pane (phenylurethan), 20439-52-5; 1,1-dichloro-2-methyl-2-ethoxymethylcyclopropane, 20439-53-6; 1,1-dichloro-2-methyl-3-chloromethylcyclopropane, 20439-54-7.

Acknowledgment.—Spectral data were obtained and largely interpreted by Dr. F. J. Impastato and Dr. D. W. Imhoff. Elemental analyses were conducted by Mr. W. J. Easley.

Bicyclobutyl Derivatives. V. Syntheses of Conjugated Perhalogenated Diolefins[1]

J. D. PARK, SAM KWON CHOI,[2] AND H. ERNEST ROMINE[2]

Department of Chemistry, University of Colorado, Boulder, Colorado 80302

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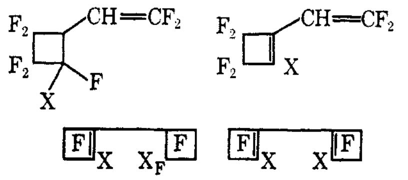
The cycloaddition of 1,1,4,4-tetrafluorobutadiene-1,3 to $CF_2{=}CFCl$ and $CF_2{=}CCl_2$, respectively, led to the formation of the following perhalogenated derivatives which have been examined and characterized.

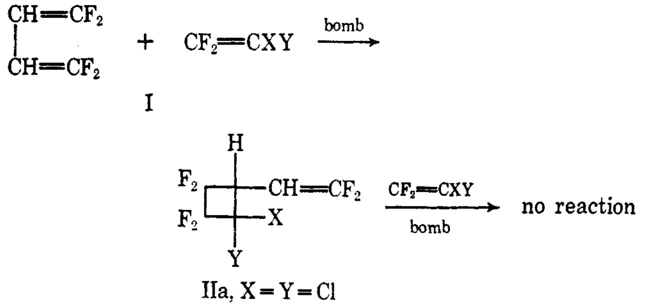


X = Cl or F

This paper reports the cycloaddition of 1,1,4,4-tetrafluorobutadiene-1,3 to $CF_2{=}CFCl$ and $CF_2{=}CCl_2$ leading to perhalogenated "dibox" compounds.[3]

Results and Discussion

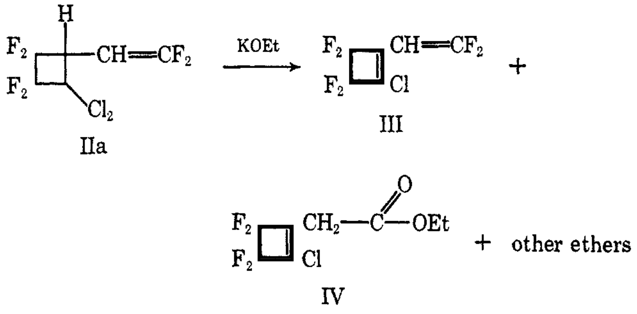
The thermal cycloaddition of 1,1,4,4-tetrafluorobutadiene-1,3 (I) with excess tetrahaloethylenes has led to the 1:1 adducts, 1-(β,β-difluorovinyl)-2,2-dihalo-3,3,4,4-tetrafluorocyclobutanes (IIa and b, 60–90%). No 1:2 diadducts were detected even in the presence of a large excess of tetrahaloethylene. The vinyl cyclobutane adducts are stable, colorless liquids. They have been characterized by microanalysis, H and ^{19}F nmr spectra, infrared spectra, and mass spectra.

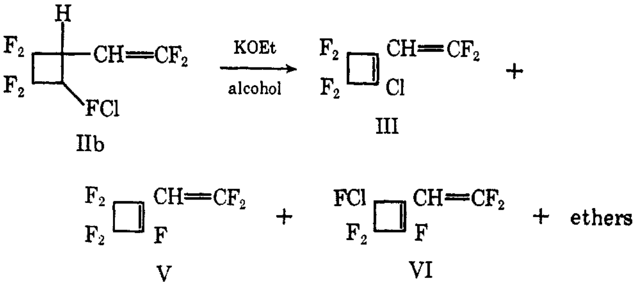


IIa, X = Y = Cl
b, X = F; Y = Cl

The observed resistance of IIa and IIb to further cycloaddition reactions implied the requirement of a diene intermediate in these highly halogenated systems. Dehydrohalogenation of IIa or IIb would lead to more reactive vinylcyclobutenes.

Several classical dehydrohalogenation media were tested on this system with limited success. Ethanolic potassium hydroxide reacts exothermically with IIa to give 1-(β,β-difluorovinyl)-2-chloro-3,3,4,4-tetrafluorocyclobutene (III, 45%) and a complex mixture of ether substitution products. The ester IV (18%) apparently stems from base-catalyzed hydrolysis of one or more product ethers. Potassium ethoxide converts IIb into a mixture of three possible dienes, III, V, and VI, along with a very complex mixture of ethers. The three vinylcyclobutenes were characterized by their infrared and mass spectra and by microanalysis. They are colorless liquids which polymerize to waxy solids within several hours at room temperature. Potassium hydroxide in mineral oil successfully dehydrohalogenates IIa to III (35%) and IIb to III (10%), V (25%), and VI





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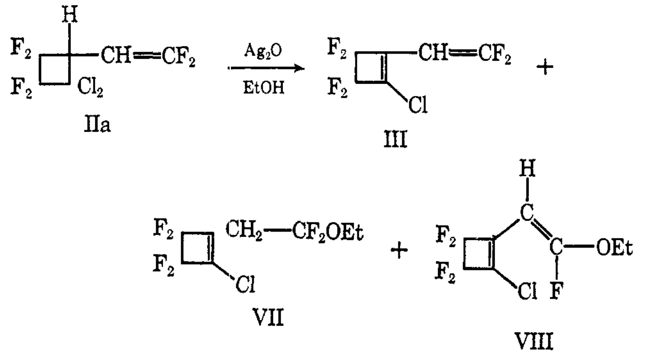
(1) Previous papers in this series: (a) J. D. Park and W. C. Frank, *J. Org. Chem.*, **29**, 1445 (1964); (b) *ibid.*, **32**, 1333 (1967); (c) *ibid.*, **32**, 1336 (1967); (d) *ibid.*, **32**, 1340 (1967).

(2) This paper represents parts of Ph.D. Theses submitted to the Graduate School, University of Colorado, Boulder, Colo., by S. K. Choi, 1969, and by H. E. Romine, 1968.

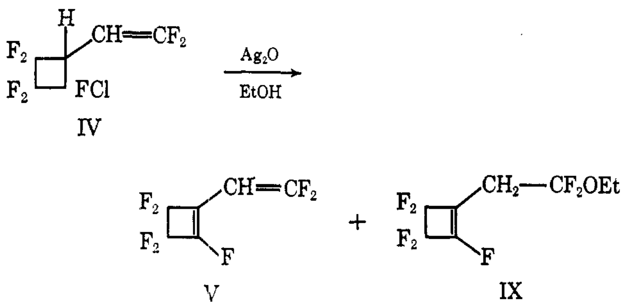
(3) "Dibox" is a trivial name used to designate dicyclobutene.

(15%) at elevated temperature, but the reaction is very exothermic once initiated and extensive polymerization frequently destroys the product. Triethylamine reacts violently with IIa or IIb in an inert solvent at −78°, giving only tars.

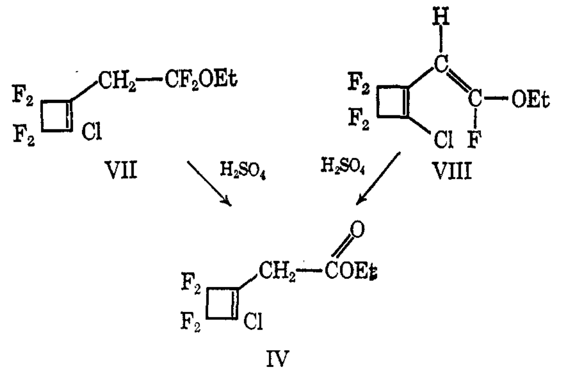
Dehydrohalogenation is best accomplished in this system through the use of silver oxide in 95% ethanol. Compound IIa reacts to give III (60%), a stable liquid VII (20%), and a white waxy solid VIII (15%).



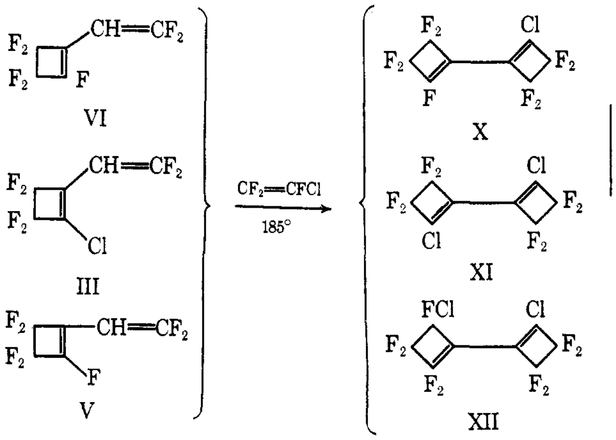
Similar to the reactions of IIa, IIb is converted to V (77%) and IX (7%) on treatment with silver oxide. IX was characterized through its mass and infrared spectra. XIII is a colorless liquid which liberates HF and darkens on standing. No dehydrofluorination products are observed in these mild silver oxide reactions, and the desired vinyl cyclobutenes are consistently prepared in good yield.



The fluorocarbon ethers VII and VIII are converted quantitatively to 1-carbethoxymethyl-2-chloro-3,3,4,4-tetrafluorocyclobutene (IV) on treatment with oleum.



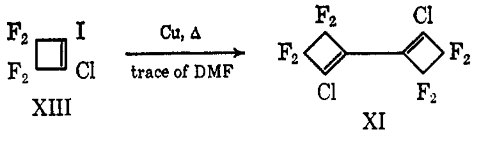
Problems in preparing and storing pure vinylcyclobutenes in quantities exceeding several grams made further codimerization studies difficult. In order to establish the reactivity of these compounds, a mixed sample of IIb, III, V, and VI was treated with a twentyfold excess of chlorotrifluoroethylene in an autoclave at 185°. Compound IIb has been shown to be inert under these reaction conditions and therefore serves as a standard against which the reactivity of the other materials can be measured. Work-up revealed 40–50% reaction of each diene and the development of three products. Preparative gas chromatography afforded 2-chlorononafluoro(bi-1,1′-cyclobut-1-enyl) (X), a pungent, colorless liquid, the related 2,2′-dichlorooctafluoro derivative (XI), and 2,4′-dichlorooctafluoro(bi-1,1′-cyclobut-1-enyl) (XII) as the three reaction products in a 4:5:6 ratio.



The simplicity of the product mixture allows an analysis of the course of the reaction. Product X could have resulted from addition of chlorotrifluoroethylene to III followed by dehydrochlorination or addition to V followed by dehydrofluorination. However, dehydrochlorination products from the adducts of chlorotrifluoroethylene with V or VI are not observed, while all products in their observed distribution can be accounted for assuming thermal dehydrofluorination from each of the required adducts. Evidence for presence of the unreacted adducts could not be found, but some polymeric material was noted in the reaction mixture.

Further work on codimerizations was rendered superfluous by the development of two alternative syntheses of dicyclobutenes incorporating coupling reactions.

Recent studies in this laboratory[4,5] outlining the preparation of vinyliodocyclobutenes by halogen exchange reactions has promoted an interest in the chemistry of these novel fluorocarbons. It was consequently discovered that 1-iodo-2-chloro-3,3,4,4-tetrafluorocyclobutene couples to form XI when passed over hot copper turnings. The presence of a trace of dimethylformamide is necessary to initiate the radical reaction.



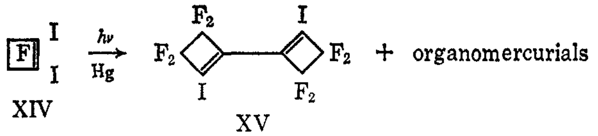
While yields vary from 30 to 60% with considerable decomposition, this one-step synthesis is convenient for small-scale laboratory preparations. The reaction is general of polyfluorinated vinyliodocycloalkenes, as will be discussed further in a forthcoming paper.[6]

(4) G. G. J. Moore, Ph.D. Thesis, University of Colorado, 1965.

(5) R. J. McMurtry, Ph.D. Thesis, University of Colorado, 1965.

(6) J. D. Park and S. K. Choi, to be published.

Photochemically initiated radical reactions of 1,2-diiodo-3,3,4,4-tetrafluorocyclobutene (XIV) have been observed to give 2,2′-diiodooctafluoro(bi-1,1′-cyclobut-1-enyl) (XV), a white crystalline solid, in 16% yield.



The major product (57%) of this mercury-sensitized reaction is a green organometallic species which was not sufficiently stable to permit characterization.

Experimental Section

Melting points were determined on a Thomas-Hoover capillary apparatus and are corrected; boiling points are uncorrected. Infrared spectra were recorded on a Perkin-Elmer Infracord. Proton nuclear magnetic resonance spectra were run on a Varian A-60 or A-60A spectrometer using tetramethylsilane as an internal reference. Fluorine nuclear magnetic resonance spectra were run on a Varian HA-100 spectrometer using $CFCl_3$ (F-11) as an internal reference. Chemical shifts are recorded as parts per million on the δ scale, with coupling constants as cycles per second. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Mass spectra were obtained from an Atlas CH-4 mass spectrometer and were measured at 70 eV.

Synthesis of 1-(β,β-Difluorovinyl)-3,3,4,4-tetrafluoro-2,2-dichlorocyclobutane (IIa).—A 500-ml stainless steel autoclave was charged with 67.8 g (0.54 mol) of 1,1,4,4-tetrafluorobutadiene, 225 g (1.70 mol) of 1,1-dichloro-2,2-difluoroethylene, and 2 ml of *d*-limonene. The mixture was brought to 220° in a shaker during 2 hr and maintained at that temperature for 36 hr. After cooling, the dark liquid contents were collected and fractionally distilled to give 126.7 g (91%) of the adduct IIa: bp 105–107° (628 mm); $n^{26}D$ 1.3784; d^{26} 1.59; ir 3100 and 2990 (C—H) and 1750 cm^{-1} (C=C); nmr ($CFCl_3$) δ 4.48 (m, 1, C=C—H) and 3.94 (m, 1, C—H); mass spectrum *m/e* 258 (2 Cl), 238 (2 Cl), 222 (1 Cl), and 160 (1 Cl).

Anal. Calcd for $C_6H_2Cl_2F_6$: C, 27.8; H, 0.8; Cl, 27.4; F, 44.0. Found: C, 27.71; H, 0.76; Cl, 27.47; F, 44.02.

Synthesis of 1-(β,β-Difluorovinyl)-2,3,3,4,4-pentafluoro-2-chlorocyclobutane (IIb).—A 500-ml stainless steel autoclave was charged with 60.1 g (0.48 mol) of 1,1,4,4-tetrafluorobutadiene, 225 g (1.94 mol) of chlorotrifluoroethylene, and 3 ml of *d*-limonene. The mixture was heated in a shaker to 260° during 8 hr and maintained at that temperature for 18 hr. After cooling, a light orange liquid was collected from the bomb which on fractional distillation gave 67.8 g (58%) of 1-(β,β-difluorovinyl)-2,3,3,4,4-pentafluoro-2-chlorocyclobutane (IIb); bp 75–78° (630 mm); $n^{26}D$ 1.3358; d^{26} 1.63; ir 3120 and 2990 (C—H) and 1750 cm^{-1} (C=C); nmr ($CFCl_3$) δ 4.47 (m, 1, C=C—H) and 3.88 (m, 1, C—H); mass spectrum *m/e* 242 (1 Cl), 223 (1 Cl), 207, 203 (1 Cl), 188, and 187.

Anal. Calcd for $C_6H_2ClF_7$: C, 29.7; H, 0.83; Cl, 14.6; F, 54.9. Found: C, 29.51; H, 0.93; Cl, 13.53; F, 54.77.

Dehydrohalogenation of 1-(β,β-Difluorovinyl)-3,3,4,4-tetrafluoro-2,2-dichlorocyclobutane (IIa). A. Reaction with Potassium Ethoxide.—A solution of 5.18 g (0.02 mol) of IIa in 10 ml of 95% ethanol in a flask was cooled to 0° prior to the dropwise addition of a solution of 1.7 g (0.03 mol) of potassium hydroxide with rapid stirring. Following an additional 6 hr of stirring at 25°, the mixture was quenched with water and the crude product isolated. Preparative gas chromatography (6 ft × 0.5 in. column packed with 15% SE-30 on 30–60 mesh Chromosorb W-HMDS at 200°) yielded 1-(β,β-difluorovinyl)-3,3,4,4-tetrafluoro-2-chlorocyclobutene (III, 45%) and 1-carbethoxymethyl-3,3,4,4-tetrafluoro-2-chlorocyclobutene (IV, 18%) along with 20% recovered IIa. Compound VII is a colorless, readily polymerized liquid: $n^{27}D$ 1.3897; d^{27} 1.64; ir 3100 (C—H) and 1720 and 1630 cm^{-1} (C=C); mass spectrum *m/e* 222 (1 Cl), 203 (1 Cl), and 187.

Anal. Calcd for C_6HClF_6: C, 32.4; H, 0.5; Cl, 15.9; F, 51.2. Found: C, 32.16; H, 0.51; Cl, 16.39; F, 52.66.

Compound IV is a stable colorless liquid: $n^{28}D$ 1.3968; d^{28} 1.40; ir 3030 (C—H), 1760 (C=O) and 1670 cm^{-1} (C=C); nmr ($CFCl_3$) δ 4.52 (d, 1, J_{HF} = 31.5 cps, —CH=CFOEt), 4.12 (q, 2, J_{HH} = 7.0 cps, —OCH_2CH_3) and 1.43 (t, 3, J_{HH} = 7.0 cps, —OCH_2CH_3); mass spectrum fragments at *m/e* 201 (1 Cl), 173 (1 Cl), 154 (1 Cl), 123 (1 Cl), and 119.

B. Reaction with Potassium Hydroxide in Mineral Oil.—To a mixture of 10 ml of light mineral oil and 2.8 g (0.05 mol) of KOH was added with stirring 8.15 g (0.031 mol) of IIa during 1 hr. A very exothermic and apparently autocatalytic reaction ensued with refluxing, discoloration, and polymerization. Following 16 hr of stirring at 25°, vacuum distillation gave III (35%) and recovered IIa (25%).

C. Reaction with Silver Oxide in 95% Ethanol.—A solution of 5.18 g (0.02 mol) of IIa in 10 ml of 95% ethanol was added with rapid stirring to a suspension of 2.32 g (0.01 mol) of Ag_2O in 10 ml of 95% ethanol during 10 min. Stirring was continued for 16 hr or until AgCl formation and mild heat evolution ceased. The pale yellow oil which separated on quenching with water was water washed and dried (Na_2SO_4). Preparative gas chromatography (6 ft × 0.5 in. column packed with 15% SE-30 on 30–60 mesh Chromosorb W-HMDS at 180°) gave recovered IIa (25%), the diene III (45%), and two new ethers, VII (15%) and VIII (12%). Compound VII has been identified as 1-(2,2-difluoro-2-ethoxy)ethyl-3,3,4,4-tetrafluoro-2-chlorocyclobutene: $n^{26}D$ 1.3777; d^{25} 1.46; ir 3070 (C—H) and 1670 cm^{-1} (C=C); ^{1}H nmr ($CFCl_3$) δ 3.97 (q, 2, J_{HH} = 7.0 cps, —O—CH_2—), 2.98 (t, 2, J_{HF} = 9.5 cps, C—CH_2—C), and 1.27 (t, 3, J_{HH} = 7.0 cps, —CH_2—CH_3); ^{19}F nmr ($CFCl_3$) δ 117.8 (m, 1, —CF_2—CF_2—C—Cl), 116.3 (m, 1, —CF_2—CF_2—C—Cl), and 114.1 (broad s, 1, —CF_2—OEt); molar refraction calcd, 42.17, and obsvd, 42.23. Compound VIII has been identified as 1-(*cis*-α-hydro-β-ethoxy-β-fluoro)-vinyl-3,3,4,4-tetrafluoro-2-chlorocyclobutene: mp 38.1–39.7°; ir 3050 (C—H) and 1695 and 1640 cm^{-1} (C=C); ^{1}H nmr ($CFCl_3$) δ 4.52 (d, 1, J_{HF} = 31.5 cps, —CH = CFOEt), 4.12 (q, 2, J_{HH} = 7.0 cps, —O—CH_2—CH_3), and 1.43 (t, 3, J_{HH} = 7.0 cps, —O—CH_2—CH_3); ^{19}F nmr ($CFCl_3$) δ 118.3 (m, 1, —CF_2—CF_2—C—Cl) and 115.2 (m, 1, —CF_2—CF_2—C—Cl). The vinylic F was not scanned. Although the presence of VIII in a single isomeric form lacks explanation, a careful analysis of the product mixture confirmed the absence of the other isomer.

Dehydrohalogenation of 1-(β,β-Difluorovinyl)-2,3,3,4,4-pentafluoro-2-chlorocyclobutane (IIb). A. Reaction with Potassium Ethoxide.—To a solution of 2.8 g (0.05 mol) of KOH in 15 ml of 95% ethanol was added during 90 min with stirring, 8.05 g (0.033 mol) of IIb. The mixture was kept below 50° with intermittent cooling in an ice bath. Stirring at ambient was continued until the fluorocarbon was consumed (90 min) while the mixture progressed from yellow to milky brown. The product was quenched, water washed, and finally dried (Na_2SO_4). Preparative gas chromatography (6 ft × 0.5 in. column packed with 15$_1$ SE-30 on 30–60 mesh Chromosorb W-HMDS at 200 and 260°) gave III (10%) and the new dienes V (12%) and VI (8%) along with a very complex mixture of by-products (70%). Compound V is the desired 1-(β,β-difluorovinyl)-2,3,3,4,4-pentafluorocyclobutene: $n^{27}D$ 1.3453; d^{27} 1.62; ir 3150 (C—H) and 1750 and 1700 cm^{-1} (C=C); ^{1}H nmr ($CFCl_3$) δ 4.96 (d, 1, J_{HF} (*trans*) = 25.0 cps); ^{19}F nmr ($CFCl_3$) δ 117.4 (m, 2, —CF_2—CF_2—C—F), 116.9 (m, 2, —CF_2—CF_2—C—F), 114.6 (m, 1, —CF_2—CF_2—C—F), 73.6 (m, 1, $—\overset{H}{C}=C<^{F}_{F}$), and 68.4 (m, 1, $—\overset{H}{C}=C<^{F}_{F}$); mass spectrum *m/e* 206, 187, 156, and 137.

Anal. Calcd for C_6HF_7: C, 35.0; H, 0.5; F, 64.5. Found: C, 33.03; H, 0.49; F, 64.01.

Compound VI has been identified as 1-(β,β-difluorovinyl)-2,3,3,4-tetrafluoro-4-chlorocyclobutene: $n^{27}D$ 1.3884; d^{27} 1.66; ir 3130 (C—H) and 1750 and 1700 cm^{-1} (C=C); mass spectrum *m/e* 222 (1 Cl), 203 (1 Cl), and 187.

Anal. Calcd for C_6HClF_6: C, 32.4; H, 0.5; Cl, 15.9; F, 51.2. Found: C, 31.31; H, 0.52; Cl, 15.65; F, 52.35.

B. Reaction with Potassium Hydroxide in Mineral Oil.—To a stirred mixture of 2.8 g (0.05 mol) of KOH in 10 ml of light mineral oil was added during 90 min 8.10 g (0.033 mol) of IIb. A very exothermic reaction ensued and a water bath was required to keep the mixture below 120°. Stirring at 75° was continued for 8 hr, after which vacuum stripping gave 4.3 g of crude product. Chromatographic analysis and separation (10 ft ×

0.25 in. column packed with 10% SE-30 on Chromosorb W at 160°) provided III (10%), V (25%), and VI (15%), identified by comparison with authentic samples prepared in the previous experiment.

C. Reaction with Silver Oxide in 95% Ethanol.—A solution of 48.4 g (0.2 mol) of IIb in 100 ml of 95% ethanol was added during 80 min to a stirred suspension of 23.2 g (0.1 mol) of Ag_2O in 100 ml of 95% ethanol. A mild exothermic reaction occurred with considerable AgCl formation during the addition and for the subsequent 16 hr of stirring at ambient. Quenching with water followed by a water wash and drying (Na_2SO_4) gave a pale yellow liquid. Chromatographic analysis (6 ft × 0.5 in. column packed with 15% SE-30 on 30–60 mesh Chromosorb W-HMDS at 160°) gave 30% recovered IIb, the desired diene, V (55%), and a new ether, IX (5%). Compound IX is identified as 1-(2,2-difluoro-2-ethoxy)ethyl-2,3,3,4,4-pentafluorocyclobutene: $n^{25}\mathrm{D}$ 1.3713; d^{25} 1.43; ir 3070 (C—H) and 1740 cm^{-1} (C═C); mass spectrum *m/e* 252, 233, 232, 224, 223, and 204.

Sulfuric Acid Hydrolysis of 1-(*cis*-α-Hydro-β-ethoxy-β-fluorovinyl-3,3,4,4-tetrafluoro-2-chlorocyclobutene (VII).—A mixture of 2.1 g (0.0085 mol) of VII and 5.0 ml of concentrated H_2SO_4 was prepared in a test tube and agitated until the cessation of gas evolution (15 min). The dark liquid was quenched carefully with ice water to give a dark oily product. Preparative gas chromatography (6 ft × 0.5 in. column packed with 15% SE-30 on 30–60 Chromosorb W-HMDS at 175°) provided IX (94%) identical with the sample prepared earlier by basic hydrolysis.

Sulfuric Acid Hydrolysis of 1-(2,2-difluoro-2-ethoxy)ethyl-3,3,4,4-tetrafluoro-2-chlorocyclobutene (VII).—In a manner analogous to the preceding reaction, 2.2 g (0.0086 mol) of VII was agitated with 5.0 ml of concentrated H_2SO_4 and the mixture quenched to give a dark oil. A 94% yield of IV was obtained on preparative chromatography of the mixture as described above.

Codimerization of Mixed Vinyl cyclobutenes with Chlorotrifluoroethylene.—A stainless steel autoclave was charged with 3.0 ml of *d*-limonene, 210 g (1.81 mol) of chlorotrifluoroethylene and 27.3 g of mixed cyclic fluorocarbons consisting of VI (30%), III (25%), 2,2,3,3-tetrafluorocyclobutene (20%), and VIb (25%) as an inert standard. The mixture was heated at 185° for 42 hr in a shaker at autogenous pressure to give a light yellow liquid. Fractional distillation to remove the 1,2-dichloro-1,2,3,3,4,4-hexafluorocyclobutane gave 24.6 g of crude liquid product. Comparative analytical gas chromatography (6 ft × 0.13 in. column packed with 10% UC W-98 on 80–100 mesh Chromosorb W at 120 and 200°; 6-ft × 0.13-in. column packed with 10% Carbowax 20 M on 80–100 mesh Chromosorb P at 140°; and a 10 ft × 0.25 in. column packed with 15% Ucon on 60–80 mesh firebrick R at 140°) indicated the presence of VI (15%), III (15%), V (10%), and IIb (25%) plus the three products, X (8%), XI (10%), and XII (12%). Vacuum fractionation of the product followed by preparative gas chromatography (6 ft × 0.50 in. column packed with 15% SE-30 on 30–60 mesh Chromosorb W-HMDS at 160°) permitted isolation of the products. Compound X is 2-chlorononafluoro(bi-1,1′-cyclobut-1-enyl): $n^{26}\mathrm{D}$ 1.3721; d^{26} 1.75; ir 1740, 1670, and 1610 cm^{-1} (unsymmetrical conjugated diene); ^{19}F nmr ($CFCl_3$) δ 117.5 (m, 2, —CF_2—$\mathbf{CF_2}$—CF═), 116.5 (m, 2,—CF_2—$\mathbf{CF_2}$—CCl═), 115 (m, 1, —CF_2—CF_2—**CF**═), 114.7 (m, 2, —$\mathbf{CF_2}$—CF_2—CCl), and 114.2 (m, 2, —$\mathbf{CF_2}$—CF_2—CF═); mass spectrum *m/e* 302 (1 Cl), 283 (1 Cl), 267, 233 (1 Cl), and 217.

Anal. Calcd for C_8F_9Cl: C, 31.7; Cl, 11.7. Found: C, 31.4; Cl, 12.43.

Compound XI is 2,2′-dichlorooctafluoro-(bi-1,1′-cyclobut-1-enyl): mp 67.8–69.1°; ir 1560 cm^{-1} (C═C); ^{19}F nmr ($CFCl_3$) δ 116.3 (m, 1, —$\mathbf{CF_2}$—CF_2—CCl═) and 112.8 (m, 1, —CF_2—$\mathbf{CF_2}$—CCl═); mass spectrum *m/e* 318 (2 Cl), 299 (2 Cl), 283 (1 Cl), 248 (2 Cl), and 247.

Anal. Calcd for $C_8F_8Cl_2$: C, 30.0; F, 47.7; Cl, 22.2. Found: C, 29.84; F, 47.88; Cl, 21.67.

Compound XII is 2,4′-dichlorooctafluoro(bi-1,1′-cyclobut-1-enyl): mp 58.4–59.9°; ir 1590 and 1550 cm^{-1} (unsymmetrical conjugated diene); mass spectrum *m/e* 318 (2 Cl), 299 (2 Cl), 283 (2 Cl), 248 (2 Cl), and 247. It is distinguished from XI by mixture melting point depression and by its infrared spectrum.

Careful analysis of the product mixture indicated only traces of higher boiling adducts and no perfluoro(bi-1,1′-cyclobut-1-enyl).

Coupling of 1-Iodo-2-chloro-3,3,4,4-tetrafluorocyclobutene (XIII) over Copper in a Hot Tube.—A 1-in.-i.d. Pyrex tube was packed with alternating 3-in. bands of fine copper turnings and copper along a 12-in. length and fitted with a condenser and dropping funnel at the top and a flask at the bottom before being suspended vertically in a tube furnace. The tube was heated to 180° and 46 g (0.16 mol) of XIII containing ~1% dimethylformamide was added dropwise at a rate of 2.0 ml per hr during 10 hr. After an additional 6 hr of heating, 13.5 g (53%) of white crystalline XI identical with that prepared previously was collected from the receiver flask.

Photochemical Reaction of 1,2-diiodo-3,3,4,4-tetrafluorocyclobutene (XIV) over Mercury.—A stirred mixture of 7.5 g (0.019 mol) of XIII and 42.6 g (0.113 mol) of mercury in a quartz vessel was irradiated by 13 clear mercury arc sources in a Rayonette photochemical reactor for 24 hr. Filtration of the mixture gave mercuric iodide, recovered mercury, 10 g of a dense green solid, and 4.2 g of colorless liquid. The unidentified green solid is unstable with respect to mercury and could not be purified for analysis. It is insoluble in water, ethanol, acetone, carbon tetrachloride, hexane, and diethyl ether. The liquid fraction was separated by gas chromatography (6 ft × 0.5 in. column packed with 15% SE-30 on 30–60 mesh Chromosorb W-HMDS at 200°) to give 2.0 g of recovered XIV and 2.2 g (32%) of 2,2′-diiodooctafluoro(bi-1,1′-cyclobut-1-enyl) (XV): mp 145.2–146.7°; ir 1520 cm^{-1} (C═C); mass spectrum *m/e* 502, 483, 375, and 325.

Anal. Calcd for $C_8F_8I_2$: C, 19.1; F, 30.3; I, 50.5. Found: C, 18.85; F, 30.91; I, 50.02.

Registry No.—IIa, 20290-60-2; IIb, 20290-61-3; III, 20290-62-4; IV, 20238-10-2; V, 20290-63-5; VI, 20290-64-6; VII, 20238-35-1; VIII, 20238-36-2; IX, 20238-11-3; X, 20290-65-7; XI, 20290-66-8; XII, 20238-12-4; XV, 20238-13-5.

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