decanoate.[41] The mixture was refluxed for six hours, cooled and acidified with 20 ml. of concentrated hydrochloric acid. A gelatinous, colorless precipitate formed immediately which was separated by filtration, washed with water and air dried. The crude material (5 g.) was recrystallized twice from ligroin and once from petroleum ether, yielding 3.0 g., m.p. 60.5–61.5°. This represented a 7.7% over-all yield.

Anal. Calcd. for $C_{12}H_{22}O_3$: C, 67.25; H, 10.35; neut. equiv., 214.3. Found: C, 67.25; H, 10.26; neut. equiv., 215.2.

CAMBRIDGE, MASS.

---

[41] This material was formed during the preparation of diethyl 6,13-diketoöctadecane-1,18-dioate. It was obtained in the preliminary purification of the C_{18} diketodiester by Procedure A as the liquid fraction boiling below 155° (1 mm.). See Table II.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE OHIO STATE UNIVERSITY]

The Synthesis and Properties of Methylenecyclopropane[1]

BY JAMES T. GRAGSON, KENNETH W. GREENLEE, JOHN M. DERFER AND CECIL E. BOORD

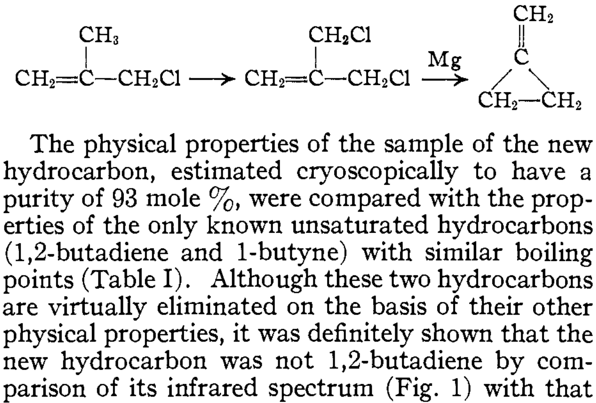
RECEIVED JUNE 13, 1952

Methylenecyclopropane has been synthesized and isolated for the first time. Some physical and chemical properties of this hydrocarbon were determined, and its infrared absorption spectrum was measured. Methylcyclopropane was prepared for use in identification work, and improved physical properties are reported for it. Evidences of interaction between the double bond and the ring of methylenecyclopropane are noted.

The synthesis of methylenecyclopropane has been attempted with little success by several workers. Merezhkovskii[2] reported that the treatment of 1,2,3-tribromo-(2-bromomethyl)-propane with zinc in 80% alcohol gave a gaseous mixture, which on oxidation with 1% potassium permanganate produced products to be expected from isobutene, as well as some oxalic acid. He postulated that the oxalic acid was derived from methylenecyclopropane; however, 1,3-butadiene, which may have been present, would also give oxalic acid. Dechlorination of a mixture of 3-chloro-(2-chloromethyl)-1-propene and its isomer 1,3-dichloro-2-methyl-1-propene with zinc in alcohol[3] also gave isobutene (75% yield) rather than methylenecyclopropane.

Dem'janov and Dojarenko[4] attempted to prepare methylenecyclopropane by the thermal decomposition of $\underline{CH_2\text{-}CH_2\text{-}CH}\text{-}CH_2\text{-}N(CH_3)_3OH$ and obtained very little hydrocarbon, most of which was 1,3-butadiene. Whitmore[5] wrote that "all attempts to prepare methylenecyclopropane have failed."

In the present work, 3-chloro-(2-chloromethyl)-1-propene, prepared by chlorination of 2-methylallyl chloride, was treated with zinc dust in molten acetamide,[6] because it was thought that this solvent, being less polar than ethanol, might alter the course of the reaction sufficiently to allow formation of methylenecyclopropane; however, isobutene (38% yield) was the only product found. The dechlorination was then attempted with magnesium in dry tetrahydrofuran at the reflux temperature of the mixture. A 17% yield of a hydrocarbon which was subsequently shown to be methylenecyclopropane was obtained by fractional distillation of the reaction product.



The physical properties of the sample of the new hydrocarbon, estimated cryoscopically to have a purity of 93 mole %, were compared with the properties of the only known unsaturated hydrocarbons (1,2-butadiene and 1-butyne) with similar boiling points (Table I). Although these two hydrocarbons are virtually eliminated on the basis of their other physical properties, it was definitely shown that the new hydrocarbon was not 1,2-butadiene by comparison of its infrared spectrum (Fig. 1) with that of authentic 1,2-butadiene[7]; that it was not 1-butyne was shown when it did not yield a yellow

TABLE I

PHYSICAL PROPERTIES OF METHYLENECYLOPROPANE AND RELATED HYDROCARBONS

	Methylene-cyclopropane	1,2-Butadiene[a]	1-Butyne[b]
B.p., °C. (749 mm.)	8.34	....	.....
B.p., °C. (760 mm.)	8.8[d]	10.9	8.07
M.p., °C.	−138.7[e]	−136.20	−125.720
ΔM.p., °C./mole % impurity	0.32	0.244	0.286
Ref. index (n^0D)	1.415	....	.....
Density (d^{20}_4)	0.718 (at 0°)	0.652[c]	0.65[c]
Purity, %	93	....	.....

[a] F. D. Rossini, *et al.*, *J. Research Natl. Bur. Standards*, **39**, 321 (1947). [b] F. D. Rossini, *et al.*, *ibid.*, **41**, 323 (1948). [c] F. D. Rossini, *et al.*, "Selected Values of Properties of Hydrocarbons," N.B.S. Circular C461, U. S. Gov. Printing Office, Washington, D. C., Tables 11a and 12a. [d] Corrected from the b.p. at 749 mm. and a dt/dp value of 0.04°/mm. [e] The m.p. for the 100% pure product was calculated from this and other cryoscopic data to be −136°.

---

[1] This paper was abstracted largely from the dissertation submitted in 1951 by J. T. Gragson to the Graduate School of The Ohio State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy. It was presented before the Organic Division of the American Chemical Society, in Buffalo, March, 1952. The investigation was sponsored by the American Petroleum Institute in coöperation with The Ohio State University Research Foundation.

[2] B. K. Merezhkovskii, *J. Russ. Phys. Chem. Soc.*, **45**, 2072 (1913).

[3] I. A. D'yakanov, *J. Gen. Chem.* (*U.S.S.R.*), **10**, 402 (1940).

[4] N. J. Dem'janov and Marie Dojarenko, *Ber.*, **56B**, 2208 (1923).

[5] F. C. Whitmore, "Organic Chemistry," 2nd edition, D. Van Nostrand Co., New York, N. Y., 1951, p. 530.

[6] H. B. Hass, E. T. McBee, G. E. Hinds and E. W. Glusenkamp, *Ind. Eng. Chem.*, **28**, 1178 (1936).

[7] Catalog of Infrared Spectral Data, American Petroleum Institute Research Project 44, F. D. Rossini, Director, Carnegie Institute of Technology.

precipitate on passage through an ammoniacal cuprous sulfate solution.

Microanalysis of a freshly distilled sample of the new hydrocarbon gave the following results: Calcd. for C_4H_6: C, 88.88; H, 11.12. Found: C, 88.2; H, 11.6. The fact that the % C is low and the % H is high reflects the presence of an impurity; however, the analysis corresponds to an empirical formula of C_2H_3, the % C being 2 to 4% removed from compounds which have empirical formulas of CH_2 or CH. On the basis of the percentage composition and the boiling point, the new hydrocarbon must have had a molecular formula of C_4H_6. In addition to 1,2-butadiene and 1-butyne, the only unsaturated hydrocarbons other than methylenecyclopropane having this formula are 1,3-butadiene, 2-butyne, cyclobutene and the two methylcyclopropenes. 1,3-Butadiene (b.p. $-4.4°$, m.p. $-108.9°$), 2-butyne (b.p. 27.0°, m.p. $-32.2°$) and cyclobutene (b.p. 2.4°, m.p. $-1.0°$) were easily eliminated on the basis of their known boiling and melting points. Neither 1-methylcyclopropene nor 3-methylcyclopropene has been prepared, but their probable boiling points can be predicted from series relationships to be much lower than that observed in the present case. The methylcyclopropene structures were also discounted by an infrared analysis of the new hydrocarbon, as will be described in detail in a separate publication.[8]

The infrared absorption spectrum of the new hydrocarbon (Fig. 1) supports the methylenecyclopropane structure. The strong absorption between 9.7 and 9.8 μ is indicative of the presence of the cyclopropyl ring,[9] and the broad absorption centered at about 11.2 μ is interpreted to result from both asymmetric deformation vibrations of the cyclopropyl ring[10] and hydrogen bending vibrations of a Type III olefinic bond. The broad band from 5.6 to 5.8 μ may be attributed to C=C stretching vibrations, the band having shifted from its usual position near 6 μ. Such a shift is not unexpected, because the cumulative effect of double bond and cyclopropyl ring would shift this band to shorter wave lengths in a manner similar to that observed in 1,2-diolefins (compare spectra of 1-butene, 1,2-butadiene and 1,3-butadiene[7]). Overtones of the 11 μ absorption probably contribute to the broadness of the 5.6 to 5.8 μ band. Although the sodium chloride optics used in determining the spectrum of the hydrocarbon do not adequately resolve the C–H vibrations in the 3 to 4 μ region, it is probable that the 3.2 and 3.3 μ bands correspond to those found by Wiberley[11] in cyclopropyl compounds, the latter being broader and intensified by contributions from the methylene group.[12] The spectrum of the hydrocarbon does not support the methylcyclopropene structure[8] which would be expected to give stronger absorption in the 6.8 μ region (methyl group) and a shift in the position of the band at 9.75 μ attributed to the cyclopropyl ring.[9]

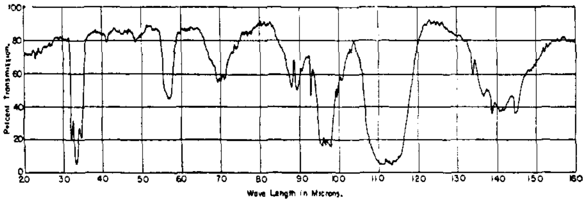


Fig. 1.—Infrared absorption spectrogram of methylenecyclopropane: state, gas; temperature, 23°; cell length, 5 cm.; pressure, 300 mm.

Determination of the new hydrocarbon's molecular refraction by appropriate substitution of experimental data into the Lorenz–Lorentz formula gave a value of 18.84. The theoretical molecular refraction, calculated by using Eisenlohr's constants and an increment of 0.69 for the cyclopropyl ring,[13] gave a value of 18.70. This represents good agreement with the observed value, especially since the magnitude of the cumulative effect of the cyclopropyl ring and double bond, which undoubtedly influences the observed molecular refraction, is unknown and, consequently, could not be included in the calculation of the theoretical value. The apparent exaltation of 0.14 may represent experimental error, but it could be due to the "cumulation" of the double bond and the cyclopropane ring, as two double bonds are cumulated in the allenes. This effect amounts to 0.57 in 1,2-pentadiene, but because a cyclopropane ring would not be expected to have as great an effect as a double bond, an exaltation of 0.14 in methylenecyclopropane (approximately one-fourth the effect of double bond cumulation) would not be unreasonable. That the cyclopropane ring has an effect similar to that of the double bond is also shown by the fact that vinylcyclopropane[14] exhibits an apparent exaltation of 0.29, due to "conjugation"; the exaltation of *cis*-1,3-pentadiene is 1.38. In this comparison the cyclopropane ring again appears to have about one-fourth of the effect of a double bond. Murray and Stevenson[15] determined the molecular refraction of spiropentane to be 22.43, (*MR* calculated, 22.27). Here we see an apparent exaltation of 0.11, which might be due to "cumulation" of the two cyclopropane rings.

An attempt to prove the structure of the new hydrocarbon by ozonolysis was not completely successful. The only fragment isolated was formaldehyde, and that in only 2% yield. The ozonide, while originally crystalline in appearance, melted and apparently polymerized when warmed to ice temperature.

Hydrogenation of the hydrocarbon over a copper chromite catalyst at 100–115° produced *n*-butane of about 83% purity, as indicated by boiling point data, infrared spectra and a mixed melting point determination with an authentic sample of *n*-

---

[8] W. J. Taylor and E. J. Blau, The Ohio State University, unpublished results.

[9] J. M. Derfer, E. E. Pickett and C. E. Boord, *ibid.*, **71**, 2482 (1949).

[10] Marie-Louise Josien, Nelson Fuson and A. S. Cary, *ibid.*, **73**, 4445 (1951).

[11] S. E. Wiberley and S. C. Bunce, *Anal. Chem.*, **24**, 623 (1952).

[12] R. S. Rasmussen and R. R. Brattain, *J. Chem. Phys.*, **15**, 120 (1947).

[13] R. G. Kelso, K. W. Greenlee, J. M. Derfer and C. E. Boord, paper in preparation.

[14] (a) Ross Van Volkenburgh, K. W. Greenlee, J. M. Derfer and C. E. Boord, THIS JOURNAL, **71**, 3595 (1949); (b) V. A. Slabey, *ibid.*, **74**, 4930 (1952).

[15] M. J. Murray and E. H. Stevenson, *ibid.*, **66**, 812 (1944).

butane. The presence of methylcyclopropane in the hydrogenate was indicated by a small peak at 9.8 μ in the infrared spectrum.

Since *n*-butane, a non-cyclic compound, was the chief hydrogenation product of the methylenecyclopropane, it is evident that rupture of the cyclopropyl ring occurred. Slabey, Wise and Gibbons[16] found that the ring in alkylcyclopropanes is unaffected by hydrogen in the presence of copper chromite under the conditions of pressure and temperature used in the present work. In order to determine whether methylcyclopropane was formed as an intermediate in the hydrogenation of the methylenecyclopropane, a sample of the cycloparaffin was subjected to hydrogenation under the same conditions used previously. No absorption of hydrogen occurred, even when the temperature was raised to 165°; 93% of the unchanged methylcyclopropane was recovered. This indicates that in the hydrogenation of methylenecyclopropane, either the cyclopropane ring was ruptured first, or the ring and the double bond were attacked simultaneously. The presence of the double bond adjoining the ring must create great strain at the non-hydrogen bearing carbon atom, thus increasing the tendency to break one of the adjacent bonds.

Methylenecyclopropane has a boiling point of 8.8°, which is 8.1° higher than that of methylcyclopropane (b.p. 0.7°); this is about as expected from comparison of an analogous pair, methylenecyclobutane and methylcyclobutane, which exhibits a difference of about 5.6°. This difference becomes progressively smaller as the size of the ring structure is increased, *i.e.*, for the cyclopentanes, the difference is 3.2°, and for the cyclohexanes, 1.1°.

Although the methylenecyclopropane was stable enough to distil, polymer residues were obtained from the distillations of the hydrocarbon, and the hydrocarbon on standing at ice temperature, or above, also slowly polymerized. The polymers were unsaturated, absorbed oxygen upon standing, and from an analysis for carbon and hydrogen, were found to contain C_4H_6 units.

The methylcyclopropane used for identification and comparison purposes was prepared from two different halides. 1-Chloro-3-bromo-2-methylpropane, obtained from the peroxide-catalyzed hydrobromination of 2-methylallyl chloride, was treated with zinc in aqueous ethanol to obtain a 95% yield of hydrocarbon. The olefinic impurity (about 7%) was removed by exhaustive permanganate treatment, before the hydrocarbon's physical properties were determined. Methylcyclopropane was also prepared from 1,3-dibromobutane in the same way. The yield of hydrocarbon in this case was 93%, and it contained about 10% olefinic impurity. The physical properties of the two purified samples compared favorably. The boiling point measured (+0.70° (760 mm.)) was an improvement over existing literature values, and a melting point (−177.0°) was determined for the first time.

Experimental

3-Chloro-(2-chloromethyl)-1-propene.—2-Methylallyl chloride (3 moles, 272 g.) was placed in a 500-ml. 3-neck flask fitted with a mercury-sealed stirrer, a gas inlet tube reaching to the bottom of the flask, an outlet tube, and a thermometer reaching below the level of the liquid. Chlorine was passed into the stirred chloride at a rate sufficient to maintain the temperature at 35–45°, the flask being surrounded by a cold water-bath. The chlorination was continued until the refractive index of the reaction mixture reached 1.4760; this required 8 hours for 5 moles of 2-methylallyl chloride.

After chlorination was complete, the product was poured into cold water, washed, dried over anhydrous sodium sulfate, and, finally, distilled at reduced pressure. The material boiling at 53° (45 mm.) and having an $n^{20}\mathrm{D}$ 1.4740–1.4754, amounted to 131 g. (1.04 moles) or a 34% yield of the desired 3-chloro-(2-chloromethyl)-1-propene; the physical properties reported in the literature[17] are b.p. 58.8 to 59.8° (50 mm.), $n^{20}\mathrm{D}$ 1.4758. Fractions corresponding to 26% of the charge appeared as headings of unchanged 2-methylallyl chloride. The tailings apparently contained a little isomeric dichloro compound (b.p. 56-60° (45 mm.)), but probably consisted chiefly of the addition product, 1,2,3-trichloro-2-methylpropane (b.p. 74° (45 mm.), $n^{20}\mathrm{D}$ 1.4760).

Methylenecyclopropane.—To 70 g. (2.8 g. atoms) of magnesium covered with dry tetrahydrofuran in a 3-liter 3-neck flask (fitted with a mercury-sealed stirrer, addition funnel and a reflux condenser connected to a Dry Ice-cooled trap) was added a crystal of iodine and a small amount of 3-chloro-(2-chloromethyl)-1-propene. Once the Grignard reaction had begun, 330 g. (2.64 moles) of 3-chloro-(2-chloromethyl)-1-propene, diluted with 2 to 3 times its volume of tetrahydrofuran, was added at such a rate as to maintain a gentle reflux. After about 30 minutes, magnesium chloride began to precipitate from the solution. After all of the dichloride had been added, the mixture was refluxed for several hours, during which time 49 g. of material collected in the trap. This product was separated into 6 fractions and a residue through a 3 ft. × 0.5 in. vacuum-jacketed column packed with $^3/_{32}$ in. metal helices and fitted with a Dry Ice-cooled reflux condenser with a built-in vapor phase take-off; fr. 1, −3.0 to +4.0° (2.7 g.); fr. 2, 4.0 to 5.9° (3.0 g.); fr. 3, 5.9 to 6.9° (3.7 g.); fr. 4, 6.9 to 7.5° (3.2 g.); fr. 5, 7.5 to 8.0° (18.0 g.); fr. 6, 8.0 to 8.0° (6.0 g.); residue (10.0 g.), $n^{20}\mathrm{D}$ 1.4105.

Distillation started at −3.0° and the temperature rose rapidly, reaching the methylenecyclopropane plateau (b.p. 8.3°) after 34% of the distillate had been collected; the residue was largely tetrahydrofuran and equal to 20% of the charge. The 7% impurity in the best sample (fractions 5 and 6, corresponding to a 17% yield) of the new hydrocarbon could not have been the solvent, tetrahydrofuran, as a similar sample which was scrubbed thoroughly with water had an identical infrared spectrum with no positive evidence for the presence of any of the cyclic ether. Rather, the impurity probably consisted chiefly of freshly-formed polymer and of isobutene which was actually found in the headings of the distillation.

On redistillation of the headings (corresponding to fractions 1 through 4 from several "original" distillations), an initial boiling point of −6.3° was noted; distillation temperature then rose gradually to that of methylenecyclopropane at which point fractions equal to 30% of the charge had been collected. Another 30% appeared as fairly pure methylenecyclopropane, and 40% appeared as a polymeric residue. The distillation indicated that isobutene was present as the chief by-product of the synthesis; it probably comprised some of the impurity present in the methylenecyclopropane after fractionation. An infrared spectrogram of the headings fraction boiling from 0.2 to 5.5° showed that isobutene was present in these fractions; there was no indication of a plateau at 2°, this indicating that cyclobutene was not present. An infrared spectrogram of the polymeric residue was quite different from that of methylenecyclopropane in that methyl group bands appeared relatively strong and the cyclopropane band at 9.8 μ and the olefin band at 11.2 μ were diminished. The band at 5.7 μ was almost completely absent, but a new band appeared at 10.4 μ. The residue ($n^{20}\mathrm{D}$ 1.5088) is believed to be a polymer of methylenecyclopropane, or possibly a copolymer with isobutene.

---

(16) V. A. Slabey, P. W. Wise and L. C. Gibbons, This Journal, **71**, 1518 (1949).

(17) W. S. Ropp, C. W. Gould, H. M. Engelmann and G. E. Hulse, *ibid.*, **73**, 3024 (1951).

Ozonolysis of Methylenecyclopropane.—The hydrocarbon was ozonized by the method of Cook and Whitmore[18] in an apparatus, essentially like that described by Henne and Perilstein.[19] A 2.7-g. sample (0.05 mole) of methylenecyclopropane in 100 ml. of *n*-pentane was treated with ozone at Dry Ice temperature, and, after standing overnight at −80°, deposited a crystalline-appearing substance. This was assumed to be the ozonide, and upon warming to ice temperature, it melted, but it was insoluble in the pentane solvent. The *n*-pentane was decanted from the viscous yellow product, which was poured into an ice-cooled metal beaker containing a stirred suspension of 4 g. of Raney nickel in 200 ml. of cyclopentane. On warming to room temperature, the product did not dissolve, but became increasingly viscous, this indicating polymerization. The cyclopentane solvent was decanted and combined with the *n*-pentane, and the composite was washed several times with small portions of cold water to extract formaldehyde. When the wash water was treated with dimedon in alcohol, a precipitate weighing 0.3 g. was obtained; it melted at 188–189°, without further purification. An authentic derivative prepared from formalin melted at 189°, and a mixed melting point caused no depression. The indicated yield of formaldehyde was about 2%.

Hydrogenation of Methylenecyclopropane—Methylenecyclopropane was hydrogenated under conditions similar to those used by Slabey, *et al.*,[16] in the hydrogenation of isopropenylcyclopropane.

Twenty-four grams (0.45 mole) of methylenecyclopropane in 28 ml. of cold, absolute alcohol and 3.7 g. of copper chromite catalyst (Harshaw Chemical Co., Cu-0102P) were charged to a 300-ml. steel bomb cooled by Dry Ice. The bomb was then heated cautiously until absorption of hydrogen began at 100° and an initial pressure of 1400 p.s.i. of hydrogen, a drop of 775 p.s.i. then occurring over a period of 30 minutes. (This was only about half the theoretical amount of hydrogen calculated to be needed for both saturation of the double bond and rupture of the cyclopropane ring, but substantial loss must have occurred in charging of the bomb, since the material recovered from the hydrogenation amounted to only 40% of theory). When the absorption of hydrogen appeared complete, the bomb was raised to a temperature of 115° for one hour before cooling to room temperature. The hydrogenate (a gaseous mixture of hydrogen and hydrocarbon) was passed through a train consisting of a scrubber filled with water (to remove alcohol), drying tower, and two Dry Ice-cooled traps which collected 5 g. of hydrocarbon. The bomb was cooled by Dry Ice, and the cold alcohol solution was removed and distilled, yielding 5 g. more of gaseous product. The total yield of hydrogenate, 10 g., was 40%. All of the product distilled at −0.5 to −0.2°. This boiling point indicated that *n*-butane (b.p. −0.5°) was the chief product rather than methylcyclopropane (b.p. +0.7°). A portion (4.62 g.) of the hydrogenate was added to 20.98 g. of authentic *n*-butane (m.p. −138.72°) and a mixed melting point was determined to be −139.80°; this indicated that the hydrogenate was *n*-butane containing about 17% impurity, as calculated from the cryoscopic constants of Rossini, *et al.* (Table I, ref. *c*).

Methylcyclopropane, Method 1.—1-Chloro-3-bromo-2-methylpropane was prepared by the hydrobromination of 2-methylallyl chloride, according to the method of Brewster.[20] The yield of product, after distillation at reduced pressure, was 80%. Physical properties determined were: b.p. 58° (24 mm.), d^{20}_4 1.4853, n^{20}_D 1.4819.

The ring closure with zinc in aqueous ethanol was done in a manner previously described,[21] the crude hydrocarbon product being collected in a Dry Ice-cooled trap. The yield from 1.6 moles of bromochloride was 86 g., or 95%. It was distilled through the same column as was the methylenecyclopropane, whereby 2.2 g. of headings (b.p. −0.1 to +0.5°) was removed. The remainder of the charge distilled at 0.7°. A center fraction was freed of olefins by repeatedly passing it as gas through scrubbers filled with saturated permanganate solution. When formation of manganese dioxide in the scrubbers ceased, the gaseous hydrocarbon was dried over calcium chloride and liquefied. The purified methylcyclopropane had the following properties: b.p. +0.70° (760 mm.), m.p. −177.16° (lit.[22] b.p. 0° (750 mm.)).

Method 2.—1,3-Dibromobutane (Columbia Organic Chemicals Co.) was cyclized by the same procedure referred to above. The crude hydrocarbon (93% yield) distilled completely between 0.6 to 0.9°. A center fraction was freed of unsaturation, as described above, and the purified methylcyclopropane had the following properties: b.p. +0.70° (760 mm.), m.p. −177.03°.

The infrared absorption spectrograms were determined on a Baird Associates, Model B, Double Beam, Recording Spectrophotometer with rock salt optics, located in the Department of Chemistry at The Ohio State University.

Acknowledgment.—The authors wish to acknowledge the assistance of Russell W. Walker in the attempted hydrogenolysis of methylcyclopropane.

COLUMBUS, OHIO

---

[18] N. C. Cook and F. C. Whitmore, THIS JOURNAL, **63**, 3540 (1941).

[19] A. L. Henne and W. L. Perilstein, *ibid.*, **65**, 2183 (1943).

[20] J. W. Brewster, *ibid.*, **73**, 366 (1951).

[21] R. W. Shortridge, R. A. Craig, K. W. Greenlee, J. M. Derfer and C. E. Boord, *ibid.*, **70**, 946 (1948).

[22] F. E. Condon and D. E. Smith, *ibid.*, **69**, 965 (1947).