Chlorocyanoacetylene and Cyanoacetylene.—The pyrolysis apparatus was the same as that used for the copyrolysis of acetonitrile and carbon tetrachloride, with a slight modification.[1a] The whole system was evacuated with an aspirator while the sample was fed by the leak method. The reaction product, most of which condensed as a crystalline mass in the first trapping tube, was dissolved in tetrachloroethylene and analyzed by gas chromatography. The column was SE-30 (10%) or TCP (10%) on Chromosorb W. The temperature of the column was 65°. Typical results are shown in Table I.

Malononitrile. General Procedure.—Four grams of chlorocyanoacetylene was dissolved in a solvent and the solution was placed in a four-necked flask equipped with a thermometer, an inlet tube for ammonia, a reflux condenser, and a mechanical stirrer. With efficient stirring, a stream of gaseous ammonia was introduced directly into this solution. The rate of feeding ammonia was *ca.* 100 ml/min, which corresponded to the rate of consumption of *ca.* 0.2 g of chlorocyanoacetylene/min. When the inside temperature reached 30°, cooling was started in order to maintain this temperature during the reaction period. After ammonia had been introduced into the reaction mixture for 20 min, the precipitated NH$_4$Cl was filtered off and most of the solvent was evaporated. A small amount of water was added and the solution was extracted with benzene. The combined benzene extract was washed, dried (Na$_2$SO$_4$), and evaporated to leave the reaction product, which was almost pure malononitrile, which, in most cases, crystallized when it was cooled to room temperature. The product obtained was further purified by distillation under reduced pressure. The yield of malononitrile was 60–87%.

Identification of β-Chloro-β-methoxyacrylonitrile.—Pure samples of the two isomers were isolated by preparative gas chromatography and their structures were confirmed by the following data, respectively, except the assignment of *cis–trans* isomerism. Sample A had shorter retention time on gas chromatography: mp 33–33.4°; ir (liquid film) 3090, 2225, 1618, 1320, 1120 cm^{-1}; nmr (CDCl$_3$) δ 4.02 (s, 3), 4.67 (s, 1).

Anal. Calcd for C$_4$H$_4$ClNO: C, 40.87; H, 3.43; N, 11.92. Found: C, 40.92; H, 3.30; N, 11.64.

Sample B had longer retention time: ir (liquid film) 3075, 2240, 1615, 1230 cm^{-1}; nmr (CDCl$_3$) δ 3.86 (s, 3), 4.73 (s, 1).

Anal. Calcd for C$_4$H$_4$ClNO: C, 40.87; H, 3.43; N, 11.92. Found: C, 40.52; H, 3.67.

Reaction of Chlorocyanoacetylene in the Presence of Additional NH$_4$Cl and Malononitrile.—In a four-necked flask equipped with a stirrer, a thermometer, an ammonia inlet tube, and Teflon Tube for feeding chlorocyanoacetylene, which was sent by means of a stroke pump, malononitrile (4 g), benzene or ethyl acetate (36 g), and powdered NH$_4$Cl (3.25 g) were placed and stirred mechanically. To this stirred suspension chlorocyanoacetylene was added in a form of 20% solution in the same solvent, at the rate of 0.2 g of chlorocyanoacetylene/min for 20 min. After 5 min, the addition of ammonia (the rate of flow was 100 ml/min) was started and continued for 20 min. Under the reaction conditions, the concentrations of the malononitrile and the chlorocyanoacetylene were kept almost constantly at 10 and 2.5%, respectively. After the reaction had finished, the analysis of the reaction mixture was carried out as described above.

Registry No.—Chlorocyanoacetylene, 2003-31-8; cyanoacetylene, 1070-71-9; malononitrile, 109-77-3.

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Fluorocyclopropanes. I. Preparation and Nuclear Magnetic Resonance Spectra

P. B. SARGEANT[1]

Contribution No. 1434 from the Central Research Department, Experimental Station,
E. I. du Pont de Nemours and Company, Wilmington, Delaware 19898

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Hexafluoropropylene epoxide transfers a difluoromethylene group to olefins in a general and convenient synthesis of fluorinated cyclopropanes. In one case the reaction was shown to be stereospecific. However, loss of stereospecificity can result from thermal isomerization of the fluorinated cyclopropane, which occurs slowly near 200°. The nmr spectra of the fluorinated cyclopropanes show that generally the vicinal coupling constants *cis* J_{HF} (9–17 Hz) and *cis* J_{FF} (5–10 Hz) are greater than *trans* J_{HF} (1–2 Hz) and *trans* J_{FF} (2–5 Hz), respectively.

Fluorinated cyclopropanes have been prepared by the pyrolysis of sodium chlorodifluoroacetate,[2] trifluoromethyl-substituted organometallics,[3–6] ketene,[7] diazomethane,[8] fluorine-substituted diazo compounds,[9–10] difluorodiazirine,[11] and selected chlorofluorocyclopropanes,[12] and base treatment of dichlorofluoromethane[13] and tetrachlorodifluoracetone[14] in the presence of olefins. These procedures suffer from either lack of generality or difficult preparation of the fluorinated starting material. This paper reports a method for the preparation of fluorinated cyclopropanes from hexafluoropropylene oxide which complements the use of sodium chlorodifluoroacetate. Both starting materials are readily available and both give stereospecific addition of CF$_2$; hexafluoropropylene oxide is useful for reaction with low-boiling olefins while sodium chlorodifluoroacetate is appropriate for reaction with solids and most liquids.

Results and Discussion

Above 170° hexafluoropropylene oxide (1) served as an apparent source of CF$_2$ which added to thio-

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[1] Dacron Research Laboratory, Textile Fibers Department, E. I. du Pont de Nemours and Co., Kinston, N. C. 28501.

[2] J. M. Birchall, G. W. Cross, and R. N. Haszeldine, *Proc. Chem. Soc.*, 81 (1960); L. Knox, *et al.*, *J. Amer. Chem. Soc.*, **85**, 1851 (1963).

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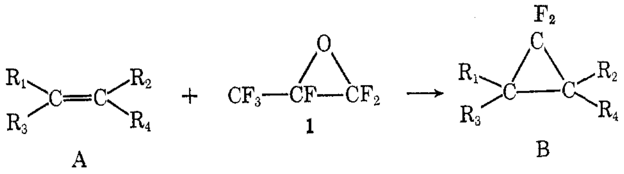
TABLE I

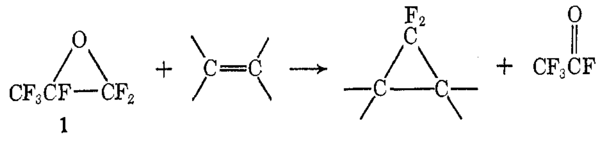
PREPARATION OF FLUORINATED CYCLOPROPANES



Isomer	R$_1$	R$_2$	R$_3$	R$_4$	Ratio of **1**/A[a]	Product	Yield, %
	CF$_3$	F	F	F	1	**2**	50[b,c]
	H	F	F	F	1.5	**3**	65[c]
	CF$_3$O	F	F	F	1.3	**4**	60
cis	H	Cl	F	F	1	**5**	75 (*cis*)[d]
trans	H	F	F	Cl	1	**6**	80 (*trans*)[d]
cis,trans	Cl	Cl(F)	F	F (Cl)	2	**7, 8**	85 (*cis,trans*)[c]
	(CH$_2$)$_4$		H	H	0.6	**9**	7[e]
	CH$_2$=CH	H	H	H	0.5	**10**	11[c]
	Single bond	Single bond	CF$_3$	CF$_3$	2	**11, 12**[f]	28[g]

[a] Moles of **1**/mole of olefin. [b] 100% yield based on recovered **1**. [c] Reference 11. [d] Product slowly isomerized to other isomer. See Results and Discussion. [e] Reference 2. [f] Isolated 12% yield of perfluoro-1,3-dimethylbicyclo[1.1.0]butane (**12**), the 2:1 adduct. [g] Reference 3.

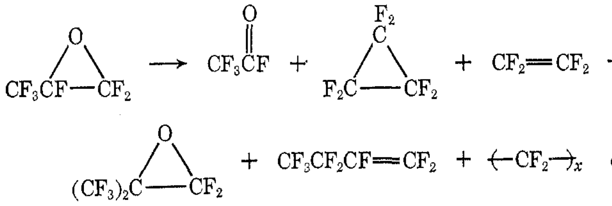
carbonyl fluoride,[15a] and this reagent has also been used to prepare difluoronorcarane from cyclohexene.[15b] Heating **1** in the presence of an olefin yields the cyclopropane derived from addition of difluoromethylene to the olefin and trifluoroacetyl fluoride as the major products (eq 1). Reaction occurred readily in sealed



(1)

equipment at autogenous pressure and 170–200° for 4–8 hr for all examples listed in Table I.

Thermal decomposition (200°, 8 hr) of **1** in the absence of added olefin gave trifluoroacetyl fluoride and hexafluorocyclopropane as major products (eq 2) along with lesser amounts of tetrafluoroethylene, perfluoro-1,2-epoxy-2-methylpropane, perfluoro-1-butene, and a solid difluoromethylene polymer. These products were also occasionally isolated and identified in the reactions of hexafluoropropylene oxide with olefins.



(2)

From Table I it is apparent that only a slight excess of **1** is required for satisfactory yields.

The stereospecificity of the reaction was examined. A mixture of **1** and *cis*- and *trans*-1-chloro-1,2-difluoroethylene (**13** and **14**, respectively) heated at 225° for 8 hr gave a mixture of 67.7% *trans*- and 32.3% *cis*-1-chloro-1,2,2,3-tetrafluorocyclopropane (**6** and **5**, respectively). The olefins were separated by preparative vpc. Heating **1** and **14** at 208° for 15 hr gave a mixture of 72.7% **6** and 27.3% **5**. Heating **1** and **13** at 208° for 15 hr gave a mixture of 68% **6** and 32% **5**. When **1** and **14** were heated at 200° and periodically examined by ^{1}H nmr, the reaction gave exclusively **6** for 4 hr; subsequently, a small amount of **5** was observed. The reaction appeared complete after *ca.* 8 hr, but the amount of **5** continued to increase at the expense of **6**. After 240 hr, the reaction was stopped and the product mixture contained 67% **6** and 33% **5**. Similarly, **1** and **13** gave exclusively **5** for 4 hr; then a small amount of **6** was noted. The reaction appeared complete at the end of 8 hr, but the amount of **6** continued to increase at the expense of **5**. After 230 hr, the reaction was stopped and the product mixture contained 67% **6** and 33% **5**. Olefins **13** and **14** were shown not to isomerize under the reaction conditions. Clearly, the reaction proceeds stereospecifically, but prolonged heating results in isomerization of the product cyclopropane to the equilibrium mixture (67:33) of **6** and **5**. This was verified by heating pure **5** and pure **6** at 200° for 23 hr to give essentially identical mixtures containing 68% **6** and 32% **5** and 70% **6** and 30% **5**, respectively. Based on the constant intensity of the nmr signal in all of the above reactions, there was no yield loss during any heating period. Therefore, the reaction is isomerization and not preferential destruction of one isomer. Table II summarizes this study.

TABLE II

REACTION STEREOSPECIFICITY AND CYCLOPROPANE ISOMERIZATION

Starting composition	Temp, °C	Time, hr	Final composition[a]	
			6	**5**
13, 14 + **1**	225	8	68	32
14 + **1**	200	4	>95	<5
14 + **1**	208	15	72	27
14 + **1**	200	240	67	33
13 + **1**	200	4	<5	>95
13 + **1**	208	15	68	32
13 + **1**	200	230	67	33
6	200	5	77	23
6	200	23	70	30
5	200	5	60	40
5	200	23	68	32

[a] Determined by ^{1}H nmr integration.

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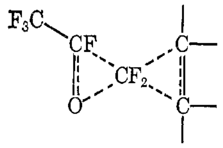
The reaction mechanism is believed either to involve "free" difluoromethylene generation or to proceed *via* a difluoromethylene transfer involving both **1** and olefin in the transition state. Either mechanism would provide a stereospecific addition.[11] A choice between these mechanisms is not possible at present.



The ease of the fluorinated cyclopropane geometrical isomerization is surprising when contrasted with the high temperatures required for hydrocarbon cyclopropane isomerizations.[16-19] One geometrical isomerization[19] of an aromatic-substituted cyclopropane near 200° is attributed to transition-state stabilization of the developing free-radical intermediate. The ready geometrical isomerizations of fluorinated cyclopropanes may be due to transition-state stabilization, but are thought to be also a manifestation of higher ground-state energy resulting from strain energy higher than that for hydrocarbon cyclopropanes.

The nmr spectra of the fluorinated cyclopropanes were used to establish their structure and stereochemistry. Many of the spectra, or considerable portions of them, were amenable to first-order analysis. The spectra of cyclopropanes **2**, **3**, **7**, and **8** have been reported previously;[11] our results agree qualitatively, although the interpretations are somewhat different.

The ^{19}F chemical-shift assignments (Table III) were based both on the spin-spin coupling constants *cis* J_{HF} and *cis* J_{FF} being larger than *trans* J_{HF} and *trans* J_{FF}, respectively (see below), and on the effect of *cis* and *trans* chlorine substituents on the fluorine chemical shifts. Using the chemical shift of the fluorine signal of perfluorocyclopropane (158.9 ppm) as a standard, the replacement of a fluorine atom by a hydrogen atom results in deshielding of the fluorine nuclei, which are *cis* and vicinal to the proton. The fluorine nuclei which are *trans* and vicinal to the proton are shielded. On the other hand, a chlorine atom deshields both *cis* and *trans* vicinal fluorine nuclei and this effect is greater on the *cis* vicinal nuclei. The substituent effect of hydrogen is similar to that observed in fluorocyclohexanes.[20] If one further assumes that the chemical-shift differences in compounds **3** and **7** are representative of the respective *cis* and *trans* substituents hydrogen and chlorine, an additive correlation similar to that of Shoolery[21-23] obtains. Thus a *trans* hydrogen shields by *ca.* 2.66 ppm, a *cis* hydrogen deshields by *ca.* 7.27 ppm, a *trans* chlorine deshields by *ca.* 2.30 ppm, and a *cis* chlorine deshields by *ca.* 9.22 ppm.

The dependence of vicinal H-H coupling constants on the H-C-C-H dihedral angle is well known.[24,25] A similar dependence of the same general trend has been noted for vicinal H-F and F-F coupling constants.[26-28] In hydrocarbon cyclopropanes, the vicinal coupling constants *cis* J_{HH} are larger than *trans* J_{HH}.[29-33] In this study of fluorinated cyclopropanes, the vicinal *cis* J_{HF} and *cis* J_{FF} coupling constants are usually larger than the respective *trans* J_{HF} or J_{FF} coupling constants (Table III). Coupling constants for compounds **3**, **5**, **6**, and **7** were calculated from at least 15 determinations and are reproducible to ±0.2 Hz. The geminal coupling constants J_{HF} (*ca.* 55 Hz) and J_{FF} (170-210 Hz) are as expected.[11,34-36] The *cis* J_{HF} values are between 9.1 and 16.8 Hz, while *trans* J_{HF} values are between 1.3 and 2.1 Hz. The range of *cis* and *trans* J_{FF} values overlaps; nevertheless, in any single compound *cis* J_{FF} > *trans* J_{FF}, except for **6**. In **6**, the double-resonance frequency sweep method was used to verify the coupling constants as indicated in Table III. Irradiation of the F_1 resonance removed the 11.1-Hz coupling from the F_4 pattern, and irradiation of F_4 removed the 11.1-Hz coupling from the F_1 pattern. Similarly, $J_{F_1F_2}$ and $J_{F_2F_4}$ were verified. Irradiation of the F_3 resonance (B resonance areas or calculated chemical shift) did not change either the F_1 or F_4 pattern. Vicinal F-F coupling constants appear to depend on substituent effects as well as dihedral angle.

Fluorine-fluorine coupling constants through four bonds are noted in **2** and through four and five bonds in **4**. In **2**, the trifluoromethyl fluorines are coupled by 7.7 Hz with the fluorines *cis* to the trifluoromethyl group and by 6.0 Hz with the *trans* fluorines. This result is interesting, since only the *trans* fluorines can assume the extended W conformation often associated with long-range coupling,[37,38] whereas the requirements for the controversial "through space" coupling are met only by the *cis* fluorines.[39-41] The "geminal" four-bond F_1-F_4 coupling constant in **4** is 4.9 Hz and the extended W conformation is possible. However, the five-bond coupling constant with the *cis* fluorines is 4.6 Hz. Again the fluorines close to one another couple more strongly than those in an extended conformation.

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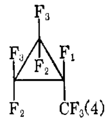
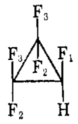
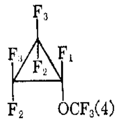
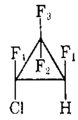
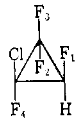
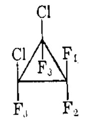
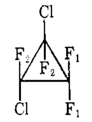
TABLE III

^{19}F NMR SPECTRA OF FLUORINATED CYCLOPROPANES[a]

Cyclopropane	Chemical shift, δ, ppm[a]				Multiplicity[b]	Coupling constants, Hz
	δ_1	δ_2	δ_3	δ_4		
 2	221.2	157.5[c]	157.5[c]	73.4	F_1 qtt F_2, F_3 complex F_4 dtt	$J_{14} = 9.2$, $J_{13} = 4.3$, $J_{12} = 2.7$ $J_{41} = 9.2$, $J_{42} = 7.7$, $J_{43} = 6.0$
 3[d]	241.9	151.6[e]	161.5[e]		F_1 dtt[f] F_2, F_3 complex H dtt	$J_{1H} = 56$, $J_{13} = 9.8$, $J_{12} = 4.9$ $J_{23} = 208$[g] $J_{H1} = 56$, $J_{H2} = 13.2$, $J_{H3} = 1.3$
 4	166.9	157.2[h]	159.9[h]	62.6	F_1 tqt F_2, F_3 complex F_4 dtt	$J_{13} = 9.2$, $J_{14} = 4.9$, $J_{12} = 3.2$ $J_{23} = 201$[i] $J_{41} = 4.9$, $J_{42} = 4.6$, $J_{43} = 1.2$
 5[j]	230.8	141.6[k]	158.1[k]	175.1	F_1 dtd F_2 A of AB, ddd F_3 B of AB, ddd F_4 dddd H ddt	$J_{1H} = 57$, $J_{13} = J_{14} = 7.5$, $J_{12} = 4.9$ $J_{23} = 184$, $J_{2H} = 10$, $J_{21} = 4.9$, $J_{24} = 2.1$ $J_{32} = 184$, $J_{31} = 7.5$, $J_{34} = 4.8$, $J_{3H} = 1.3$ $J_{41} = 7.5$, $J_{43} = 4.8$, $J_{42} = 2.1$, $J_{4H} = 1.3$ $J_{H1} = 57$, $J_{H2} = 10$, $J_{H3} = J_{H4} = 1.3$
 6[l]	226.7	148.3[m]	150.2[m]	162.0	F_1 ddd F_2 A of AB, ddd F_3 B of AB, m F_4 ddd H dddd	$J_{1H} = 57$, $J_{14} = 11.1$,[n] $J_{12} = 2.8$[n] $J_{23} = 190$, $J_{2H} = 9.1$, $J_{24} = 5.7$,[n] $J_{21} = 2.8$[n] $J_{32} = 190$ $J_{4H} = 16.8$, $J_{41} = 11.1$,[n] $J_{42} = 5.7$[n] $J_{H1} = 57$, $J_{H4} = 16.8$, $J_{H2} = 9.1$, $J_{H3} = 2.1$
 7	140.5[o]	154.4[o]	166.5		F_1 A of AB, t F_2 B of AB, t F_3 dd	$J_{12} = 174$, $J_{13} = 5.3$ $J_{21} = 174$, $J_{23} = 5.6$ $J_{32} = 5.6$, $J_{31} = 5.3$
 8	146.7	157.8			F_1 t F_2 t	Separation = 2.6[p]

[a] Neat liquid referenced to externally substituted fluorotrichloromethane at 56.4 Hz. [b] Multiplicity is indicated as follows: d, doublet; t, triplet; q, quartet; m, multiplet. Ordered in terms of decreasing coupling constant. [c] The center of strongly overlapped F_2 and F_3 resonance. [d] Proton chemical shift centered at τ 5.43. [e] AA′BB′ pattern approximated to AB using centers of peaks at 149.5, 153.2, 160.0, and 163.7 ppm. [f] Appears as doublet to septets; actually doublet to triplets to triplets which overlap. [g] J_{AB} of approximated AB pattern. [h] AA′BB′ pattern approximated to AB using centers of peaks at 154.6, 158.1, 159.0, and 162.6 ppm. [i] J_{AB} of approximated AB pattern. [j] Proton chemical shift centered at τ 5.80. [k] AB pattern resonance at 139.8, 143.1, 156.7, and 160.0 ppm. [l] Proton chemical shift centered at τ 5.50. [m] AB pattern resonance at 145.2, 148.6, 149.0, and 152.4 ppm. [n] Coupling constant verified by the double-resonance experiment. [o] AB pattern resonance at 138.8, 141.9, 153.0, and 156.1 ppm. [p] Must be analyzed as AA′BB′ system to obtain coupling constants.

The fluorocyclopropanes were also characterized by their mass spectra; the major ion fragments are reported in the Experimental Section. The mass spectra of fluorocarbons are characterized by the abundance of CF_3, CF_2, and CF fragments;[42] the CF_3 fragment is frequently the base (100) peak even when no CF_3 group is present in the molecule. This is true for fluorocyclopropanes. Fluorocyclopropanes are also characterized by a large parent minus CF_2 ion which is consistent with the reported thermal generation of CF_2 from selected fluorocyclopropanes.[12] Chlorofluorocyclopropanes exhibited a large parent minus chlorine ion which is consistent with the relative C–Cl and C–F bond strengths.

Experimental Section

General.—Proton nmr spectra were obtained on a Varian Associates A-60 spectrometer. Fluorine nmr spectra were obtained with Varian Associates high-resolution spectrometers operating at 56.4 and 94.1 Hz. Chemical shifts were referenced to internal TMS (^1H) and externally substituted trichlorofluoromethane (^{19}F). Spectral parameters are reported in Table III. Infrared spectra were obtained on a Perkin-Elmer Infracord spectrophotometer calibrated with polystyrene. Mass spectra were obtained on a Bendix time-of-flight mass spectrometer. The ionizing voltage was 70 eV, with a 0.125-V trap current and 25° inlet temperature. Hexafluoropropylene oxide was prepared by the method of Biggs and Warnell.[43] The olefins were either purchased or synthesized as described below.[44] Three examples

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(42) J. R. Majer, *Advan. Fluorine Chem.*, **2**, 55 (1961).

(43) H. H. Biggs and J. L. Warnell, French Patent 1,322,597 (1963).

(44) Perfluoromethyl vinyl ether was supplied by Dr. B. Yates of E. I. du Pont de Nemours and Co.

of the cyclopropane synthesis are also given; the other cyclopropanes were prepared by similar procedures.

1,1,2-Trichloro-1,2-difluoroethane.—Chloral (252 g, 1.7 mol) and sulfur tetrafluoride (300 g, 2.8 mol) were charged to a 1-l. Hastelloy bomb and heated at 150° for 6 hr. The liquid product was washed with water (1 l.), dried over anhydrous magnesium sulfate, and distilled through a 45-cm spinning-band distillation column. Two such runs produced 357 g (62%) of product: bp 70–74° (lit.[45] bp 70–72°); $n^{25}\text{D}$ 1.3940; ^{1}H nmr (neat) δ 6.25 (d, $J = 49$ Hz, d, $J = 4$ Hz); ^{19}F nmr (neat) δ 70.6 (d, $J = 22.5$ Hz, d, $J = 4$ Hz, CCl_2F) and 140.2 (d, $J = 49$ Hz, d, $J = 22.5$ Hz, CHClF).

1-Chloro-1,2-difluoroethylene (13 and 14).—1,1,2-Trichloro-1,2-difluoroethane (277 g, 1.6 mol) in dry THF (160 ml) was added to a vigorously stirred mixture of magnesium (40 g, 1.9 g-atoms) in THF (240 ml) in a 2-l., three-necked, round-bottomed flask equipped with addition funnel, mechanical stirrer, and water condenser which led to a trap cooled in Dry Ice–acetone, all under N_2, at a rate sufficient to maintain reflux. After half the ethane had been introduced, THF (250 ml) was added to the reaction mixture to increase fluidity. The total addition time was 4 hr. The stirring mixture was heated at reflux for 3 hr. After standing overnight, the product in the Dry Ice–acetone trap was transferred to a 200-ml flask and distilled through a low-temperature still to give 95 g (60%) of *cis* (**13**) and *trans* (**14**) isomers: bp −19 to −10° (lit.[46] bp −15°); ^{1}H nmr (neat) δ 6.05 (d, $J = 73$ Hz, d, $J = 12$ Hz, *trans*) and 6.90 (d, $J = 74$ Hz, d, $J = 1.2$ Hz, *cis*); ^{19}F nmr (neat) *trans* isomer δ 132.4 (d, $J = 132$ Hz, d, $J = 1.2$ Hz, CClF) and 176.4 (d, $J = 132$ Hz, d, $J = 74$ Hz, CHF), *cis* isomer 107.6 (d, $J = 12$ Hz, d, $J = 11$ Hz, CClF) and 159.1 (d, $J = 73$ Hz, d, $J = 11$ Hz, CHF). Two such reactions gave 67% **14** and 33% **13** and 65% **14** and 35% **13**, respectively, by vpc analysis (6-ft Kel F, 25°) and ^{1}H and ^{19}F nmr integration.

1,2-Dichloro-1,2-difluoroethylene.—Zinc dust (600 g) and zinc bromide (50 g) were suspended in absolute ethanol (400 ml) in a 2-l., three-necked, round-bottomed flask equipped with mechanical stirrer, 250-ml addition funnel, and a hot-water condenser leading to a 100-ml trap cooled in Dry Ice–acetone, and heated to 55° under nitrogen. 1,1,2,2-Tetrachloro-1,2-difluoroethane (250 g, 1.2 mol) in absolute ethanol (75 ml) was slowly added to the stirring mixture. After 18 hr, the system was swept with N_2 for 15 min to give 105 ml of product in the Dry Ice trap. Distillation through a 40-cm low-temperature column gave *cis* and *trans* isomers: bp 15–23° (lit.[47] bp 21–22°); ^{19}F nmr (neat) δ 106 (*cis*) and 120.7 (*trans*).

1,2-Dichloro-1,2,3,3-tetrafluorocyclopropane (7, 8).—1,2-Dichloro-1,2-difluoroethylene (144 g, 1.08 mol) and **1** (332 g, 2.0 mol) were charged to a 1-l. stainless steel bomb and heated at 185° for 8 hr. The bomb was cooled to −78°, opened, and warmed to 0°, bleeding through a trap cooled in wet ice. The bomb and trap contents were combined and distilled to give recovered 1,2-dichloro-1,2-difluoroethylene (14.0 g, 0.105 mol, 91.5% conversion) and *cis-* (**7**) and *trans*-cyclopropane (**8**) (155 g, 0.846 mol, bp 37–40°, 85% yield).[11] Preparative vpc (Kel F ester) provided pure isomers (**8** eluted before **7**).

1-Chloro-1,2,2,3-tetrafluorocyclopropane (5, 6).—A 1-l. stainless steel bomb was charged with 1-chloro-1,2-difluoroethylene (98.5 g, 1.0 mol) and **1** (250 g, 1.5 mol) and heated at 180° for 6 hr. The bomb was cooled to −80° and warmed slowly to 60°, bleeding through a Dry Ice trap. Distillation of the trap contents gave a mixture of trifluoroacetyl fluoride (44 g, bp −55 to −45°), unreacted **1** (90 g, bp −45 to −23°), unreacted olefin, and *cis-* (**5**) and *trans*-cyclopropane (**6**): yield 85 g (57%); bp 25–28°; ir 3050 (w), 1480 (m), 1310 (s), 1260 (s), 1195 (s), 1085 (s), 960 (m), 858 (w), 790 (m), and 730 cm^{-1} (m). The band at 1480 cm^{-1} has been attributed to a fluorocyclopropane containing a CF_2 group.[11]

Perfluoromethyl Cyclopropyl Ether (4).—Perfluoromethyl vinyl ether (25 g, 0.15 mol) and **1** (33.6 g, 0.20 mol) were sealed in a Carius tube and heated at 210° for 8 hr. Distillation through a low-temperature column gave 21.2 g (60%) of **4**: bp −4 to −2°; ir 1480 (w), 1250 (s), 1170 (s), 1080 (m), 1020 (m), 965 (w), 920 (s), 890 (s), 835 (s), 814 (m), 743 (m), and 715 cm^{-1} (w).

Major fragments of fluorocyclopropane mass spectra[48,49] follow: perfluorocyclopropane (C_3F_6), C_2F_4 (65, p − CF_2), CF_3 (85), CF_2 (35), and CF (100); **3** (C_3HF_5), C_3HF_4 (35, p − F), C_2HF_3 (70, p − CF_2), CF_3 (100), CHF_2 (35), and CF (55); **5** (C_3HClF_4), C_3HF_4 (85, p − Cl), C_2HClF_2 (60, p − CF_2), CF_3 (85), CHF_2 (40), and CF (100); **6** (C_3HClF_4), C_3HF_4 (45, p − Cl), C_2HClF_2 (45, p − CF_2), CF_3 (55), CHF_2 (35), and CF (100); **7** ($C_3Cl_2F_4$), C_3ClF_4 (45, p − Cl), CF_3 (40), and CF (100); **8** ($C_3Cl_2F_4$), C_3ClF_4 (55, p − Cl), $C_2Cl_2F_2$ (30, p − CF_2), CF_3 (45), and CF (100).

Registry No.—**2**, 379-16-8; **3**, 872-58-2; **4**, 19448-33-0; **5**, 22430-74-6; **6**, 22430-75-7; **7**, 22430-76-8; **8**, 22430-77-9.

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[48] Relative abundance compared with base (100) peak, and source of the fragment; p = parent ion.

[49] The author acknowledges Mrs. N. P. Hillyard and Mr. C. B. Matthews for assistance in obtaining and interpreting the mass spectra.