

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 $\text{C}_5\text{F}_8\text{H}_2\text{O}_2$: 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 $\text{C}_{10}\text{H}_{12}\text{F}_4\text{O}_2$: 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

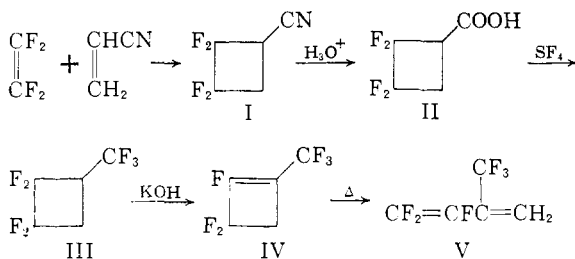
BY R. E. PUTNAM AND J. E. CASTLE

RECEIVED JUNE 8, 1960

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. \times 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).

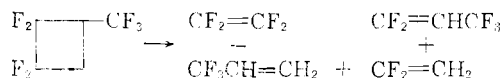
(2) W. R. Hasek, W. C. Smith, Jr., and V. A. Engelhardt, *ibid.*, **82**, 543 (1960).

(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.

by cleavage of III present as an impurity in IV. Accordingly, a sample of the cyclobutane III was passed through a hot tube at 750° and 5 mm. pressure. Under these conditions a 50% yield of a mixture of four olefins in approximately equal amounts was obtained. Three of these olefins were



shown to be tetrafluoroethylene, vinylidene fluoride and 3,3,3-trifluoropropene by comparison with authentic samples. An attempt to brominate the mixture gave a mixture of dibromides that could not be separated by distillation. However, the proton and fluorine nuclear magnetic resonance (n.m.r.) spectra⁶ of the mixture showed the presence of $\text{BrCF}_2\text{CHBrCF}_3$, as well as the dibromides of tetrafluoroethylene, vinylidene fluoride and trifluoropropene. This evidence, together with the work of Anderson⁵ on pyrolysis of other fluorinated cyclobutanes, indicates that the unidentified olefin was 1,1,3,3,3-pentafluoropropene.

Experimental⁷

2,2,3,3-Tetrafluorocyclobutanecarbonitrile.—The preparation of this compound has previously been described.³ This procedure consistently gave yields of 80–82%.

2,2,3,3-Tetrafluorocyclobutanecarboxylic Acid.—Hydrolysis of tetrafluorocyclobutanecarbonitrile³ on a 250–500-g. scale gave the corresponding acid in yields of 85–95%.

1-Trifluoromethyl-2,2,3,3-tetrafluorocyclobutane.—In a 400-ml. stainless steel lined shaker tube was placed 100 g. (0.58 mole) of tetrafluorocyclobutanecarboxylic acid. The tube was closed, cooled to –80°, evacuated, and charged with 185 g. (1.7 moles) of sulfur tetrafluoride. The tube was heated to 130° for 16 hours, cooled to room temperature and bled slowly in a hood to remove HF, SO_2 and excess SF_4 . The 98 g. of brownish liquid that remained was poured into a mixture of 100 ml. of xylene and 10 g. of sodium fluoride to remove dissolved HF. The mixture was filtered and distilled to give 76 g. (67%) of 1-trifluoromethyl-2,2,3,3-tetrafluorocyclobutane, b.p. 61–62°, n_D^{25} 1.2925; n.m.r. proton and F^{19} spectra were consistent with the assigned structure. The proton spectrum exhibited a group of overlapping peaks centered at –95.5 c.p.s. The F^{19} spectrum consisted of a single peak at 344 c.p.s. (CF_3), a widely split quadruplet (–1140, –1365, –1895, –2125 c.p.s.; CF_2 adjacent to CHCF_3) and a second quadruplet (–1260, –1480, –1550, –1770 c.p.s.; CF_2 adjacent to CH_2).

Anal. Calcd. for $\text{C}_5\text{F}_7\text{H}_3$: C, 30.63; H, 1.54; F, 67.83. Found: C, 31.00; H, 1.72; F, 67.67.

1-Trifluoromethyl-2,3,3-trifluorocyclobutene.—In a flask equipped with a stirrer, dropping funnel and Vigreux column attached to a solid carbon dioxide-cooled trap were placed 42 g. of powdered KOH (10–15% H_2O) and 90 ml. of Primol D mineral oil. The mixture was stirred rapidly and 31 g. of 1-trifluoromethyl-2,2,3,3-tetrafluorocyclobutane was added dropwise at a rate such that slow distillation occurred. When all the material had been added, the pot temperature was gradually raised to 100° until distillation ceased. There was obtained 20 g. (72%) of water-white distillate which proved to be nearly pure 1-trifluoromethyl-2,3,3-trifluorocyclobutene, b.p. 34–35°, n_D^{25} 1.2943; n.m.r. proton and F^{19} spectra were consistent with the assigned structure. The proton spectrum consisted of a doublet at –99.5 and –111 c.p.s. while the F^{19} spectrum exhibited three single peaks at 452 (CF_3), –950 ($=\text{CF}$) and –1560 c.p.s. (CF_2) with an intensity ratio of 3/1/2. An infrared spectrum of the material showed strong fluorovinyl absorption at 1755 cm^{-1} .

Anal. Calcd. for $\text{C}_5\text{F}_6\text{H}_2$: C, 34.11; H, 1.15; F, 64.74. Found: C, 34.27; H, 1.19; F, 64.20.

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

(7) All boiling points are uncorrected.

1,1,2-Trifluoro-3-trifluoromethylbutadiene.—Pyrolysis of 1-trifluoromethyl-2,3,3-trifluorocyclobutene was accomplished in a vertical Vycor tube, 2 ft. long and 0.75 in. in diameter, packed with 8-mm. quartz tubing cut into 5-mm. lengths and equipped with a thermocouple well extending up through the packing to the center of the heated section of the tube. The tube was heated to 700° (measured at center of heated zone) by means of a standard 110-volt tube furnace, evacuated to 5 mm., and 61 g. of 1-trifluoromethyl-2,3,3-trifluorocyclobutene was added dropwise over a period of 2 hours. There was obtained 60 g. of water-white pyrolyzate in a solid carbon dioxide trap, connected to the base of the pyrolysis tube, essentially no product was found in a liquid N_2 trap attached in series with the solid carbon dioxide trap. No carbonization occurred in the tube during pyrolysis. Infrared and nuclear magnetic resonance spectra indicated the presence of a mixture of trifluoromethyltrifluorocyclobutene (42%) and trifluoro-trifluoromethylbutadiene (58%). A vapor phase chromatogram of the mixture confirmed these proportions. The mixture could not be separated by distillation because of similar boiling points of the components and because of the tendency of the diene to polymerize on prolonged heating. Vapor phase chromatography, as described below, gave pure diene, b.p. 39°. An infrared spectrum of the diene exhibited the strong band at 1760 cm^{-1} characteristic of a highly fluorinated double bond.

Anal. Calcd. for $\text{C}_5\text{F}_8\text{H}_2$: C, 34.11; H, 1.15. Found: C, 33.80; H, 0.99.

Vapor Phase Chromatographic Separation of Diene-Cyclobutene Mixtures.—A simple column⁸ for the v.p.c. separation of large quantities of the diene-cyclobutene mixture described above was constructed as follows. The large end of a Büchner funnel was inserted in the bottom of a vertical glass tube (6' × 2.5") and was fixed in position by means of a rubber stopper. The tube was packed with firebrick-supported silicone 200 oil on a bed of glass wool in the funnel. To the spout of the Büchner funnel was attached a preheater consisting of a chamber 6 in. × 0.5 in., packed with quartz chips and having an inlet for helium and an orifice through which samples could be injected with a hypodermic syringe. To the top of the column was taped the upper half of a polyethylene bottle of appropriate size. In the neck of the bottle was inserted a rubber stopper holding a brass tee. In the two remaining orifices of the tee were mounted a thermistor and a hypodermic needle, which, for sample collection, was inserted through rubber serum caps into spiral traps. The preheater was heated to 100° by means of a heating tape; the helium flow was adjusted to 500 ml. per minute; and the fractions were detected as eluted by thermal conductivity change as measured by the thermistor element of a Wheatstone bridge circuit.

In the above system it was possible to separate 12-g. samples of the pyrolysis mixture containing 60% diene and 40% cyclobutene, together with trace amounts of five impurities. Separation was quantitative in about 20 minutes. Larger samples could not be used because of the difficulty in introducing the entire sample quickly. In a typical run, 79.5 g. of pyrolysis mixture was separated in 12-g. portions giving 45.5 g. of diene and 29 g. of cyclobutene. Recovery of charged material was 94%, the loss being mainly the more volatile cyclobutene.

Pyrolysis of 1-Trifluoromethyl-2,2,3,3-tetrafluorocyclobutane.—A 19-g. sample of the cyclobutane was pyrolyzed at 750° and 5 mm. in the apparatus described previously. From the solid carbon dioxide cooled trap was recovered 7 g. of cyclobutane. A liquid nitrogen trap contained 10 g. of colorless solid, all of which boiled below 0°. A vapor phase chromatographic analysis of this fraction showed it to consist of four compounds, including tetrafluoroethylene, vinylidene fluoride and 3,3,3-trifluoropropene (by comparison with authentic samples).

The entire gas sample was condensed in a Carius tube with 11 g. of bromine and was heated to 120° for 12 hours. The excess bromine was removed by distillation and the last traces by shaking with mercury. Distillation gave three fractions: A, b.p. 72–82°; B, 82–87°; C, 87–104°. Proton and fluorine nuclear magnetic resonance spectra indicated the compositions: A, $\text{BrCF}_2\text{CF}_2\text{Br}$ 10%, $\text{BrCH}_2\text{CF}_2\text{Br}$ 80%,

(8) The authors wish to express their appreciation to Dr. B. C. Anderson of this Laboratory for construction of this column and for his assistance in the chromatographic separations.

CF₃CHBrCF₂Br 10%; B, BrCH₂CF₂Br 20%, CF₃CHBrCF₂Br 50%, CF₃CHBrCH₂Br 30%; C, CF₃CHBrCF₂Br 20%, CF₃CHBrCH₂Br 80%. Although pentafluoropropene was not positively identified, there is little doubt of its presence. It was produced in an amount equivalent to vinylidene fluoride (v.p.c.).

Polymerization of 1,1,2-Trifluoro-3-trifluoromethylbutadiene. (a) **Azo Catalyst.**—In a glass Carius tube were charged 0.1 g. of azobisisobutyronitrile and 10 g. of 1,1,2-trifluoro-3-trifluoromethylbutadiene. The tube was cooled to -80°, evacuated, sealed and heated to 90° for 24 hr. The solid mass was removed from the tube, broken up in a Waring blender with methanol, and dried *in vacuo* at 90°. There was obtained 9.4 g. (94%) of a white, acetone-soluble polymer that was somewhat elastic but tacky.

Anal. Calcd. for (C₅F₆H₂)_x: C, 34.11; H, 1.15. Found: C, 34.10; H, 1.39.

(b) **Ultraviolet Light.**—In a quartz Carius tube was charged 7 g. of trifluorotrifluoromethylbutadiene. The tube was cooled to -80°, evacuated, sealed and irradiated 24 hr. with a General Electric A-H-3 ultraviolet lamp placed 3 in. from the Carius tube. There was obtained an extremely viscous sirup from which excess monomer was removed *in vacuo*. There remained 2.4 g. (34%) of tough, elastic polymer that could be pressed to a clear, elastic film at 70° and 4000 lb. ram pressure. An infrared spectrum of the polymer was identical to that of a sample prepared using azoisobutyronitrile catalyst and showed the polymer to be exclusively 1,4 in orientation (no =CF₂ or =CH₂ absorption).

[CONTRIBUTION NO. 543 FROM THE CENTRAL RESEARCH DEPARTMENT, EXPERIMENTAL STATION, E. I. DU PONT DE NEMOURS AND CO., WILMINGTON 98, DEL.]

Fluorodienes. IV. 2,3-Bis-(trifluoromethyl)-1,3-butadiene¹

BY R. E. PUTNAM, R. J. HARDER AND J. E. CASTLE

RECEIVED JUNE 8, 1960

A four-step synthesis of 2,3-bis-(trifluoromethyl)-butadiene from acetylenedicarboxylic acid is described. Radical-initiated polymerization of the diene gave a high-melting, stable polymer.

The thermal cleavage of cyclohexenes (reverse Diels-Alder reaction) to butadienes and ethylenes is a reaction of wide applicability in the hydrocarbon series.² Utilization of this reaction for the preparation of fluorine-containing dienes has not been described, however, presumably because of difficulties in the preparation of the required intermediates. Recent work in this Laboratory has shown that pyrolysis of 1,2-bis-(trifluoromethyl)-cyclohexene (II), leads to the expected 2,3-bis-(trifluoromethyl)-butadiene (III)³ and ethylene, with trifluoromethylbenzene and 1,2-bis-(trifluoromethyl)-benzene as by-products.

Reaction of acetylenedicarboxylic acid with sulfur tetrafluoride,⁴ using titanium tetrafluoride catalyst, afforded hexafluoro-2-butyne in excellent yield. This acetylene was found to react quantitatively with butadiene at room temperature to give 1,2-bis-(trifluoromethyl)-1,4-cyclohexadiene (I). A similar product, IV, was prepared from the butyne and 2,3-dimethylbutadiene. Reaction of trifluoropropyne with butadiene has previously been reported to give a cyclohexadiene.⁵ Catalytic reduction of I with hydrogen over platinum oxide gave 1,2-bis-(trifluoromethyl)-cyclohexene (II) in 94% yield.

Pyrolysis of II by passage through an evacuated tube maintained at 800° and 5 mm. pressure produced 2,3-bis-(trifluoromethyl)-butadiene (III) in 44% yield, together with a mixture of higher boiling materials. Careful fractionation of these latter compounds yielded three major fractions

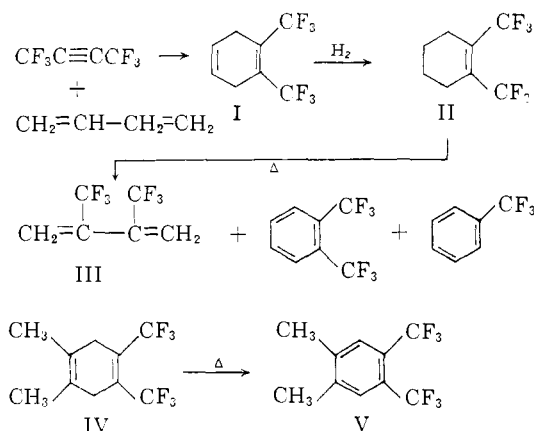
(1) For the previous paper in this series, see R. E. Putnam and J. E. Castle, *THIS JOURNAL*, **83**, 389 (1961).

(2) M. C. Kloetzel, "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., Vol. IV, 1948, p. 9.

(3) Unsuccessful attempts to prepare this diene by different routes have been reported by A. L. Henne and P. E. Hincamp, *THIS JOURNAL*, **76**, 5147 (1954), and P. Tarrant, ASTIA Document 21,734, p. 6 (1955).

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

(5) R. L. K. Carr, *Dissertation Abs.*, Ohio State, **16**, 653 (1956).



boiling at 102–105°, 138–142° and 145–146°. Comparison of proton and fluorine nuclear magnetic resonance spectra of these fractions with those of authentic samples served to identify them. The material boiling at 102–105° was trifluoromethylbenzene.⁶ The fraction boiling at 138–142° proved to be a mixture of 1,2-bis-(trifluoromethyl)-benzene (reported⁴ b.p. 143°) and 1,2-bis-(trifluoromethyl)-cyclohexene (II), while the 145–146° fraction was pure II.

An attempt was also made to prepare 2,3-bis-(trifluoromethyl)-butadiene (III) by pyrolytic cleavage of 1,2-bis-(trifluoromethyl)-4,5-dimethyl-1,4-cyclohexadiene (IV). However, the only reaction that occurred was dehydrogenation, a fluorinated durene (V) being produced in good yield.

Initiation of polymerization of 2,3-bis-(trifluoromethyl)-butadiene with azobisisobutyronitrile at 80° yielded 10% polymer. This polymer has been shown to have remarkable chemical and thermal stability. It was not soluble in common solvents and was not attacked by refluxing con-

(6) Boiling point reported, 102°; F. Swarts, *Chem. Zentr.*, **69**, II, 26 (1896).