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The Preparation of Ethylenes with Polyfluorocyclobutenyl and Polyfluorocyclopentenyl Groups

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The new ethylenes, with a 2-hydroperfluorocyclobutyl, 2-chlorotetrafluoro-1-cyclobutenyl or 2-chlorohexafluoro-1-cyclopentenyl group, were synthesized in good yields by the dehydration of the 1 : 1 adducts prepared by the addition of the alcohols to perfluorocyclobutene, 1, 2-dichlorotetrafluorocyclobutene or 1, 2-dichlorohexafluorocyclopentene respectively. The dehydrofluorination of 2-hydroperfluorocyclobutylalkylethylenes gave a mixture of perfluoro-1-cyclobutenyl- and perfluoro-2-cyclobutenylethylene. In the mixture, the former was predominant over the latter. Some polyfluorocycloalkenylethylenes prepared polymerized in the presence of peroxide to yield transparent polymers.

Several ethylenes containing polyfluorocyclobutenyl groups have been synthesized, mainly by the cycloaddition of fluoroolefin with conjugated enyne[1] or diene[2], followed by dehydrohalogenation. No papers have, however, been published on the syntheses of polyfluorocyclopentenyl ethylenes.

In a previous report,[3] the radiation-induced addition reactions of alcohols to perfluorocyclobutene were found to produce the corresponding

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[1] D. D. Coffman, P. L. Barrick, R. D. Cramer and M. S. Raasch, *J. Am. Chem. Soc.*, **71**, 490 (1949).

[2] J. D. Park and W. C. Frank, *J. Org. Chem.*, **29**, 1445 (1964).

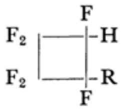
[3] H. Muramatsu, S. Moriguchi and K. Inukai, ibid., **31**, 1306 (1966).

TABLE I. THE DEHYDRATION OF 2-HYDROPERFLUOROCYCLOBUTYLALKYLCARBINOLS (I)

Carbinol				P_2O_5	Ethylene		
R	R′	g.	*trans*/*cis*[a]	g.	g.	Yield, %	*trans*/*cis*[a]
H	H	215.9	2.7	225	140	71	2.3
H	CH_3	315.0	1.6	312	183.9	63	1.8
CH_3	H	81.0		78	58.5	79	5.0

a) *Trans* and *cis* forms in the halocyclobutyl group.

TABLE II. (2-HYDROPERFLUOROCYCLOBUTYL)ETHYLENES,



R	B. p. °C	n_D^{20}	d_4^{20}	F, % Found	F, % Calcd.	$\nu_{C=C}$ μ
			Trans form[a]			
$-CH=CH_2$[3]	63.5	1.3303	1.358	59.7	60.0	6.06
$-C(CH_3)=CH_2$	91	1.3460	1.340	56.2	55.9	6.05
$-CH=CHCH_3$ *trans*	92	1.3454	1.324	55.8	55.9	5.98
cis	93.5	1.3458	1.321	56.0	55.9	5.98
$-CH_2CH=CH_2$	89.5	1.3429	1.320	55.9	55.9	6.07
			Cis form[a]			
$-CH=CH_2$[3]	86.5	1.3348	1.378	59.8	60.0	6.00
$-C(CH_3)=CH_2$	105.5	1.3500	1.319	56.0	55.9	6.03
$-CH=CHCH_3$ *trans*	116.5	1.3514	1.332	55.5	55.9	5.98
cis	118	1.3530	1.337	55.0	55.9	5.98
$-CH_2CH=CH_2$	110	1.3482	1.325	55.8	55.9	6.08

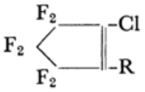
a) In the halocyclobutyl group.

TABLE III. (2-CHLOROTETRAFLUORO-1-CYCLOBUTENYL)ETHYLENES,

R	B. p. °C	n_D^{20}	d_4^{20}	F, % Found	F, % Calcd.	Cl, % Found	Cl, % Calcd.	$\nu_{C=C}$,[a] μ
$-CH=CH_2$	104	1.4030	1.350	41.0	40.7	20.3	19.0	6.03, 6.19
$-C(CH_3)=CH_2$	126	1.4155	1.321	37.7	37.9	18.3	17.7	6.10, 6.18
$-CH=CHCH_3$[b]	131	1.4249	1.316	37.9	37.9	17.6	17.7	6.00, 6.21,[c] 6.27[d]

a) The first absorption bands are due to the C=C of the cyclobutenyl groups and second bands due to the C=C of the ethylenes.
b) A mixture of *trans* and *cis* form.
c) *Trans.*
d) *Cis.*

TABLE IV. (2-CHLOROHEXAFLUORO-1-CYCLOPENTENYL)ETHYLENES,



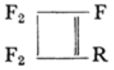
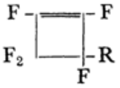
R	B. p. °C	n_D^{20}	d_4^{20}	F, % Found	F, % Calcd.	Cl, % Found	Cl, % Calcd.	$\nu_{C=C}$,[a] μ
$-CH=CH_2$	121	1.3983	1.490	48.7	48.2	15.2	15.0	6.09, 6.26
$-C(CH_3)=CH_2$	132	1.3968	1.428	44.3	45.5	14.3	14.2	6.14, 6.25
$-CH=CHCH_3$ *trans*	152	1.4185	1.438	46.0	45.5	14.2	14.2	6.05, 6.23
cis	138	1.3986	1.418	45.8	45.5	13.7	14.2	6.09, 6.30
$-CH_2CH=CH_2$	134	1.3872	1.414	46.5	45.5	14.2	14.2	6.04, 6.09

a) The first absorption bands are due to the C=C of the cyclopentenyl groups and the second bands due to the C=C of the ethylenes.

TABLE V. THE DEHYDROFLUORINATION OF 2-HYDROPERFLUOROCYCLOBUTYLETHYLENES (IV)

Ethylene			KOH	Products			
R	R′	g.	g.	V, g.	VI, g.	V/VI	Total yield, %
H	H	90	87	17.8	5.8	3.1	29
H	CH_3	31	34	12.6	3.7	3.4	58
CH_3	H	81.5	40.5	21.7	3.0	7.2	49

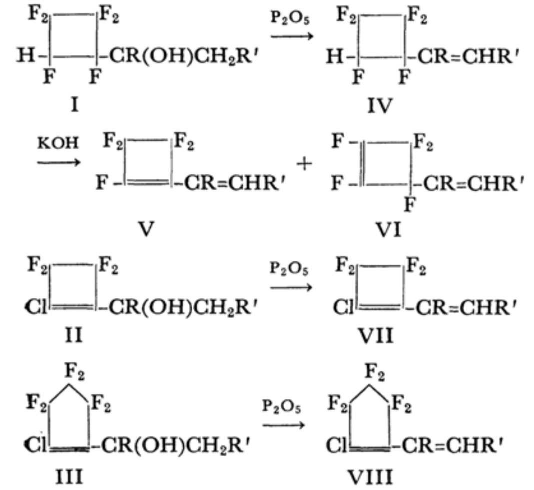
TABLE VI. (PERFLUOROCYCLOBUTENYL)ETHYLENES

R	B. p. °C	n_D^{20}	d_4^{20}	F, % Found	F, % Calcd.	$\nu_{C=C}$,[a] μ
						
$-CH=CH_2$	68	1.3558	1.304	55.7	55.9	5.84, 6.20
$-C(CH_3)=CH_2$	92	1.3698	1.260	51.4	51.6	5.87, 6.16
$-CH=CHCH_3$	105	1.3820	1.262	50.5	51.6	5.83, 6.11
						
$-CH=CH_2$	58	1.3382	1.311	56.4	55.9	5.60
$-C(CH_3)=CH_2$	76	1.3554	1.242	51.2	51.6	5.60, 5.81
$-CH=CHCH_3$	89	1.3579	1.265	51.0	51.6	5.59, 5.78

a) The first absorption bands are due to the C=C of the cyclobutenyl groups and the second bands due to the C=C of the ethylenes.

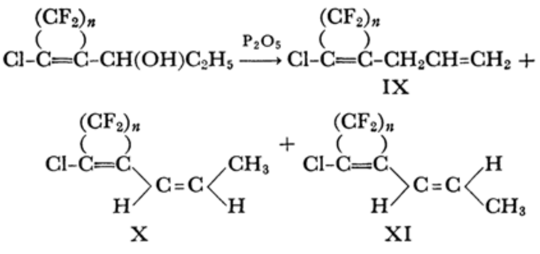
1 : 1 adducts, the carbinols with a 2-hydroperfluorocyclobutyl group (I). Similar additions of alcohols to 1, 2-dichlorotetrafluorocyclobutene or 1, 2-dichlorohexafluorocyclopentene[4] gave mainly the dehydrochlorinated 1 : 1 adducts, 2-chloro-3,3,4,4-tetrafluoro-1-cyclobutenylcarbinol (II) and 2-chloro-3, 3, 4, 4, 5, 5-hexafluoro-1-cyclopentenylcarbinol (III) respectively.

By the dehydration of these 1 : 1 adducts with phosphorus pentoxide, new ethylenes, with polyfluorocyclobutyl (IV), polyfluorocyclobutenyl (VII), or polyfluorocyclopentenyl (VIII) groups, were prepared in good yields.



(R, R′=H or CH_3)

Since the (2-hydroperfluorocyclobutyl)alkylcarbinol (I) two stereoisomers[5] (the *trans* and *cis* forms in the halocyclobutyl group), the product, (2-hydroperfluorocyclobutyl)ethylene (IV), was a mixture of the *trans* and *cis* forms. In the dehydration of the *cis* or *trans* form of (2-hydroperfluorocyclobutyl)ethylcarbinol, the proton rearrangement was observed, yielding a mixture of three isomers in each case. The proton rearrangement occured also in the dehydration of (2-chlorotetrafluoro-1-cyclobutenyl)- or (2-chlorohexafluoro-1-cyclopentenyl)ethylcarbinol.



(n=2 or 3)

The compositions of the isomers, IX, X, and XI, were calculated from the areas under each peak of the gas chromatograms of the products; they

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

[5] The stereoisomers were assigned to the *trans* and *cis* form from the dipole moment of the isomers of 2-hydroperfluorocyclobutylethylene, which were derived from 2-hydroperfluorocyclobutylmethylcarbinol. See Ref. 3.

were found to be 6%, 5%, and 89% in the case of the chlorotetrafluorocyclobutenylcarbinol and 9%, 13%, and 78% in the case of the chlorohexafluorocyclopentenylcarbinol respectively. The structures of the isomers were determined from their infrared spectra.

The conditions and yields for the dehydration of I are summarized in Table I. Each stereoisomer was isolated by a Shimadzu 10A preparative gas chromatograph. The physical properties of the (2-hydroperfluorocyclobutyl)ethylene (IV), (2-chlorotetrafluoro-1-cyclobutenyl)ethylene (VII), and (2-chlorohexafluoro-1-cyclopentenyl)ethylene (VIII) are shown in Tables II, III, and IV respectively. The *cis* form of 2-hydroperfluorocyclobutylethylene has a boiling point higher by about 20°C than the *trans* form.

The dehydrofluorination of (2-hydroperfluorocyclobutyl)ethylenes was accomplished using powdered potassium hydroxide; this gave two isomers, (perfluoro-1-cyclobutenyl)ethylene (V) and (perfluoro-2-cyclobutenyl)ethylene (VI). The isomer V, which has the conjugated double bonds, was predominant over the isomer VI. The conditions for dehydrofluorination and the physical properties of the (perfluorocyclobutenyl)ethylenes prepared are summarized in Tables V and VI respectively.

The peroxide-induced polymerization was attempted on these ethylenes. Only the ethylenes which have a $-CH=CH_2$ group conjugated with the double bond in the halocycloalkenyl group were found to be polymerized to give the transparent polymers.

Experimental[6]

The Dehydration of the (2-Hydroperfluorocyclobutyl)alkylcarbinols. — To 312 g. (2.18 mol.) of phosphorus pentoxide in a flask with a reflux condenser there was added, drop by drop, 315 g. (1.42 mol.) of (2-hydroperfluorocyclobutyl)ethylcarbinol (a mixture of the *trans* and *cis* in a molar ratio of 1.6 : 1.0) over a 2 hr. period. The reaction mixture was then heated to reflux for 3 hr. and distilled. Since a gas chromatogram[7] of the distillate has six peaks, the compounds of each peak were isolated using preparative gas chromatography. The stereoisomer was assigned on the basis of the products obtained in the dehydration of the clean *trans* or *cis* form of the carbinol. During dehydration, no conversion between the *trans* and *cis* forms was observed. The structures of the isomers were determined from elemental analyses and from a study of their infrared spectra. Thus, the products were 35.5 g. of the *trans* form of 3-(2-hydroperfluorocyclobutyl)-1-propene (retention time, 3.0 min.), 83.7 g. of the *trans* form of 1-(2-hydroperfluorocyclobutyl)-1-propene (a mixture of the *trans* and *cis* forms in a double bond; retention times, 3.6 and 3.8 min. respectively), 19.4 g. of the *cis* form of 3-(2-hydroperfluorocyclobutyl)-1-propene (retention time, 5.3 min.), and 45.5 g. of the *cis* form of 1-(2-hydroperfluorocyclobutyl)-1-propene (a mixture of the *trans* and *cis* forms in a double bond; retention times, 6.8 and 8.1 min. respectively). Upon standing at room temperature, the isolated *cis* forms (in a double bond) gradually changed to the *trans* forms.

Other (2-hydroperfluorocyclobutyl)alkylcarbinols were dehydrated under similar conditions; they are shown in Table I.

The Dehydration of the (2-Chloro-3, 3, 4, 4-tetrafluoro-1-cyclobutenyl)carbinols. — To 24.7 g. (0.17 mol.) of phosphorus pentoxide there was added, drop by drop, 23.1 g. (0.11 mol.) of the halocyclobutenylmethylcarbinol. A reaction mixture was then heated in an oil bath at about 130°C for 20 min. and distilled. The distillation of the product gave 13.8 g. (0.074 mol., 65% yield) of 2-chloro-3, 3, 4, 4-tetrafluoro-1-cyclobutenylethylene, b. p. 103—104°C.

Under similar conditions, the reaction of 29.2 g. (0.21 mol.) of phosphorus pentoxide and 30.0 g. (0.14 mol.) of the halocyclobutenyldimethylcarbinol yielded 16.6 g. (0.083 mol., 60% yield) of 2-(2-chloro-3, 3, 4, 4-tetrafluoro-1-cyclobutenyl)-1-propene. In the dehydration of the halocyclobutenylethylcarbinol (12.8 g., 0.059 mol.) with phosphorus pentoxide (12.5 g., 0.088 mol.), 8.9 g. (0.048 mol.; 82% yield) of the products were obtained. The products were found from gas chromatogram[8] to be a mixture of three isomers, 3-(2-chloro-3, 3, 4, 4-tetrafluoro-1-cyclobutenyl)-1-propene (retention time, 3.5 min.), the *cis* form (4.3 min.), and the *trans* form (6.3 min.) of 1-(2-chloro-3, 3, 4, 4-tetrafluoro-1-cyclobutenyl)-1-propene. The products were fractionated in order to separate a mixture of the *cis* and *trans* isomers. Though not each isomer was isolated, their structures were determined from the infrared spectra.

The physical properties and analyses of the ethylenes containing 2-chlorotetrafluoro-1-cyclobutenyl group are listed in Table III.

The Dehydration of the (2-Chloro-3, 3, 4, 4, 5, 5-hexafluoro-1-cyclopentenyl)carbinols.—A mixture of 52 g. (0.20 mol.) of the halocyclopentenylmethylcarbinol and 43.5 g. (0.31 mol.) of phosphorus pentoxide was heated at about 135°C for 35 min. and then distilled to give 42.5 g. (0.18 mol.; 88% yield) of 2-chloro-3, 3, 4, 4, 5, 5-hexafluoro-1-cyclopentenylethylene, b. p. 119—121°C. Using the same procedure, 32.5 g. (0.12 mol.) of the halocyclopentenyldimethylcarbinol was reacted with 25.8 g. (0.18 mol.) of phosphorus pentoxide to yield 26.6 g. (0.11 mol.; 88% yield) of 2-(2-chloro-3, 3, 4, 4, 5, 5-hexafluoro-1-cyclopentenyl)-1-propene.

The dehydration of 31.0 g. (0.12 mol.) of the halocyclopentenylethylcarbinol with 24.6 g. (0.17 mol.) of phosphorus pentoxide gave 25.5 g. (0.10 mol.; 83% yield) of the products, which were found to consist of three isomers, 3-(2-chloro-3, 3, 4, 4, 5, 5-hexafluoro-1-cyclopentenyl)-1-propene (retention time,[9] 3.0 min.),

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6) All temperature readings are uncorrected.

7) A Hitachi-KGL-2 was employed using helium carrier gas at flow rate of 60 ml./min. and column temperature of 64°C; 2 m. of column packed with 25% Silicone DC-550 was used.

8) The same conditions as Ref. 7 except a helium flow rate 55 ml./min.; column temperature, 93°C.

9) A helium flow rate 50 ml./min.; column temperature 98°C.

the *cis* form (3.9 min.), and the *trans* form (5.9 min.) of 1-(2-chloro-3, 3, 4, 4, 5, 5-hexafluoro-1-cyclopentenyl)-1-propene. The isomers were separated by preparative gas chromatography, and their structures were determined from their infrared spectra.

The physical properties and analyses of the ethylenes containing 2 - chloro-3, 3, 4, 4, 5, 5-hexafluoro-1-cyclopentenyl group are shown in Table IV.

The Dehydrofluorination of (2-Hydroperfluorocyclobutyl)ethylenes.—To 87 g. (1.55 mol.) of powdered potassium hydroxide there was added 90 g. (0.47 mol.) of (2-hydroperfluorocyclobutyl)ethylene. The reaction mixture was then heated under reflux for 1 hr. and distilled. The gas chromatogram of the distillate (23.6 g., 0.14 mol., 29% yield) had two peaks, showing the existence of two isomers. They were isolated by preparative gas chromatography and found to be perfluoro-1-cyclobutenylethylene and perfluoro-2-cyclobutenylethylene from their elemental analyses and from a study of their infrared spectra. The perfluoro-1-cyclobutenylethylene was readily polymerized upon standing in the air.

Other (2-hydroperfluorocyclobutyl)ethylenes, dehydrofluorinated under similar conditions, are summarized in Table V.

The Peroxide-Induced Polymerization of the Halocyclobutenylethylene and Halocyclopentenylethylene.—2-Chloro-3, 3, 4, 4-tetrafluoro-1-cyclobutenylethylene (2 g.) and benzoyl peroxide (0.1 g.) were placed in a glass tube. The tube was then sealed and kept at 100°C for 3 hr. The ethylene polymerized to give a transparent solid. Upon heating, the polymer (0.8 g.) was dissolved in *o*-chlorobenzotrifluoride (7 ml.), and the solution was poured into methanol (80 ml.). The polymer thus precipitated (0.6 g.) was washed with methanol and dried. In its infrared spectrum, the absorption bands of 3.23 (=CH_2), 3.30 (=CH–), and 6.19 μ (C=C) in the ethylene disappeared, and a band due to the C=C stretching in the halocyclobutenyl group shifted from 6.03 μ to 6.07 μ.

In a similar procedure, 2-chloro-3, 3, 4, 4, 5, 5-hexafluorocyclopentenylethylene was polymerized in the presence of benzoyl peroxide to give a transparent solid. The polymer was dissolved in trifluorotrichloroethane and precipitated in methanol. The absorption bands of 3.205 (=CH_2), 3.29 (=CH–), and 6.26 μ (C=C) in the ethylene disappeared, and a band due to C=C stretching in the halocyclopentenyl group shifted from 6.09 μ to 6.11 μ.

In a similar way, (perfluoro-1-cyclopentenyl)ethylene was polymerized to give a pale brown solid. The polymer was dissolved in acetone and precipitated in methanol. The absorption bands of 3.205 (=CH_2) and 6.20 μ (C=C) in the ethylene disappeared, and a band due to C=C stretching in the perfluorocyclobutenyl group shifted from 5.84 μ to 5.81 μ.