

$\text{CF}_3\text{CHBrCF}_2\text{Br}$ 10%; B, $\text{BrCH}_2\text{CF}_2\text{Br}$ 20%, $\text{CF}_3\text{CHBrCF}_2\text{Br}$ 50%, $\text{CF}_3\text{CHBrCH}_2\text{Br}$ 30%; C, $\text{CF}_3\text{CHBrCF}_2\text{Br}$ 20%, $\text{CF}_3\text{CHBrCH}_2\text{Br}$ 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 $(\text{C}_5\text{F}_8\text{H}_2)_x$: 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 $=\text{CF}_2$ or $=\text{CH}_2$ 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

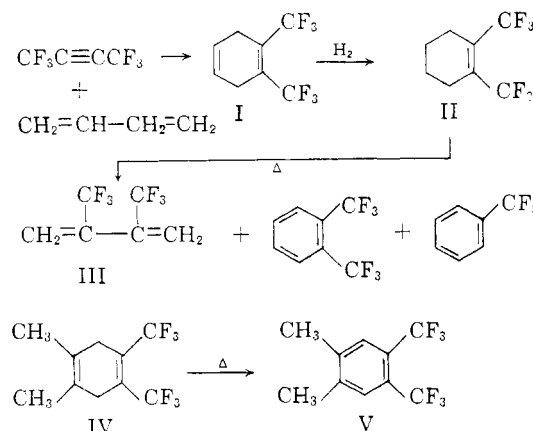
RECEIVED JUNE 8, 1960

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



boiling at $102-105^\circ$, $138-142^\circ$ and $145-146^\circ$. 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 $102-105^\circ$ was trifluoromethylbenzene.⁶ The fraction boiling at $138-142^\circ$ proved to be a mixture of 1,2-bis-(trifluoromethyl)-benzene (reported⁴ b.p. 143°) and 1,2-bis-(trifluoromethyl)-cyclohexene (II), while the $145-146^\circ$ 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-

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

(2) M. C. Klotzel, "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).

(6) Boiling point reported, 102° ; F. Swarts, *Chem. Zentr.*, **69**, II, 26 (1898).

centrated nitric acid or organic bases. At temperatures above 350° it melted and seemed to depolymerize. These properties are most likely attributable to shielding of the hydrocarbon chain and double bonds of the polymer by the bulky trifluoromethyl groups.

Acknowledgment.—The authors wish to thank Dr. B. C. McKusick for helpful suggestions.

Experimental⁷

Hexafluoro-2-butyne.—In a 145-ml. Hastelloy-lined, high-pressure tube were placed 14.2 g. (0.125 mole) of acetylenedicarboxylic acid and 2 g. of titanium tetrafluoride. The bomb was closed, cooled in a solid carbon dioxide-acetone mixture, evacuated and charged with 81 g. (0.75 mole) of sulfur tetrafluoride. The bomb was heated to 170° over a period of 2 hours and then was heated at 170° for 8 hours. It was cooled to room temperature, and the volatile product (96 g.) was transferred to a steel gas cylinder cooled in liquid nitrogen. In the bomb there remained 2 g. of dark solid. A mass spectrometric analysis of the volatile product indicated the presence of 14–18% of hexafluoro-2-butyne, with only a trace of $\text{CF}_3\text{C}\equiv\text{CCOF}$ and $\text{FCOC}\equiv\text{CCOF}$. The gas was passed through an absorption train of two towers of 40% KOH (in polyethylene bottles) and one tower of Drierite, the exit gas being condensed in a solid carbon dioxide-acetone-cooled trap. Comparison of the product (16 g., 80%), b.p. –25 to –24°, with authentic hexafluoro-2-butyne⁸ by gas chromatography indicated a purity of ca. 99%.

1,2-Bis-(trifluoromethyl)-1,4-cyclohexadiene (I).—A 500-ml. stainless-steel high-pressure tube was evacuated, cooled to –78°, and charged with 50 g. (0.31 mole) of hexafluoro-2-butyne and 27 g. (0.5 mole) of butadiene. The tube was closed and allowed to stand at 28° for 48 hours. There was obtained 65 g. of liquid product. Distillation gave 64 g. (96% yield) of 1,2-bis-(trifluoromethyl)-1,4-cyclohexadiene, b.p. 135°, n_D^{20} 1.3778. The infrared spectrum of the pure liquid had double bond absorption bands at 1670 and 1710 cm^{-1} . The ultraviolet spectrum (EtOH) had λ_{max} 2270 and 2110 Å., both with $\log \epsilon_{\text{max}}$ 2.44. The proton n.m.r. spectrum showed two peaks at 15 and –92 c.p.s. These peaks had an intensity ratio of 1:2 and are assignable to the vinyl and methylene hydrogens, respectively.

Anal. Calcd. for $\text{C}_8\text{F}_8\text{H}_6$: C, 44.45; H, 2.80; F, 52.75. Found: C, 44.86; H, 3.17; F, 52.55.

1,2-Bis-(trifluoromethyl)-cyclohexene (II).—In a 500-ml. hydrogenation bottle were placed 112 g. (0.52 mole) of 1,2-bis-(trifluoromethyl)-1,4-cyclohexadiene and 0.5 g. of platinum oxide. The bottle was placed on a Parr hydrogenation apparatus and pressured with 10–40 lb./sq.in. of hydrogen. The reaction was quite exothermic and shaking had to be stopped several times to keep the temperature below 40°. The hydrogen absorption was 0.53 mole. Filtration to remove catalyst yielded 105 g. (94%) of 1,2-bis-(trifluoromethyl)-cyclohexene, b.p. 145–146°, n_D^{20} 1.3708. The infrared spectrum of the pure liquid had strong double bond absorption at 1675 cm^{-1} . The proton n.m.r. spectrum exhibited two peaks of equal intensity at –113 and –139 c.p.s.

Anal. Calcd. for $\text{C}_8\text{F}_8\text{H}_4$: C, 43.96; H, 3.87; F, 52.17. Found: C, 44.00; H, 3.96; F, 52.25.

1,2-Bis-(trifluoromethyl)-4,5-dimethyl-1,4-cyclohexadiene (IV).—An 80-ml. stainless-steel, high-pressure tube was charged with 12 g. (0.146 mole) of 2,3-dimethylbutadiene and 0.5 g. of hydroquinone. The bomb was cooled to –78°, evacuated, charged with 26 g. (0.16 mole) of perfluoro-2-butyne, closed and heated at 100° for 6 hours. There was obtained, after evaporation of volatile material, 28 g. of crystalline solid mixed with a small amount of oil. The material was pressed on a clay plate, dissolved in pentane and filtered. Evaporation of the pentane gave pure 1,2-bis-(trifluoromethyl)-4,5-dimethyl-1,4-cyclohexadiene,

m.p. 49.5–50.5°, in 69% yield. The proton n.m.r. spectrum contained two peaks at –90 and –139 c.p.s. These peaks, having an intensity ratio of 2:3, are assignable to the methylene and methyl hydrogens, respectively. The infrared spectrum (CCl_4) had double bond absorption bands at 1690 and 1720 cm^{-1} ; ultraviolet spectrum (EtOH) λ_{max} 2420 Å., $\log \epsilon_{\text{max}}$ 2.36.

Anal. Calcd. for $\text{C}_{10}\text{H}_{10}\text{F}_6$: C, 49.19; H, 4.13; F, 46.68. Found: C, 49.19; H, 4.50; F, 46.08.

1,2-Bis-(trifluoromethyl)-4,5-dimethylbenzene (V).—Pyrolytic dehydrogenation of 1,2-bis-(trifluoromethyl)-4,5-dimethyl-1,4-cyclohexadiene was accomplished in a pyrolysis apparatus such as described in ref. 1; 9.5 g. of molten diene (maintained above 50° by warming with an infrared lamp) was added dropwise into the pyrolysis tube maintained at 700° and 3 mm. From the solid carbon dioxide-cooled trap was isolated 6 g. of crystalline solid, m.p. 38–40°. Sublimation at 85° and 1 atmosphere gave pure bis-(trifluoromethyl)-dimethylbenzene, m.p. 39.5–40°. Infrared, n.m.r. and ultraviolet spectra were consistent with the assigned structure. The proton n.m.r. spectrum contained two peaks at 82 and –125 c.p.s. These peaks, having an intensity ratio of 1:3, are assignable to the aromatic and methyl hydrogens, respectively. The ultraviolet spectrum exhibited peaks at 2200 Å. (ϵ_{max} 8230), 2640 Å. (ϵ_{max} 508) and 2730 Å. (ϵ_{max} 291).

Anal. Calcd. for $\text{C}_{10}\text{H}_8\text{F}_6$: C, 49.61; H, 3.32; F, 47.07. Found: C, 49.83; H, 3.55; F, 46.53.

Pyrolysis of 1,2-Bis-(trifluoromethyl)-cyclohexene.—Pyrolysis of 1,2-bis-(trifluoromethyl)-cyclohexene was accomplished in an apparatus such as described in ref. 1. The pyrolysis tube was heated to 800° and evacuated to a pressure of 5 mm. The cyclohexene (46.2 g., 0.21 mole) was added dropwise over a period of several hours, and the products were caught in a solid carbon dioxide-acetone-cooled trap and a liquid nitrogen-cooled trap arranged in series. From the solid carbon dioxide trap there was recovered 34.7 g. of liquid product; the product in the liquid N_2 trap boiled below –80° and its infrared spectrum showed the major component to be ethylene, together with at least one fluorine-containing compound. The crude liquid product was separated by distillation into three cuts: A, b.p. 50–60°, 19.5 g.; B, b.p. 60–119°, 4.7 g.; C, b.p. 119–141°, 7.5 g. Vapor phase chromatograms of the cuts showed A and B to be predominantly single compounds, while C was a mixture of three compounds, one of which was identical with B. Fractionation of A yielded 17.5 g. (44%) of 2,3-bis-(trifluoromethyl)-butadiene (III), b.p. 59–61°, n_D^{20} 1.3236. The infrared spectrum of the diene exhibited absorption bands at 1615(w), $\text{C}\equiv\text{C}$; 1295(vs), 1130–1200(vs), 1090(vs), $\text{C}=\text{F}$; 955–965(s) cm^{-1} . The n.m.r. (proton) spectrum had resonances at 22 and 31 c.p.s. of approximately equal intensity and a weak resonance at 77 c.p.s. apparently due to a trace of an impurity. The n.m.r. F^{19} spectrum had a single resonance at 348 c.p.s.

Anal. Calcd. for $\text{C}_8\text{F}_8\text{H}_4$: C, 37.90; H, 2.12; F, 59.98. Found: C, 37.81; H, 2.41; F, 59.54.

Fractions B and C were combined and carefully fractionated. A series of fractions boiling from 61 to 146° were obtained with the three major components boiling at 102–105°, 138–142° and 144–146°. The n.m.r. (proton and fluorine) spectra of these fractions were compared with those of authentic materials. In this way the 102–105° fraction was shown to be trifluoromethylbenzene (b.p. 102°), the 138–142° fraction was a 60/40 mixture of 1,2-bis-(trifluoromethyl)-benzene (b.p. 143°) and 1,2-bis-(trifluoromethyl)-cyclohexene (b.p. 145–146°), and the 144–146° fraction was mainly 1,2-bis-(trifluoromethyl)-cyclohexene. The weights and yields of the by-products were not estimated.

Polymerization of 2,3-Bis-(trifluoromethyl)-butadiene.—A small glass tube was charged with 3.0 g. of 2,3-bis-(trifluoromethyl)-butadiene and 0.01 g. of azobisisobutyronitrile, cooled with solid carbon dioxide, evacuated and sealed. It was then heated to 80° for 20 hours. Evaporation of excess monomer left 0.3 g. (10%) of white, granular polymer. The polymer did not soften appreciably below 355° at which temperature it melted and seemed to depolymerize. Attempts to press films at temperatures up to 325° and pressures of 15,000 lb. (ram pressure) were only partially successful because of poor flow. The polymer was

(7) All melting and boiling points are uncorrected. Spectra were obtained as described in paper I of this series.

(8) C. I. Cochenour, U. S. Patent 2,546,997.

completely unaffected by refluxing in concentrated nitric acid, aniline, *n*-butylamine or dimethylformamide. The infrared spectrum (KBr) had strong CF_2 absorption bands at 1185, 1275 and 1310, a CH_2 band at 1480(m) and bands

at 855(m) and 770(m) cm^{-1} . There was only a trace of absorption in the double bond region (1640 cm^{-1}).

Anal. Calcd. for $(\text{C}_6\text{H}_4\text{F}_6)_x$: C, 37.90; H, 2.12; F, 59.98. Found: C, 37.29; H, 2.41; F, 59.19.

[CONTRIBUTION NO. 2497 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, PASADENA, CALIF.]

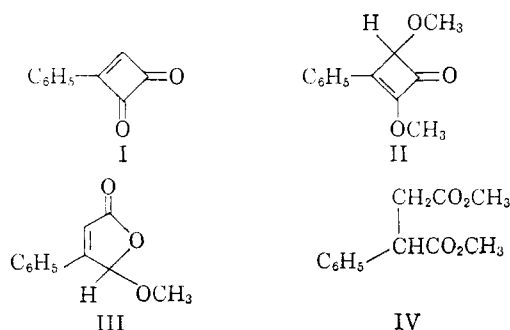
Small-Ring Compounds. XXX. Reactions of Phenylcyclobutadienoquinone with Methanol^{1,2}

BY FRANK B. MALLORY³ AND JOHN D. ROBERTS

RECEIVED AUGUST 4, 1960

The thermal reaction of phenylcyclobutadienoquinone (I) with methanol gives 2,4-dimethoxy-3-phenylcyclobutenone (II), 3-phenyl-4-hydroxy-4-methoxy-2-butenic acid lactone (III) and dimethyl phenylsuccinate (IV). The relative yields of the three products depend on the reaction temperature. A possible mechanism is presented that accounts for the formation of the three products by way of a common intermediate: 2-hydroxy-2-methoxy-3-phenylcyclobutenone (V). The structures of II and III were established by spectroscopic analysis, chemical degradation and independent synthesis.

Phenylcyclobutadienoquinone^{4,5} (I) reacts thermally with methanol to give three principal products. Evidence will be presented for the formulation of these products as 2,4-dimethoxy-3-phenylcyclobutenone (II), 3-phenyl-4-hydroxy-4-methoxy-2-butenic acid lactone (III) and dimethyl phenylsuccinate (IV).



The relative yields of II-IV were found to depend mainly on the reaction temperature. Thus, when a solution of the quinone I in methanol was maintained at reflux for 12 days in the dark,⁶ the product was the dimethoxyketone II, slightly contaminated with the diester IV. Substantially the same result was obtained when the reaction was carried out in a stainless-steel bomb heated⁷ to 90–135° for 5–12

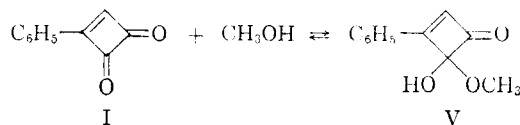
hours with or without acid catalyst. The highest yield (49%) of the dimethoxyketone II was obtained from the acid-catalyzed reaction.

A series of reactions in a stainless-steel bomb at somewhat higher temperatures (*ca.* 150°⁷) for 1 to 2 days gave equimolar mixtures of the methoxylactone III (*ca.* 40% yield) and the diester IV (*ca.* 40% yield); no dimethoxyketone II was detected.

When the bomb was heated in an electric furnace⁸ at 150°, which constitutes the highest reaction temperature used, the predominant product was the diester IV (64% yield), along with a small amount of the methoxylactone III (8% yield). That the diester IV was not formed from the methoxylactone III as precursor was demonstrated by recovering III unchanged after heating with methanol at 145–170° for 24 hours.

The absence of excess pressure in the bomb when it was opened at the completion of each reaction indicated that no appreciable amounts of gaseous products were formed.⁹

Although no detailed mechanistic study was undertaken, it is possible to formulate reasonable reaction paths for the formation of the several products by way of a common intermediate, the hemiketal of I, 2-hydroxy-2-methoxy-3-phenylcyclobutenone (V), which could exist in equilibrium with methanol and the quinone I.



The dimethoxyketone II could arise from V by reaction with methanol of the carbonium ion resulting from the acid-induced loss as water of the hemiketal hydroxyl.

Ring opening of the hemiketal V could occur at higher temperatures to form the stereoisomeric vinylketenes VI and VII.

ways somewhat lower since only the lower part of the bomb was immersed in the bath.

(8) In this case the effective reaction temperature was undoubtedly the same as the furnace temperature.

(9) It has been shown previously¹⁰ that carbon monoxide is evolved when pure I is heated to its melting point.

(1) Supported in part by the National Science Foundation.

(2) Presented before the Organic Section at the Second Delaware Valley Regional Meeting of the American Chemical Society, February 5, 1958, Philadelphia, Penna.

(3) General Electric Co. Predoctoral Fellow, 1956–1957.

(4) E. J. Smutny and J. D. Roberts, *THIS JOURNAL*, **77**, 3420 (1955).

(5) E. J. Smutny, M. C. Caserio and J. D. Roberts, *ibid.*, **82**, 1793 (1960).

(6) A photochemical reaction of I with methanol was discovered that gave 15–25% of dimethyl phenylsuccinate (IV) and 10–30% of a rather unstable white crystalline solid of m.p. 219° dec., which had the elemental composition $\text{C}_{11}\text{H}_{10}\text{O}_3$ and which contained one methoxyl group per molecule. The reaction was typically carried out at reflux temperature with irradiation for 15 min. in a Pyrex flask with a General Electric A-H6 mercury arc. Considerable work was done toward the elucidation of the structure of the compound of composition $\text{C}_{11}\text{H}_{10}\text{O}_3$, but the results are not now correlatable in terms of any single structural formula; cf. F. B. Mallory, Ph.D. Thesis, Calif. Inst. of Technology, 1958.

(7) The temperature of the oil-bath used to heat the bomb is specified; the effective reaction temperatures in this arrangement were al-