluoroethyl Ethers.—Ethyl and allyl chlorotrifluoroethyl ethers were prepared by the method of Park, *et al.*,⁸ which consisted of passing the olefin through a solution of potassium hydroxide in the appropriate alcohol until absorption of the olefin ceased. Methyl and *t*-butyl chlorotrifluoroethyl ethers were prepared in the same apparatus, using as catalysts solutions of the sodium or potassium alkoxide in the corresponding alcohol.

The ethers were recovered by washing out the catalyst and unreacted alcohol with water, after which they were dried over sodium carbonate and distilled at atmospheric pressure to give yields of the indicated boiling ranges: methyl chlorotrifluoroethyl ether, 68%, 67.2–69.0°; ethyl chlorotrifluoroethyl ether, 47%, 87.1–88.0°; and allyl chlorotrifluoroethyl ether, 45%, 109.1–109.2°. The 93% yield given in Table I for *t*-butyl chlorotrifluoroethyl ether is for the crude, washed, dried material.

The *t*-butyl chlorotrifluoroethyl ether proved to be less stable than the *n*-alkyl ethers. Even at reduced pressures the presence of sodium carbonate in the still-pot prevented decomposition only during the early part of the distillation. For this reason only a small part of the material was purified by distillation for the determination of physical properties. A relatively stable material with the same refractive index was obtained by passing the crude material through a small column containing a 1/8-inch layer of Norite A below six inches of activated silica gel. Toward the end of this purification the concentration of the hydrogen fluoride in the Norite layer became great enough to start decomposition, and so the last few fractions were discarded. Once freed of the hydrogen fluoride by this method, the material was stored unchanged for several months in the presence of sodium carbonate and was stable toward aqueous mineral acids at room temperature. It was immediately decomposed by heat or concentrated sulfuric acid to give isobutylene and a mixture of acidic compounds.

The Reaction of Methanol with Hexafluorocyclobutene.

1. Potassium Hydroxide as Catalyst.—A solution of 15 g. of potassium hydroxide (0.27 mole) in 135 g. of methanol was charged into a pressure reactor to which was added 53 g. of hexafluorocyclobutene (0.33 mole). The reactor was allowed to stand overnight at 20°, during which time the pressure fell from 10 to 1 p.s.i. The contents were poured into two volumes of water, and the lower layer was separated, washed and dried. Distillation gave 29.7 g. (0.17 mole) of 1-methoxy-2,3,3,4,4-pentafluorocyclobutene boiling at 35–39° at 112 mm., 52% of the theoretical, based on the amount of hexafluorocyclobutene added, and 8.5 g. (0.046 mole, 12% of theoretical) of 1,2-dimethoxy-3,3,4,4-tetrafluorocyclobutene boiling at 53–55° at 20 mm. A small amount of unreacted butene was recovered during the distillation.

2. Benzyltrimethylammonium Hydroxide as Catalyst.

—One hundred fifty grams of 30% benzyltrimethylammonium hydroxide in methanol, equivalent to 45 g. (0.29 mole) of base, was placed in a 30-inch glass tube, 20 mm. i. d., fitted with a gas dispersion disk in the lower end. One hundred fifty-five grams of hexafluorocyclobutene (0.96 mole) was passed through during the course of 3.5 hours. The rate of addition of the butene was such that absorption was essentially complete at all times. The addition was stopped while the butene was still being absorbed. The reaction mixture was poured into two volumes of water, and the lower layer was separated, washed thoroughly and dried over sodium carbonate. Distillation gave 48 g. (0.28 mole, 29% yield) of 1-methoxy-2,3,3,4,4-pentafluorocyclobutene boiling at 35.5–38° at 110 mm. and 15 g. (0.07 mole, 7.5% yield) of 1,2-dimethoxy-3,3,4,4-tetrafluorocyclobutene boiling at 45.5–47.5° at 15 mm. Upon standing, the sweetish odor of the

diether became masked by the formation of hydrogen fluoride.

From a comparison of these two runs it may be seen that slightly more than 0.26 mole of hydrogen fluoride was formed when methanol and hexafluorocyclobutene reacted in the presence of 0.27 mole of potassium hydroxide, while 0.42 mole of hydrogen fluoride was formed when the same reaction was carried on in the presence of 0.29 mole of benzyltrimethylammonium hydroxide, a weaker base. This would seem to indicate that the relatively unstable saturated addition product can exist for a short time in the presence of weaker bases, allowing these bases to catalyze the formation of a relatively greater amount of the addition product per mole of base. Subsequent splitting out of hydrogen fluoride neutralizes the catalyst and stops the reaction.

The Reaction of Ethanol and Hexafluorocyclobutene.—A mixture of 248 g. of 40% aqueous benzyltrimethylammonium hydroxide and 47 g. of ethanol was sealed in a 500 ml. stainless steel reactor and the reactor was cooled in a Dry Ice-trichloroethylene slush and evacuated. After 98 g. of hexafluorocyclobutene was added by gaseous transfer, the reactor was allowed to stand overnight and then shaken by a mechanical shaker for four hours at 21°. At that time the pressure had fallen from 15 to 5 p.s.i. Unreacted hexafluorocyclobutene (15 g.) was recovered and the liquid contents were removed. The colorless lower layer was separated, washed and placed over calcium chloride. The next morning the material had assumed a red color and emitted clouds of hydrogen fluoride when the bottle was opened. It was again washed and dried, and distilled to give only 32 g. of 1-ethoxy-2,3,3,4,4-pentafluorocyclobutene boiling at 99–103° at 745 mm., a 33% yield based on unrecovered butene, and 2.5 g. of 1,2-diethoxy-3,3,4,4-tetrafluorocyclobutene boiling at 70–72° at 20 mm., a 5% yield.

The Reaction of Phenolic Compounds with Hexafluorocyclobutene.—An ethereal solution of equimolar quantities of triethylamine and 2-naphthol or phenol was charged into a pressure reactor, and slightly more than one molar equivalent of hexafluorocyclobutene was gradually forced in while shaking, keeping the pressure between 0–15 p.s.i. The reactor and contents were allowed to stand overnight, then the ether was removed and the product was recrystallized from dilute methanol or distilled. This procedure gave an 81% yield of 1-(2-naphthoxy)-2,3,3,4,4-pentafluorocyclobutene, a white crystalline solid, and a 67% yield of 1-phenoxy-2,3,3,4,4-pentafluorocyclobutene boiling at 38–40° at 0.5–0.6 mm., a colorless liquid.

Summary

The addition of allyl and *t*-butyl alcohols to chlorotrifluoroethylene and the properties of the resulting chlorotrifluoroethyl ethers are described. The *t*-butyl ether is not as stable as the *n*-alkyl chlorotrifluoroethyl ethers and, because of this, purification by distillation is difficult. A method of purification by adsorption is described.

Alcohols and hexafluorocyclobutene react to give mono- and dialkoxy polyfluorocyclobutenes. By proper choice of catalyst and reaction conditions, it is possible to control the relative amounts of these products. An addition mechanism is proposed for this reaction, and supporting evidence is given.

Only monoaryloxy pentafluorocyclobutenes are obtained from the reaction of phenolic compounds and hexafluorocyclobutene.

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