with iodine vapor for each of the compounds examined. The compounds listed in Table I gave the corresponding R_f values: I (0.39), II (0.36), III (0.42), IV (0.38), V (0.40), VI (0.38), VII (0.39), and VIII (0.34).

The Addition Reactions of Aldehydes, Alcohols, and Ethers to Perfluorocyclobutene

HIROSHIGE MURAMATSU, SOYAO MORIGUCHI,[1]
AND KAN INUKAI

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

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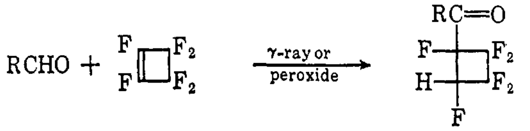
Earlier reports have described the radiation- or peroxide-induced addition reactions of aldehydes,[2] alcohols,[3,4] and ethers[5,6] to chlorofluoroethylenes, 1,2-dichlorotetrafluorocyclobutene, and 1,2-dichlorohexafluorocyclopentene to yield the corresponding 1:1 adducts and the dehydrochlorinated 1:1 adducts. In this paper, these addition reactions were extended further to perfluorocyclobutene to prepare the new ketones, alcohols, and ethers containing 2-hydroperfluorocyclobutyl group, which are the interesting intermediates in the syntheses of the derivatives of polyfluorocyclobutane and polyfluorocyclobutene.

The addition reactions were carried out under irradiation of γ-ray. The same products were obtained in the peroxide-induced addition reaction using *t*-butyl perbenzoate as a catalyst as in the irradiation-induced addition.

Addition Reactions of Aldehydes.—The general reaction is shown in eq 1. The irradiation conditions and yields[7] for each run are listed in Table I.

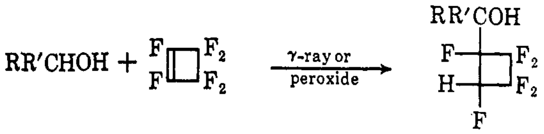


(1)

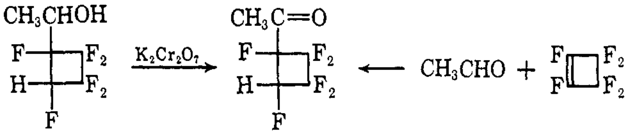
The gas chromatogram of the 1:1 adducts exhibited the presence of *cis* and *trans* form in the 2-hydroperfluorocyclobutyl group. The two stereoisomers were separated by using a preparative gas chromatograph. The physical properties of the 1:1 adducts, 2-hydroperfluorocyclobutyl alkyl ketones, and their 2,4-dinitrophenylhydrazones are shown in Table II.

The distinct difference of the physical properties is found between isomer A and B. While the isomer A has a lower boiling point by about 10° and a smaller retention time compared with isomer B, the melting point of the 2,4-dinitrophenylhydrazone of the isomer A is higher than that of the corresponding isomer B. The specific gravity and refractive index of the isomer A are smaller than those of the isomer B. The infrared spectra of the isomer A showed the C=O absorption band at 1731-1735 cm^{-1}, and those of isomer B at 1739-1742 cm^{-1}. In the proton nmr spectra, absorption bands of the proton in the cyclobutyl group of the isomer A showed a rather simple multiplet due to the coupling with fluorines (τ 4.34-4.38). On the other hand, the corresponding absorption bands of the isomer B exhibited the complicated multiplet (τ 4.61-4.64).

Addition Reactions of Alcohols.—The general reaction is shown in eq 2. The irradiation conditions and yields for each run are listed in Table III. The gas chromatograms of the 1:1 adducts obtained from ethanol and 1-propanol consisted of four peaks, showing the presence of two stereoisomers (*trans* and *cis*) and conformers (*trans* and *gauche*). Their assignment to the A and B isomers was done by comparison of the infrared spectra and retention times (gas chromatogram) of the oxidation products of each stereoisomer with those of the corresponding 1:1 adducts obtained in the addition of aldehydes (for example, eq 3). During the oxidation of each stereoisomer of methyl- or ethyl(2-hydroperfluorocyclobutyl)carbinol with potassium dichromate, no conversion occurred between isomers A and B, yielding only the corresponding pure stereoisomers of the ketone.

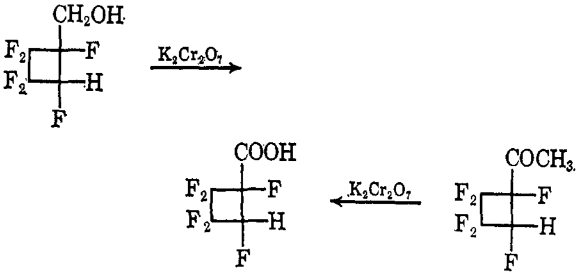


(2)



(3)

The assignment of stereoisomers of the 1:1 adduct of methanol was attempted as shown in eq 4. Though each isomer of the carbinol was converted to the corresponding carboxylic acid with potassium dichromate, oxidation of 2-hydroperfluorocyclobutyl methyl ketone was rather difficult, yielding only a small amount of the carboxylic acid which was found to be a mixture of both stereoisomers. An attempt to oxidize the 1:1 adduct of 2-propanol to get the carboxylic acid was also unsuccessful. Therefore the stereoisomers of 1:1 adducts from methanol and 2-propanol were assigned to isomers A and B from the proton nmr spectra of the acetate of the 1:1 adducts. The physical properties of 2-hydroperfluorocyclobutylalkylcarbinols are shown in Table IV.



(4)

Addition Reactions of Ethers.—While the addition of tetrahydrofuran gave only the 1:1 adduct, dioxane and diethyl ether produced both the 1:1 adduct and

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[1] On leave from the Central Research Laboratory of Showa Denko Co., Tokyo, Japan.

[2] H. Muramatsu and K. Inukai, *J. Org. Chem.*, **27**, 1572 (1962); *Kogyo Kagaku Zasshi*, **65**, 1992 (1962).

[3] H. Muramatsu, *J. Org. Chem.*, **27**, 2325 (1962).

[4] H. Muramatsu, K. Inukai, and T. Ueda, *ibid.*, **30**, 2546 (1965).

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

[6] H. Muramatsu and K. Inukai, *ibid.*, **30**, 544 (1965).

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

Table I

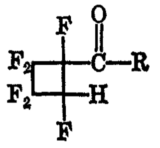
Irradiation Conditions and Yields in Addition of Aldehydes

Aldehyde (moles)	Olefin, mole	Molar ratio of aldehyde/olefin	Irradiation: Time, hr	Irradiation: Total dose, r × 10⁶	Yield of 1:1 adduct: Isomer,[a] % B	Isomer,[a] % A	Total yield, %	B/A
CH_3CHO (2.93)	0.96	3.04	493	8.5	20.3	5.1	25.4	4.0
C_2H_5CHO (1.86)	0.68	2.74	515	8.9	52.1	10.3	62.4	5.1
C_3H_7CHO (2.22)	0.94	2.37	493	8.5	63.4	13.2	76.5	4.8

[a] Isomer A, *cis;* isomer B, *trans.*

Table II

2-Hydroperfluorocyclobutyl Alkyl Ketones



R	Isomer[a]	Bp, °C	$n^{20}D$	d^{20}_4	MR Calcd	MR Found	C, % Calcd	C, % Found	H, % Calcd	H, % Found	F, % Calcd	F, % Found	$\nu_{C=O}$, cm⁻¹	2,4-Dinitrophenylhydrazone Mp, °C	N, % Calcd	N, % Found
CH_3	A	97.5	1.3364	1.471	28.69	29.08	34.97	34.90	1.96	1.50	55.3	55.2	1735	175–176.5	14.51	14.51
	B	115	1.3410	1.498	28.69	28.92	34.97	35.00	1.96	1.83	55.3	54.8	1742	113–113.5	14.51	14.75
C_2H_5	A	116	1.3465	1.400	33.31	33.52	38.20	38.12	2.75	2.85	51.8	51.5	1735	130–131	14.00	13.83
	B	127	1.3539	1.404	33.31	34.08	38.20	38.01	2.75	2.79	51.8	51.6	1742	86.5–88	14.00	13.37
C_3H_7	A	132	1.3549	1.335	37.93	38.22	41.03	40.59	3.44	3.46	48.7	48.5	1731	102–104	13.53	13.38
	B	145	1.3610	1.352	37.93	38.31	41.03	40.70	3.44	3.55	48.7	47.8	1739	95–97	13.53	13.38

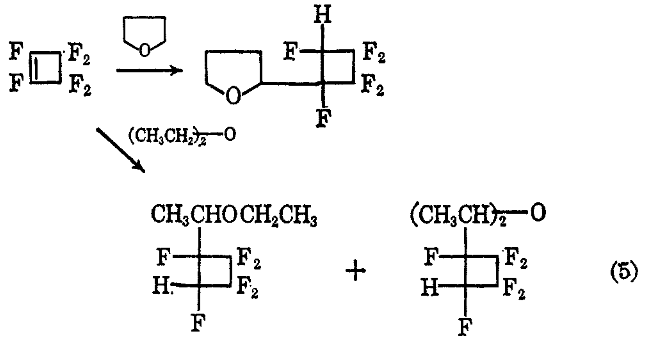
[a] Isomer A, *cis;* isomer B, *trans.*

Table III

Irradiation Conditions and Yields in Addition of Alcohols

Alcohol (moles)	Olefin, moles	Molar ratio of alcohol/olefin	Irradiation: Time, hr	Irradiation: Total dose, r × 10⁷	Peak no.[a] of gas chromatogram	Yield of 1:1 adduct: Isomer,[b] %	Total yield, %	B/A
CH_3OH (3.47)	1.15	3.01	496	2.7	1	B 70.6	84.7	5.0
					2	A 14.1		
C_2H_5OH (3.00)	1.00	3.00	526	2.9	1, 2	B 50.3	69.7	2.6
					3	A 7.7		
					4	A 11.8		
n-C_3H_7OH (2.22)	0.74	2.99	526	2.9	1, 2	B 43.2	67.0	1.8
					3, 4	A 23.8		
i-C_3H_7OH (1.50)	0.49	3.04	438	2.3	1, 2	B, A	79.9	5.0[c]

[a] The peak numbers are assigned in the order of the peak appearance in the gas chromatogram. [b] Isomer A, *cis;* isomer B, *trans.* [c] The ratio was determined from the peak areas in the gas chromatogram of the isomers of 1-(2-hydroperfluorocyclobutyl)-1-methylethylene derived from the carbinol.

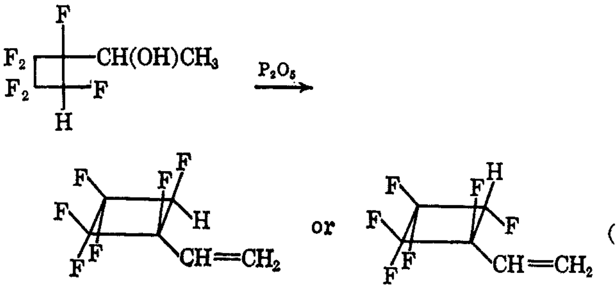


(5)

1:2 adduct (see eq 5). Table V lists the irradiation conditions and yields in the addition reaction of ethers.

The 1:1 adducts were shown to consist of two stereoisomers and conformers as did those obtained in the addition of alcohols. Each stereoisomer was assigned to *cis* or *trans* by using the characteristic absorption bands of the proton of the cyclobutyl group in the nmr spectra. The gas chromatogram of the 1:2 adduct of dioxane or diethyl ether was composed of several overlapped peaks, showing that the adduct was a mixture of stereoisomers and conformers. The physical properties of the 1:1 and 1:2 adduct of ethers are shown in Table VI.

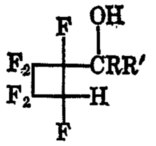
Assignment of Stereoisomers to *cis* and *trans* Forms.—The assignment of isomers A and B to the *cis* and *trans* forms was made by the dipole moments of stereoisomers of 2-hydroperfluorocyclobutylethylene derived from the corresponding isomers of 2-hydroperfluorocyclobutylmethylcarbinol by dehydration with phosphorus pentoxide (eq 6). During dehydration, no isomerization on the cyclobutyl groups was observed. The isomer A of 2-hydroperfluorocyclobutylethylene has a dipole moment of 3.09 D. and the isomer B, 1.76



(6)

TABLE IV

2-HYDROPERFLUOROCYCLOBUTYLALKYLCARBINOLS

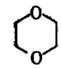


R	R′	Peak no. of gas chromatogram	Isomer[a]	Bp, °C	$n^{20}D$	d^{20}_4	MR Calcd	MR Found	C, % Calcd	C, % Found	H, % Calcd	H, % Found	F, % Calcd	F, % Found
H	H	1	B	127.5	1.3442	1.625	25.58	25.31	30.94	30.81	2.08	2.12	58.7	59.3
		2	A	140.5	1.3498	1.624	25.58	25.71	30.94	30.75	2.08	2.06	58.7	57.9
CH_3	H	1, 2	B	133[b]					34.63	34.31	2.91	3.13	54.8	55.3
		3	A	137.5	1.3552	1.496	30.20	30.33	34.63	34.52	2.91	2.80	54.8	53.9
		4	A	144[c]					34.63	34.60	2.91	2.95	54.8	55.2
C_2H_5	H	1, 2	B	144.5	1.3636	1.433	34.82	34.51	37.85	37.89	3.63	3.75	51.3	51.2
		3	A	152	1.3662	1.419	34.82	35.09	37.85	37.75	3.63	3.80	51.3	50.4
		4	A	162	1.3681	1.425	34.82	35.11	37.85	37.62	3.63	3.62	51.3	50.4
CH_3	CH_3	1, 2	B, A	135.5	1.3632	1.436	34.82	34.41	37.85	37.65	3.63	3.57	51.3	52.1

[a] Isomer A, *cis;* isomer B, *trans.* [b] Mp 35–42°. [c] Mp 48–50.5°.

TABLE V

IRRADIATION CONDITIONS AND YIELDS IN ADDITION OF ETHERS

Ether (mole)	Olefin, mole	Molar ratio of ether/olefin	Irradiation Time, hr	Irradiation Total dose, r × 10^7	Peak no.[a] of gas chromatogram	Yield of 1:1 adduct Isomer,[b] %	Yield of 1:1 adduct Total yield, %	B/A	Yield of 1:2 adduct, %
 (0.93)	0.34	2.74	321	1.7	1, 2	B 72.1	76.3	17	
					3	A 4.2			
 (0.93)	0.33	2.78	321	1.7	1	B 15.5	80.1	4	8.6
					2	B 48.7			
					3	A 6.9			
					4	A 9.0			
$CH_3CH_2)_2O$ (0.92)	0.30	3.09	321	1.7	1	B 20.4	67.9	8	21.6
					2	B 39.9			
					3	A 3.0			
					4	A 4.6			

[a] The peak numbers are assigned in the order of the peak appearance of gas chromatogram. [b] Isomer A, *cis;* isomer B, *trans.*

D. These results show that isomer A should be *cis* and isomer B *trans.*

Experimental Section[8]

Additions of Aldehydes to Perfluorocyclobutene.—A mixture of 129 g (2.93 moles) of acetaldehyde and 156 g (0.96 mole) of perfluorocyclobutene was sealed in a glass tube and irradiated to a total dosage of 8.5 × 10^6 r for a period of 493 hr. Distillation of the irradiation products, after the removal of the unchanged aldehyde and olefin, gave 55 g of a distillate, bp 82–110°, which was found to be a mixture of crotonaldehyde (retention time,[9] 7 min) and *trans* (5.5 min) and *cis* (3 min) isomers of 2-hydroperfluorocyclobutyl methyl ketone. Their yields were determined from the areas of a gas chromatogram. Crotonaldehyde yielded 4.7 g (0.067 mole), the *cis* isomer of 2-hydroperfluorocyclobutyl methyl ketone 10.0 g (0.049 mole, 5.1% yield), and the *trans* isomer 40.3 g (0.196 mole, 20.3% yield). Each product was separated by using a preparative gas chromatograph. Boiling points of the products were measured using a micro boiling point tube.[10] The 2,4-dinitrophenylhydrazones of the ketones obtained were prepared by a conventional procedure.[11]

The addition reactions of propionaldehyde and *n*-butyraldehyde were carried out under the similar conditions and treated the same way as mentioned above.

Additions of Alcohols to Perfluorocyclobutene.—In a glass tube were sealed 111 g (3.47 moles) of methanol and 187 g (1.15 moles) of perfluorocyclobutene. The contents of the tube was irradiated to a total dosage 2.7 × 10^7 r for 496 hr. Distillation of the reaction mixture yielded 189.6 g (0.98 mole, 84.7% yield) of 2-hydroperfluorocyclobutylcarbinol, bp 69–71.5° (80 mm), whose gas chromatogram showed two peaks, those of the *trans* isomer (retention time,[12] 3.5 min) and of the *cis* isomer (5.5 min). The yields of the two isomers were calculated from the areas of the peaks and the *trans* isomer was obtained in a yield of 70.6% and the *cis* isomer, 14.1%.

Using the same procedure, ethanol and 1- and 2-propanol were added to perfluorocyclobutene.

Additions of Ethers to Perfluorocyclobutene.—A mixture of 68.5 g (0.92 mole) of diethyl ether and 48.5 g (0.30 mole) of perfluorocyclobutene was irradiated to a total dosage of 1.7 × 10^7 r for 321 hr. Distillation of the irradiation products gave 48.0 g (0.20 mole, 67.9% yield) of α-(2-hydroperfluorocyclobutyl)-diethyl ether, bp 50–64° (80 mm), and 12.8 g (0.032 mole, 21.6% yield) of α,α′-bis(2-hydroperfluorocyclobutyl)diethyl ether. The gas chromatogram of the 1:1 adduct had four peaks and each component was isolated by using a preparative gas chromatograph.

Oxidation of Alkyl(2-hydroperfluorocylobutyl)carbinols.—A mixture of 0.5 g of the *trans* isomer of methyl(2-hydroperfluorocyclobutyl)carbinol, 0.7 g of potassium dichromate, 0.5 g of concentrated sulfuric acid, and 2 ml of water was stirred at about 90° for 6 hr. The mixture was extracted with diethyl ether. After removal of the ether, 0.4 g of a residue remained. Infrared spectral analysis and gas chromatography of the residue showed that the product was the mixture of the unchanged carbinol and the *trans* isomer of 2-hydroperfluorocyclobutyl methyl ketone, which was prepared in the addition of acetalde-

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[8] All temperature readings are uncorrected.

[9] A Hitachi-KGL-2 was employed using helium as the carrier gas at a flow rate of 60 cc/min and a column temperature of 63°; a 2-m column packed with 25% silicone DC-550 was used.

[10] R. L. Shriner, R. C. Fuson, and D. Y. Curtin, "The Systematic Identification of Organic Compounds," 4th ed, John Wiley and Sons, Inc., New York, N. Y., 1956, p 32.

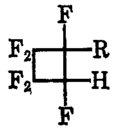
[11] Reference 10, p 219.

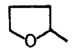
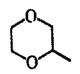
[12] Flow rate of helium, 50 cc/min; column temperature, 82.5°.

Table VI

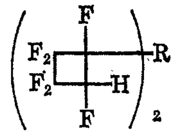
Ethers Containing 2-Hydroperfluorocyclobutyl Group

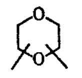
The 1:1 Adduct:



R	Peak no. of gas chromatogram	Isomer[a]	Bp, °C	n^{20}_D	d^{20}_4	MR Calcd	MR Found	C, % Calcd	C, % Found	H, % Calcd	H, % Found	F, % Calcd	F, % Found
	1, 2	B	156	1.3740	1.446	37.36	36.98	41.03	40.81	3.44	3.46	48.7	48.3
	3	A	166	1.3759	1.442	37.36	37.26	41.03	40.90	3.44	3.40	48.7	48.3
	1	B	169.5	1.3823	1.500	39.00	38.84	38.41	38.60	3.22	3.32	45.6	45.9
	2	B	172.5[b]					38.41	38.38	3.22	3.10	45.6	45.4
	3	A	177.5	1.3821	1.498	39.00	38.86	38.41	38.55	3.22	3.25	45.6	44.5
	4	A	182[c]					38.41	38.30	3.22	3.20	45.6	45.5
$CH_3\underset{\vert}{C}HOCH_2CH_3$	1	B	126	1.3495	1.295	39.56	39.21	40.68	40.62	4.27	4.25	48.3	48.8
	2	B	130	1.3509	1.297	39.56	39.26	40.68	40.60	4.27	4.23	48.3	48.6
	3	A	140.5	1.3541	1.319	39.56	38.94	40.68	40.71	4.27	4.15	48.3	47.9
	4	A	150	1.3541	1.339	39.56	38.36	40.68	40.65	4.27	4.25	48.3	48.2

The 1:2 Adduct:



R	Bp, °C (mm)	n^{20}_D	d^{20}_4	MR Calcd	MR Found	F, % Calcd	F, % Found	Mol wt Calcd	Mol wt Found
	93–93.5 (15)	1.3801	1.637	56.24	58.33	55.3	54.4	412	414
$CH_3\underset{\vert}{C}HO\underset{\vert}{C}HCH_3$	102–104 (25)	1.3565	1.539	56.80	56.61	57.3	57.6	398	395

[a] Isomer A, *cis;* isomer B, *trans.* [b] Mp 36–37°. [c] Mp 82–84°.

hyde. In the product of oxidation reaction, no *cis* isomer of 2-hydroperfluorocyclobutyl methyl ketone was detected.

In a similar way, the *cis* isomer of the carbinol was oxidized to give only the *cis* isomer of the corresponding ketone.

Oxidation of 2-Hydroperfluorocyclobutylcarbinol.—A mixture of 29 g (0.15 mole) of the *trans* isomer of 2-hydroperfluorocyclobutylcarbinol, 44 g (0.15 mole) of potassium dichromate, 30 g of concentrated sulfuric acid, and 150 ml of water was stirred at 60–80° for 3 hr. The mixture was extracted with diethyl ether. The extract was dried and distilled to give 25.5 g (0.12 mole, 82% yield) of the crude *trans* isomer of 2-hydroperfluorocyclobutanecarboxylic acid, bp 75–77.5° (17 mm). When the distillate was allowed to remain at room temperature, white needle crystals precipitated, which were filtered and recrystallized from benzene; mp 47–48°.

Anal. Calcd for $C_5H_2F_6O_2$: C, 28.86; H, 0.97; F, 54.8. Found: C, 28.41; H, 1.05; F, 52.8.

Acylation of 2-Hydroperfluorocyclobutylcarbinol.—To a mixture of 27 g (0.14 mole) of the *trans* isomer of the carbinol and 16.5 g (0.21 mole) of pyridine, 16.5 g (0.21 mole) of acetyl chloride was added dropwise at room temperature for 5 min. The reaction mixture was poured into water. An organic layer was separated, dried, and distilled to give 29 g (0.12 mole, 88% yield) of the *trans* isomer of (2-hydroperfluorocyclobutyl)methyl acetate, bp 146–148°, n^{20}_D 1.3528, d^{20}_4 1.461.

Anal. Calcd for $C_7H_6F_6O_2$: C, 35.61; H, 2.56; F, 48.3; MR, 34.95. Found: C, 35.70; H, 2.45; F, 48.5; MR, 35.04.

The *cis* isomer of the carbinol was treated with acetyl chloride as mentioned above to yield the *cis* isomer of (2-hydroperfluorocyclobutyl)methyl acetate, bp 160.5–163°, n^{20}_D 1.3574, d^{20}_4 1.462.

Anal. Calcd for $C_7H_6F_6O_2$: C, 35.61; H, 2.56; F, 48.3; MR, 34.95. Found: C, 35.67; H, 2.40; F, 48.1; MR, 34.95.

Acylation of 2-Hydroperfluorocyclobutyldimethylcarbinol.—Fifteen grams (0.19 mole) of acetyl chloride was added dropwise to 6.9 g (0.031 mole) of 2-hydroperfluorocyclobutyldimethylcarbinol in 8 g (0.10 mole) of pyridine for 5 min. The reaction mixture was heated at about 40° for 8 hr and poured into water. An organic layer was separated and 4.9 g (0.019 mole, 60% yield) of 1-methyl-1-(2-hydroperfluorocyclobutyl)ethyl acetate was obtained. The *trans* and *cis* isomers of the acetate were separated by a preparative gas chromatograph. The physical properties of the isomer are as follows: *trans* isomer, bp 157.5°, n^{20}_D 1.3668, d^{20}_4 1.353 (*Anal.* Calcd for $C_9H_{10}F_6O_2$: C, 40.92; H, 3.82; F, 43.2; MR, 44.19. Found: C, 40.57; H, 3.68; F, 43.5; MR, 43.81); *cis* isomer, bp 166°, n^{20}_D 1.3667, d^{20}_4 1.346 (*Anal.* Calcd for $C_9H_{10}F_6O_2$: C, 40.92; H, 3.82; F, 43.2; MR, 44.19. Found: C, 40.81; H, 3.40; F, 43.3; MR, 44.03.).

Dehydration of Ethyl(2-hydroperfluorocyclobutyl)carbinol.—To 31 g (0.22 mole) of phosphorus pentoxide was added dropwise 29 g (0.14 mole) of the *trans* isomer of ethyl(2-hydroperfluorocyclobutyl)carbinol for 30 min. A reaction mixture was refluxed for 4 hr and distilled. The distillate was washed with sodium bicarbonate solution and dried with anhydrous sodium sulfate. Fractionation of the product yielded 16 g (0.084 mole, 60% yield) of the *trans* isomer of 2-hydroperfluorocyclobutylethylene, bp 63.5–65°, n^{20}_D 1.3303, d^{20}_4 1.358.

Anal. Calcd for $C_6H_4F_6$: C, 37.91; H, 2.12; F, 60.0; MR, 28.21. Found: C, 37.55; H, 2.05; F, 59.7; MR, 28.57.

The *cis* isomer of the carbinol was dehydrated using the same procedure. The *cis* isomer of 2-hydroperfluorocyclobutylethylene had the following physical properties: bp 86.5–88°, n^{20}_D 1.3348, d^{20}_4 1.378.

Anal. Calcd for $C_6H_4F_6$: C, 37.91; H, 2.12; F, 60.0; MR, 28.21. Found: C, 37.95; H, 2.00; F, 59.8; MR, 28.51.

The dipole moment[13] of the isomer was calculated from the dielectric constants of carbon tetrachloride solutions and found to be *trans* 1.76 D. and *cis* 3.09 D., respectively.

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