

[CONTRIBUTION NO. 541 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO., WILMINGTON 98, DEL.]

Fluorodienes. II. Cycloalkylation Reactions of 1,1,4,4-Tetrafluorobutadiene

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Tetrafluorobutadiene has been found to polymerize when heated to give a mixture composed of a dimer, a trimer and higher polymers. The dimer was shown to be a divinylcyclobutane while the trimer was identified as a vinylcyclobutylcyclohexene. Reaction of the diene with tetrafluoroethylene, acrylonitrile and azodiformic ester gave cyclobutanes as the sole products.

In the previous paper¹ in this series, the synthesis of a number of fluorinated butadienes was described. Because of the ease with which tetrafluoroethylene undergoes cycloalkylation,² it was of interest to determine whether these fluorodienes would undergo similar cycloalkylations in preference to forming cyclohexenes by the Diels-Alder reaction. 1,1,4,4-Tetrafluorobutadiene was chosen for these studies because of its ease of preparation from tetrafluoroethylene and either acetylene or vinyl acetate.¹

Thermal polymerization of perfluorobutadiene to polycyclobutanes has been described by Prober and Miller.³ These authors reported that heating of perfluorobutadiene to 150–180° yielded a mixture of hexafluorocyclobutene, several dimers and trimers and small amounts of higher polymers. In contrast to Prober's and Miller's work, we have found that 1,1,4,4-tetrafluorobutadiene, when heated to 175°, yields a single dimer I, a mixture of the optical isomers of a single trimer II, and a number of higher polymers (see Fig. 1). No tetrafluorocyclobutene could be detected.

The dimer was shown to be a divinylcyclobutane, I, by nuclear magnetic resonance⁴ (n.m.r.) and infrared spectra. Infrared absorption at 1755 cm.⁻¹ confirmed the presence of a difluorovinyl group while bands at 3080 and 2950 cm.⁻¹ indicate vinyl hydrogens and hydrogens attached to saturated carbon atoms, respectively. The fluorine n.m.r. spectrum exhibited bands characteristic of the vinyl fluorines at -378 to -234 c.p.s. and also contained a quadruplet at -1235, -1450, -2095 and -2325 c.p.s., having the characteristic weak/strong/strong/weak pattern of the 1,1,2,2-tetrafluorocyclobutyl group. This structure was confirmed chemically by permanganate oxidation of the dimer to tetrafluorosuccinic acid. The dimer was also converted to the dibasic acid III by acid hydrolysis.

The trimer was presumed to have structure II on the basis of infrared analysis and conversion to derivatives. Infrared absorption at 1755 and 1640 cm.⁻¹ showed the presence of a difluorovinyl group and an unfluorinated double bond, respectively. The spectrum also contained a strong vinyl C-H band at 3080 cm.⁻¹ and a weak saturated C-H band at 2950 cm.⁻¹. Oxidation with chromic acid gave a monobasic acid, IV, that did not have the difluorovinyl group as indicated by absence of

infrared absorption near 1755 cm.⁻¹. Hydrolysis with sulfuric acid gave a monobasic acid, V, having one more methylene group than IV and having an infrared spectrum very similar to that of IV. Reduction of II with hydrogen over a Pd-C catalyst yielded a liquid product, VI (trimer, a solid, m.p. 40–42°), whose infrared spectrum indicated a difluorovinyl group only. In addition, the intensity of the saturated carbon-hydrogen band at 2950 cm.⁻¹ was now greater than that of the vinyl hydrogen band at 3080 cm.⁻¹.

Structures of the higher polymers obtained in the thermal polymerization of tetrafluorobutadiene have not been determined. Preliminary evidence indicates that one of the products is a solid tetramer having at least one difluorovinyl group and that there are other higher-boiling fractions having no CF₂=CH absorption in the infrared.

Although the presumed presence of a cyclohexene ring in II suggests that the diene is capable of undergoing the Diels-Alder reactions, we have not been able to uncover any other examples. Efforts to obtain Diels-Alder adducts from tetrafluorobutadiene and maleic anhydride, tetracyanoethylene, quinone and 1,4-naphthaquinone were unsuccessful. Products were obtained by reaction of the diene with acrylonitrile, azodiformic ester and tetrafluoroethylene, but in each case they were the cyclobutanes VII, VIII and IX. The failure of the diene to undergo the Diels-Alder reaction may indicate an inability to assume a "cis"-planar configuration because of steric hindrance. This inference is supported by a Stuart-Briegleb-type molecular model of the diene which shows it to be incapable of assuming a "cis"-planar configuration. If this rationalization is correct, then the structure assigned to the trimer of tetrafluorobutadiene will require more rigorous proof than that available at this time.

Reaction of tetrafluorobutadiene with acrylonitrile gave a single product, the infrared spectrum of which showed strong absorption at 1755 cm.⁻¹ for the difluorovinyl group. It has not been established which of the structures depicted by VII (Fig. 2) correctly represents this cyclobutane. When the diene was heated with the ethyl ester of azodiformic acid, a 12% yield of the diazacyclobutane VIII was obtained. As in the other cases, the structure of the diazo compound was assigned on the basis of infrared absorption which occurred at 1755 cm.⁻¹ for difluorovinyl and at 1780 cm.⁻¹ for ethoxycarbonyl. These reactions are similar to the previously reported cycloalkylations of tetrafluoroethylene with acrylonitrile² and with azodiformic ester.⁵

(1) J. L. Anderson, R. E. Putnam and W. H. Sharkey, *THIS JOURNAL*, **83**, 382 (1961).

(2) D. D. Coffman, P. L. Barrick, R. D. Cramer and M. S. Raasch, *ibid.*, **71**, 490 (1949).

(3) M. Prober and W. T. Miller, Jr., *ibid.*, **71**, 598 (1949).

(4) Spectra were obtained as described in paper I of this series.

Identity of the 1:1 adduct obtained from tetrafluorobutadiene and tetrafluoroethylene as the cyclobutane IX (Fig. 2) was established by infrared analysis and conversion to a monobasic acid. The adduct showed strong absorption at 1755 cm^{-1} , denoting the presence of the difluorovinyl group. Hydrolysis with concentrated sulfuric acid yielded the monobasic acid X which, when treated with SF_4 ,⁶ gave the corresponding trifluoromethyl compound XI. Perfluorobutadiene also reacts with tetrafluoroethylene to give a cyclobutane. The infrared spectrum of this product has a very strong band at 1785 cm^{-1} , which is indicative of the trifluorovinyl group.

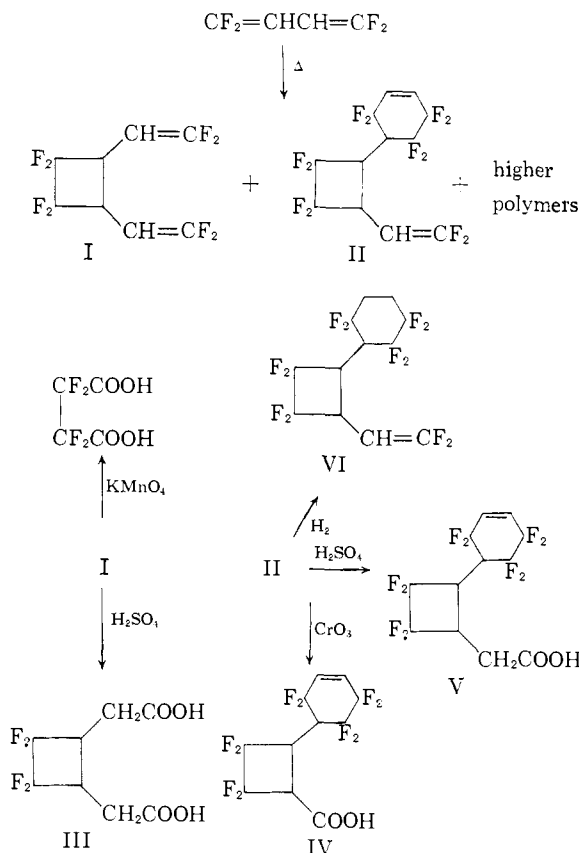


Fig. 1.—Thermal polymerization of 1,1,4,4-tetrafluorobutadiene.

In an attempt to convert IX to the ethyl ester of X by reaction with alcoholic sodium ethoxide, it was found that elimination of HF from the ring occurred in addition to reaction at the double bond. The only products that could be identified were the cyclobutenyl ester XII obtained in 17% yield and the corresponding ethoxycyclobutene XIII obtained in 14% yield. The reaction of alkoxides with fluorinated double bonds has been described previously.¹⁷

(5) R. D. Cramer, U. S. Patent 2,456,176, December 14, 1948.

(6) W. R. Hasek, W. C. Smith, Jr., and V. A. Engelhardt, THIS JOURNAL, **82**, 543 (1960).

(7) R. Meier and F. Bohler, *Ber.*, **90**, 2342, 2344 (1957); I. L. Knunyants, L. S. German and B. L. Dyatkin, *Bull. Acad. Sci. U.S.S.R.*, **1387** (1956); R. A. Sheppard, H. Lessoff, J. D. Domijen, D. B. Hilton and T. F. Finnegan, *J. Org. Chem.*, **23**, 2011 (1958), and references therein.

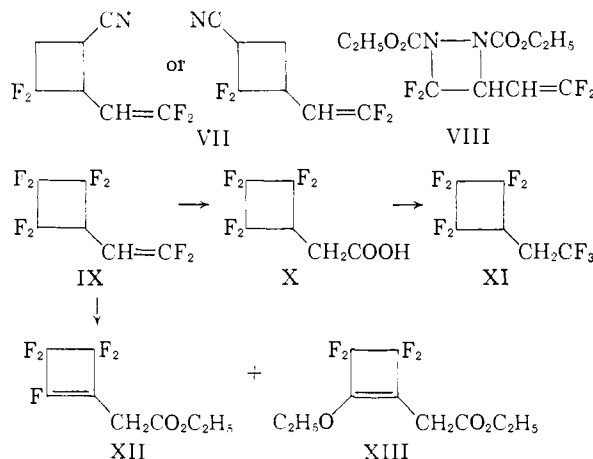


Fig. 2.—Cyclobutanes from 1,1,4,4-tetrafluorobutadiene.

Experimental⁸

Thermal Polymerization of Tetrafluorobutadiene.—An evacuated stainless-steel bomb cooled in a solid carbon dioxide-acetone mixture was charged with 104 g. of 1,1,4,4-tetrafluorobutadiene. The bomb was closed and heated to 175° for 16 hours. The product was fractionated to give 38 g. (36.5%) of liquid dimer I, b.p. 108° , n_D^{20} 1.3458. An infrared spectrum of the dimer exhibited the major bands: 3080 cm^{-1} (vinyl hydrogen), 2950 (saturated carbon-hydrogen), 1755 (difluorovinyl), 1405 , 1350 , 1305 , 1255 , 1165 , 1080 , 922 , 906 , 814 , 759 . A fluorine nuclear magnetic resonance spectrum showed 5 peaks in the region -378 to -234 c.p.s. (difluorovinyl) and a quadruplet at -1235 , -1450 , -2045 and -2325 c.p.s. (1,1,2,2-tetrafluorocyclobutyl).

Anal. Calcd. for $\text{C}_8\text{H}_4\text{F}_8$: C, 38.11; H, 1.60; F, 60.29. Found: C, 37.90; H, 2.15; F, 60.36.

A second fraction boiling at 143 – 144° (93 mm.) weighed 23 g. (22%) and proved to be a trimer of tetrafluorobutadiene, 3,3,5,5,6,6-hexafluoro-4-[2-(2,2-difluorovinyl)-3,3,4,4-tetrafluorocyclobutyl]-cyclohexene (II). The trimer melted at 40 – 42° after recrystallization from *n*-hexane.⁹ An infrared spectrum exhibited the major bands: 3080 cm^{-1} (vinyl hydrogen), 2950 (saturated carbon-hydrogen), 1755 (difluorovinyl), 1640 ($\text{CH}=\text{CH}$), 1385 , 1350 , 1305 , 1255 , 1170 , 925 , 906 , 815 , 758 .

Anal. Calcd. for $\text{C}_{12}\text{H}_6\text{F}_{12}$: C, 38.11; H, 1.60; F, 60.29. Found: C, 37.65; H, 1.70; F, 59.53.

After distillation of dimer and trimer, there remained 22.5 g. of a high-boiling residue presumed to be a mixture of higher polymers of the diene.

Oxidation of I to Tetrafluorosuccinic Acid.—To a stirred suspension of 80 g. of KMnO_4 , 80 g. of NaHCO_3 , 250 ml. of H_2O and 80 ml. of acetone was added dropwise a solution of 18 g. of I in 80 ml. of acetone. The temperature was maintained at 20 – 25° by cooling with ice. The resulting mixture was neutralized with H_2SO_4 , and excess permanganate was decomposed with SO_2 . Acetone was removed by distillation and the aqueous residue was exhaustively extracted with ether. Evaporation of the ether gave 2.5 g. of tetrafluorosuccinic acid, m.p. 114 – 115° , identified by analysis and identity of its infrared spectrum with that of an authentic sample.

Anal. Calcd. for $\text{C}_4\text{F}_4\text{O}_4\text{H}_2$: C, 25.28; H, 1.05. Found: C, 25.35; H, 1.50.

Hydrolysis of I to 1,2-Bis-(carboxymethyl)-3,3,4,4-tetrafluorocyclobutane (III).—A mixture of 33 g. of tetrafluorobutadiene dimer, 60 ml. of water and 300 ml. of sulfuric acid was stirred and heated to reflux (110°). After about 2 hours the entire organic layer had dissolved and refluxing had ceased. The mixture was poured onto 1.5 kg. of ice and the resulting solution was extracted with

(8) All melting and boiling points are uncorrected.

(9) Redistilled samples of the trimer melted as high as 50° . This behavior is best explained as the result of a difference in isomer distribution depending on purification procedure. Infrared spectra of fractions of different melting points were nearly identical.

four 100-ml. portions of ether. The ether layer was dried over magnesium sulfate, filtered, and the ether was removed on a steam-bath. There remained 23 g. of a tan solid, m.p. 139–142°. Two recrystallizations from water gave pure white crystals of 1,2-bis-(carboxymethyl)-3,3,4,4-tetrafluorocyclobutane, m.p. 142°. The yield was 60%. An infrared spectrum of the acid exhibited the major bands: 3030 cm^{-1} (broad, bonded OH), 1725 (COOH), 1385, 1340, 1285, 1225, 1170, 1085, 1030, 973, 779.

Anal. Calcd. for $\text{C}_8\text{H}_8\text{F}_4\text{O}_4$: C, 39.35; H, 3.30; F, 31.13. Found: C, 39.66; H, 3.43; F, 30.80.

Oxidation of II to 3,3,5,5,6,6-Hexafluoro-4-(2-carboxy-3,3,4,4-tetrafluorocyclobutyl)-cyclohexene (IV).—To a solution of 10 g. (0.026 mole) of tetrafluorobutadiene trimer in 100 ml. of glacial acetic acid was added dropwise a solution of 15 g. (0.15 mole) of chromium trioxide in 15 ml. of water and 100 ml. of acetic acid. During the addition (10 minutes) the temperature rose to 35°. The mixture was heated to 100° for 1 hour; 30 ml. of methanol was added to decompose excess chromic acid. The solution was evaporated to dryness *in vacuo*, 300 ml. of water was added, and the solution was extracted with three 100-ml. portions of ether. The combined ether extracts were extracted with three 50-ml. portions of 10% Na_2CO_3 . The combined aqueous extracts were acidified with hydrochloric acid, extracted with ether and the ether extract was dried over calcium chloride. On evaporation of the ether, there was obtained 2.3 g. (25%) of a solid, m.p. 137–143°. Two recrystallizations from benzene gave white needles of IV, m.p. 145–146°. An infrared spectrum of the acid exhibited the major adsorption bands: 3040 cm^{-1} (broad, bonded OH), 1735 (COOH), 1405, 1295, 1265, 1220, 1185, 1115, 1075, 985, 913, 826, 750.

Anal. Calcd. for $\text{C}_{11}\text{H}_8\text{F}_{10}\text{O}_2$: C, 35.69; H, 1.63. Found: C, 36.01; H, 1.84.

Reduction of II to 2,2,3,3,6,6-Hexafluoro-1-[2-(2,2-difluorovinyl)-3,3,4,4-tetrafluorocyclobutyl]-cyclohexane (VI).—In a low-pressure hydrogenation apparatus, a mixture of 10 g. of tetrafluorobutadiene trimer, 100 ml. of ethanol and 0.5 g. of 10% Pd-on-carbon was treated with 45 lb./sq. in. hydrogen at room temperature. Absorption of hydrogen occurred during 15 minutes. The catalyst was removed by filtration, the solvent was removed *in vacuo* and the residual liquid (8 g.) was fractionated. There was obtained 5.8 g. (58%) of liquid, VI, b.p. 125–129° (35 mm.); infrared spectrum 3100 cm^{-1} (vinyl hydrogen), 2980 (saturated carbon-hydrogen), 1755 (difluorovinyl), 1355, 1310, 1283, 1227, 1165, 1075, 980, 933, 794.

Anal. Calcd. for $\text{C}_{12}\text{H}_8\text{F}_{12}$: C, 37.90; H, 2.13. Found: C, 38.28; H, 2.39.

Hydrolysis of II to 3,3,5,5,6,6-Hexafluoro-4-(2-carboxymethyl-3,3,4,4-tetrafluorocyclobutyl)-cyclohexene (V).—A mixture of 62 g. of tetrafluorobutadiene trimer, 40 ml. of water and 200 ml. of sulfuric acid was stirred and heated to 100° for 1 hour at which time the entire organic layer solidified. The product was poured into 1 liter of water and filtered. The solid was washed twice with water and was then treated with a solution of 30 g. of sodium carbonate in 400 ml. of water. After this treatment there remained 18.1 g. of a light brown solid, the identity of which was not established.

The sodium carbonate solution was acidified with concentrated hydrochloric acid and the precipitated solid was washed twice with water and air-dried. It weighed 34.1 g. (55%) and melted from 120–155°. Fractional crystallization from benzene gave a series of fractions melting in the range 149–166°. All of these fractions had nearly identical infrared spectra and analyses indicated that they were probably mixtures of the four theoretically possible *dl*-pairs of the expected acid V. An infrared spectrum of a fraction melting at 155–166° exhibited major bands at 3030 cm^{-1} (broad, bonded OH), 1730 (COOH), 1400, 1350, 1278, 1250, 1225, 1108, 995, 889, 750.

Anal. Calcd. for $\text{C}_{12}\text{H}_8\text{F}_{10}\text{O}_2$: C, 38.52; H, 2.16; F, 50.78. Found: C, 38.09; H, 2.43; F, 50.68.

(2,2-Difluorovinyl)-cyanodifluorocyclobutane (VII).—In an 80-ml. stainless-steel, high-pressure vessel were charged 20 g. of tetrafluorobutadiene and 17 g. of acrylonitrile. The bomb was heated to 175° for 16 hours. The crude reaction mixture (24 g.) was filtered to remove polyacrylonitrile and distilled. There was obtained, after a

forerun of acrylonitrile and tetrafluorobutadiene dimer, 7 g. (25%) of liquid cyclobutane, b.p. 68–70° (10 mm.). An infrared spectrum of the product exhibited major bands at 3100 cm^{-1} (vinyl CH), 2990 (saturated CH), 2250 (CN), 1755 (difluorovinyl), and twelve major bands between 820 and 1430 cm^{-1} .

Anal. Calcd. for $\text{C}_7\text{H}_5\text{F}_4\text{N}$: C, 46.93; H, 2.81. Found: C, 46.54; H, 3.01.

1,2-Bis-(ethoxycarbonyl)-3-(2,2-difluorovinyl)-4,4-difluoro-1,2-diazacyclobutane (VIII).—A glass Carius tube was charged with 25 g. (0.15 mole) of the ethyl ester of azodiformic acid and 12.6 g. (0.1 mole) of tetrafluorobutadiene. The tube was sealed and heated to 90° for 12 hours. Distillation of the viscous, nearly colorless reaction product gave 3.5 g. (12%) of VIII, b.p. 90° (0.4 mm.). An infrared spectrum of VIII exhibited major bands at 3100 cm^{-1} (vinyl CH), 2950 (saturated CH), 1780 (ester CO), 1755 (difluorovinyl) and ten strong bands in the 910–1430 cm^{-1} region.

Anal. Calcd. for $\text{C}_{10}\text{H}_{12}\text{F}_4\text{O}_4\text{N}_2$: C, 40.00; H, 4.04; N, 9.35. Found: C, 39.76; H, 4.37; N, 9.76.

2,2,3,3,4,4-Hexafluoro-1-(2,2-difluorovinyl)-cyclobutane (IX).—In an evacuated 200-ml. stainless-steel high-pressure vessel, cooled in a solid carbon dioxide-acetone mixture, was condensed 30 g. of tetrafluorobutadiene. There was then added 60 g. of tetrafluoroethylene, and the bomb was closed and heated to 190° for 16 hours. There was obtained 41 g. of liquid product which on distillation yielded 30 g. (56%) of difluorovinylhexafluorocyclobutane, b.p. 56–57°, and 8 g. of tetrafluorobutadiene dimer I, b.p. 108°. An infrared spectrum of IX exhibited the major bands: 3090 cm^{-1} (vinyl hydrogen), 2960 (saturated CH), 1755 (difluorovinyl), 1405, 1305, 1200, 1155, 1112, 927, 905, 785.

Anal. Calcd. for $\text{C}_6\text{F}_8\text{H}_2$: C, 31.87; H, 0.89; F, 67.04. Found: C, 31.63; H, 1.20; F, 66.55.

Perfluoro-(vinylcyclobutane).—In a 200-ml. stainless-steel high-pressure vessel were heated 30 g. of perfluorobutadiene and 60 g. of tetrafluoroethylene for 16 hours at 190°. There was obtained 24.5 g. of product liquid at room temperature. Fractionation gave 11.2 g. (21%) of perfluorovinylcyclobutane boiling at 50–51°; infrared major bands at 1785 cm^{-1} (trifluorovinyl), 1410, 1334, 1300, 1212, 1180, 1144, 1037, 945.

Anal. Calcd. for C_6F_{10} : C, 27.50; F, 72.50. Found: C, 28.07; F, 72.24.

1-Carboxymethyl-2,2,3,3,4,4-hexafluorocyclobutane (X).—In a flask equipped with a reflux condenser were placed 200 g. of 90% sulfuric acid and 30 g. of difluorovinylhexafluorocyclobutane VIII. The mixture was refluxed for 45 hours during which time the temperature rose from 60 to 140°. The reaction mixture was poured onto ice and filtered. After drying *in vacuo* at room temperature the gray solid weighed 21.5 g. (67%) and melted at 70–75°. Sublimation at 50° and 5 mm. gave pure white crystals of carboxymethylhexafluorocyclobutane, m.p. 73–73.5°.

Anal. Calcd. for $\text{C}_6\text{H}_4\text{F}_6\text{O}_2$: C, 32.45; H, 1.82; F, 51.33. Found: C, 32.42; H, 1.86; F, 51.27.

2,2,3,3,4,4-Hexafluoro-1-(2,2,2-trifluoroethyl)-cyclobutane (XI).—A 145-ml. Hastelloy pressure vessel was charged with 17 g. of carboxymethylhexafluorocyclobutane and 32 g. of sulfur tetrafluoride. The bomb was heated to 160° for 16 hours. There was obtained 14 g. of light yellow liquid which gave on distillation 9.5 g. (51%) of trifluoroethylhexafluorocyclobutane, b.p. 81–82°.

Anal. Calcd. for $\text{C}_6\text{H}_5\text{F}_9$: C, 29.28; H, 1.23. Found: C, 29.75; H, 1.36.

Reaction of Difluorovinylhexafluorocyclobutane with Sodium Ethoxide.—To a pressure bottle was added 100 ml. of absolute ethanol containing 0.16 mole of sodium ethoxide and 37 g. of difluorovinylhexafluorocyclobutane. The bottle was capped and heated to 90° for 16 hours. The solid sodium fluoride and sodium hydrogen fluoride were removed by filtration and the acidic filtrate was neutralized with solid sodium carbonate. After filtering to remove inorganic material, most of the ethanol was removed by distillation. The residual oil was poured into 300 ml. of water, the organic layer was taken up in ether, dried with magnesium sulfate and distilled. There were obtained two fractions of b.p.

48° (7 mm.) and 74° (1 mm.). The lower boiling fraction (6.5 g., 17%) is thought to be 1-ethoxycarbonylmethyl-2,3,3,4,4-pentafluorocyclobutene (XII). An infrared spectrum of the ester exhibited major bands at 3000 cm.⁻¹ (saturated CH), 1755 (ester CO), 1665 (cyclobutene C=C), and twelve strong bands in region 870-1430 cm.⁻¹.

Anal. Calcd. for C₅F₈H₂O₂: C, 41.75; H, 3.07; F, 41.28. Found: C, 41.72; H, 3.22; F, 41.48.

The higher boiling fraction (5.5 g., 14%) was presumed to be 1-ethoxycarbonylmethyl-2-ethoxy-3,3,4,4-tetrafluorocyclobutene (XIII). An infrared spectrum of XIII exhibited major bands at 2990 cm.⁻¹ (saturated CH), 1750 (ester CO), 1695 (cyclobutene C=C), and twelve strong bands in the region 950-1430 cm.⁻¹.

Anal. Calcd. for C₁₀H₁₂F₄O₂: C, 46.88; H, 4.72; F, 29.66. Found: C, 47.13; H, 4.84; F, 29.29.

[CONTRIBUTION NO. 542 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO., WILMINGTON 98, DEL.]

Fluorodienes. III. 1,1,2-Trifluoro-3-trifluoromethylbutadiene

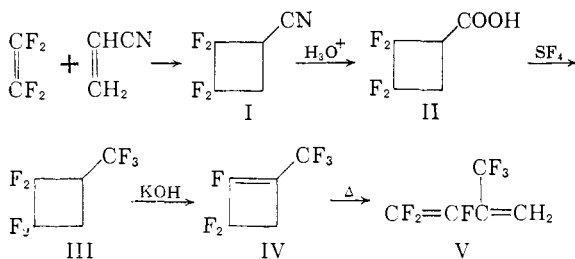
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A five-step synthesis of 1,1,2-trifluoro-3-trifluoromethylbutadiene from tetrafluoroethylene and acrylonitrile is described. Purification of the diene on a large scale was accomplished by vapor phase chromatography. The diene polymerized to an elastomer when initiated with azobisisobutyronitrile or irradiated with ultraviolet light.

In the previous papers¹ in this series the preparation of highly fluorinated dienes by pyrolysis of cyclobutenes and cyclobutyl acetates was described. However, these studies were limited to cyclobutenes derived from tetrafluoroethylene and chlorotrifluoroethylene, *i.e.*, those having no allylic hydrogens. Recent work² in this Laboratory has shown sulfur tetrafluoride to be a versatile fluorinating agent and has provided a route to 1-trifluoromethyl-2,3,3-trifluorocyclobutene (IV). Pyrolysis of this cyclobutene proceeded normally to give the new fluorodiene, 1,1,2-trifluoro-3-trifluoromethylbutadiene (V).

Reaction of tetrafluoroethylene with acrylonitrile has previously been described.³ The product, 2,2,3,3-tetrafluorocyclobutanecarbonitrile (I), was hydrolyzed to the corresponding acid II in excellent yield.³ Treatment of II with sulfur tetra-



fluoride⁴ at 130° gave 1-trifluoromethyl-2,2,3,3-tetrafluorocyclobutane (III) in 67% yield, together with tetrafluorocyclobutanecarbonyl fluoride as the only by-product. Attempted dehydrofluorinations of III with aqueous alkali or molten KOH were unsuccessful. However, when the cyclobutane was added dropwise to a slurry of powdered KOH in mineral oil a vigorous reaction ensued and 1-trifluoromethyl-2,3,3-trifluorocyclobutene

was produced in 72% yield. Pyrolysis of IV by passage through a tubular reactor at 700° and 5 mm. pressure yielded a mixture of 1,1,2-trifluoro-3-trifluoromethylbutadiene (V) and the starting material IV in a ratio of 3:2. The pyrolysis was exceptionally clean when run at a rate of 30 g./hr. At higher rates, the yield decreased and some carbonization occurred.

Attempts to separate the diene-cyclobutene mixture by distillation were unsuccessful. The diene polymerized rapidly during distillation even in the presence of polymerization inhibitors such as hydroquinone and *p-t*-butyl-*o*-cresol. Small samples of the diene obtained by careful fractionation in a 10-inch column packed with glass helices were contaminated with the cyclobutene. However, it was possible to separate the mixture by vapor phase chromatography using a column 6 ft. × 2.5 in. packed with silicone "200" oil supported on firebrick. In this apparatus 12-g. samples of the mixture could be separated quantitatively in 20 minutes.

1,1,2-Trifluoro-3-trifluoromethylbutadiene was polymerized in bulk by using azobisisobutyronitrile catalyst at 90° or by irradiation with ultraviolet light at room temperature. The polymer obtained by ultraviolet irradiation was a logy elastomer that could be pressed to a clear film at 70°. Infrared spectra indicated the absence of either methylene or difluoromethylene groups, thus showing the polymer to have been formed exclusively by 1,4-polymerization, $[\text{CF}_2\text{CF}=\text{C}(\text{CF}_3)\text{CH}_2]_n$.

During the vapor phase chromatographic purification of the mixture obtained by pyrolysis of trifluoromethyltrifluorocyclobutene IV the presence of five minor impurities was noted. Three of these impurities were identified as trifluoromethyltetrafluorocyclobutane (III), tetrafluoroethylene and 3,3,3-trifluoropropene by comparison of their retention times with those of authentic samples. Since it has been shown that fluorinated cyclobutanes can be cleaved pyrolytically to olefins⁵ it was suspected that these impurities arose

(1) (a) J. L. Anderson, R. E. Putnam and W. H. Sharkey, *THIS JOURNAL*, **83**, 382 (1961); (b) R. E. Putnam, W. H. Sharkey and J. L. Anderson, *ibid.*, **83**, 386 (1961).

(2) W. R. Hasek, W. C. Smith, Jr., and V. A. Engelhardt, *ibid.*, **82**, 543 (1960).

(3) D. D. Coffman, P. L. Barrick, R. D. Cramer and M. S. Raasch, *ibid.*, **71**, 490 (1949).

(4) Prepared by the method of C. W. Tullock, F. S. Fawcett, W. C. Smith and D. D. Coffman, *ibid.*, **82**, 539 (1960).

(5) J. L. Anderson, U. S. Patents 2,733,278, Jan. 31, 1956, and 2,773,089, Dec. 4, 1956.