bers indicate some molecular freedom below the freezing point, but no Maxwell–Wagner polarization due to conductivity was encountered in the cases of the three longer molecules. The dielectric properties of the alcohols and amines have been compared, and tentative reasons advanced for the absence of the rotator state in the amines.

PRINCETON, NEW JERSEY RECEIVED MARCH 29, 1949

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

A Synthesis of Vinylcyclopropane[1]

BY ROSS VAN VOLKENBURGH, K. W. GREENLEE, J. M. DERFER AND C. E. BOORD

The hydrocarbon vinylcyclopropane is interesting from both the synthetic and theoretical points of view. In 1922, Demjanov and Dojarenko[2] prepared it by exhaustive methylation of the amine obtained from the oxime of methyl cyclopropyl ketone, and they stated that this hydrocarbon could not be prepared by the dehydration of methylcyclopropylcarbinol. It has sometimes been assumed that vinylcyclopropane is "*incapable of existence.*"[3] Recently there has been speculation concerning the possible utility of the hydrocarbon in the manufacture of synthetic rubber.[4] In the present work methylcyclopropylcarbinol was successfully dehydrated to vinylcyclopropane, and some of the hydrocarbon's properties were observed.

The methylcyclopropylcarbinol was prepared by reduction of methyl cyclopropyl ketone; four different methods were tried. Catalytic hydrogenation gave the desired carbinol along with a nearly equal amount of the close-boiling 2-pentanol. Reduction by sodium and ammonium sulfate in liquid ammonia gave ring-opening products exclusively. The Meerwein–Ponndorf method gave the desired carbinol in low yield along with large amounts of condensation products. The only method which gave methylcyclopropylcarbinol exclusively and in high yield was reduction with lithium aluminum hydride.

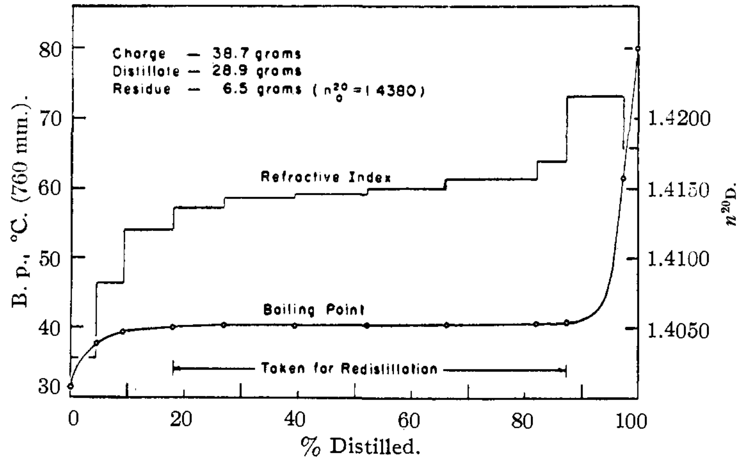

Fig. 1.—Distillation of crude vinylcyclopropane.

The dehydration of methylcyclopropylcarbinol was accomplished by refluxing it with a catalytic amount of sulfuric acid, giving 39% yield of vinylcyclopropane with 0.8° boiling range (Fig. 1). The dehydration was extremely slow, apparently because of the influence of the cyclopropane ring adjacent to the carbinol group; this may explain the failure of previous workers to observe it. The structure of the hydrocarbon was proved by an ozonolysis experiment from which both formaldehyde and cyclopropanecarboxaldehyde were identified. The physical properties listed in Table I were determined on a sample of vinylcyclopropane, estimated from a time–temperature freezing curve to be 96 ± 2 mole % pure.

Evidence for conjugation between the double bond and the cyclopropane ring of vinylcyclopropane is seen in the boiling point which is 4.5° higher than that of ethylcyclopropane; by contrast, the double bond produces a 7.8° lowering when the related 2-methylbutane is converted to 3-methyl-1-butene. Similarly, the refractive index of vinylcyclopropane shows an elevation of 0.0264 (at 20°) which approaches the elevation of 0.0332 exhibited by 2-methyl-1,3-butadiene.

TABLE I

VINYLCYCLOPROPANE

	This work	Literature[2]
F. p., °C.	−112.6	....
B. p., °C. (760 mm.)	40.41	40.0 to 40.2 (755 mm.)
d^{20}_4	0.7160	0.723 at 18°
n^{20}_D	1.4156	1.4172 at 15°

A small portion of the hydrocarbon was hydrogenated over Raney nickel. The product, insufficient for purification by distillation, was identi-

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[1] This paper forms part of the dissertation submitted in 1949 by Ross Van Volkenburgh 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 at the 116th meeting of the American Chemical Society. The investigation was sponsored by the American Petroleum Institute Research Project 45 in coöperation with The Ohio State University Research Foundation.

[2] Demjanov and Dojarenko, *Ber.*, **55B**, 2718 (1922).

[3] Whitmore, "Organic Chemistry," D. Van Nostrand Company, Inc., New York, N. Y., 1937, p. 632.

[4] Jones, *Chem. Eng. News*, **27**, No. 7, 454 (1949).

fied spectroscopically as ethylcyclopropane containing *n*-pentane as impurity (about 30 mole % on the basis of refractive index). The *n*-pentane was formed by hydrogenolysis of the cyclopropane ring through "1,4-addition" of hydrogen as in the case of a conjugated diene.[5] Other reactions in which the cyclopropane ring appears to possess many of the attributes of a double bond have been observed.[6]

The infrared absorption spectrogram of the vinylcyclopropane on which physical properties were determined is given in Fig. 2. The band at 9.9 μ, believed to be characteristic of the cyclopropane ring,[7] appears to be present, although obscured by strong olefin absorption in this region (type I olefins characteristically show absorption at 9.5 and 10.1 μ).

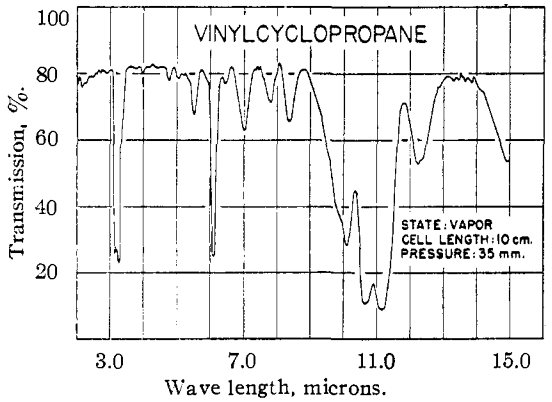

Fig. 2.—Infrared absorption spectrogram of vinylcyclopropane.

Unlike typical conjugated diolefins, vinylcyclopropane does not react with maleic anhydride at temperatures up to 100°. However, preliminary experiments indicate that it does polymerize rapidly in the presence of benzoyl peroxide when exposed to ultraviolet light.

Experimental

Reduction of Methyl Cyclopropyl Ketone

By Catalytic Hydrogenation.—Hydrogenation of methyl cyclopropyl ketone[8] over nickel-on-kieselguhr at 50 to 60° and 600–1100 p. s. i. gave a mixture of 2-pentanol (b. p. 119.85°) and methylcyclopropylcarbinol in the ratio of 2:3; distillation at about 20-plate efficiency indicated the composition but was not nearly adequate for a quantitative separation.

By Sodium and Ammonium Sulfate in Liquid Ammonia.—It has been found previously in this Laboratory that certain ketones are reduced to the corresponding carbinols by sodium in liquid ammonia in the presence of ammonium sulfate. The details of this type of reaction will be published later. When the method was applied to methyl cyclopropyl ketone, distillation of the reaction product gave no evidence for methylcyclopropylcarbinol, the desired product; only 2-pentanone and 2-pentanol were isolated. It is believed that "1,4-addition" of hydrogen first occurs, yielding 2-pentanone in its enolic form; further reduction of this ketone would then yield 2-pentanol.

By Aluminum Isopropoxide.—This reaction was carried out on methyl cyclopropyl ketone by essentially the same procedure given by Wilds[9] for the reduction of crotonaldehyde. Crude methylcyclopropylcarbinol (b. p. 119.2 to 124.1°, n^{20}D 1.4394 to 1.4323) was obtained in 23% yield, along with higher boiling by-products, believed to be carbinols of higher molecular weight.

By Lithium Aluminum Hydride.—The procedure followed was essentially that described by Nystrom and Brown.[10] Distillation of the reaction product gave an 80% yield of methylcyclopropylcarbinol (b. p. 121.8 to 123.7°, n^{20}D 1.4283 to 1.4317). Of this carbinol, about three-fourths had a constant boiling point and refractive index; the physical properties of this material are listed in Table II.

TABLE II

METHYLCYCLOPROPYLCARBINOL

	This work	Henry[11]
B. p., °C. (760 mm.)	123.5	123–124
M. p., °C.	−32.1	....
d^{20}_4	0.8893	0.88778
n^{20}D	1.4316	1.42966

From a sample of this material, the phenyl urethan derivative was prepared by the method of Shriner and Fuson.[12] After two recrystallizations from "Skellysolve C," the melting point of the derivative was 69.6–70.5° (cor.).

Vinylcyclopropane

Preparation.—Methylcyclopropylcarbinol (65.8 g., 0.76 mole), along with 12 drops of concentrated sulfuric acid, was placed in a flask attached to a small fractionating column packed with glass helices. The olefin material distilled as it formed, and the dehydration proceeded steadily but very slowly, yielding only 45 ml. of crude product during two days at reflux temperature (about 120°). Addition of 12 drops of *p*-toluenesulfonic acid gave no noticeable increase in rate, but slow dehydration continued for another day. A considerable amount of carbonaceous material remained in the flask.

After percolation through a 10-cm. column of silica gel, Dry-Ice-cold, the crude product (38.7 g.) was distilled at about 20-plate efficiency to obtain 20.0 g. (a 39% yield from carbinol) of good vinylcyclopropane (b. p. 40.0 to 40.8°, n^{20}D 1.4136 to 1.4170); the curves describing this distillation are given in Fig. 1.

Several differences are to be noted between the dehydration of methylcyclopropylcarbinol and dimethylcyclopropylcarbinol.[6a] The latter, a tertiary alcohol, dehydrated easily over sulfuric acid, giving nearly pure isopropenylcyclopropane in 80% yield. By contrast, methylcyclopropylcarbinol appears to dehydrate very slowly and to give a mixture containing a number of components. The impurity which caused the low initial boiling point in the distillation may have been 1,4-pentadiene, isoprene or fragmentation products. The higher boiling impurity probably was 1,3-pentadiene (*cis* and/or *trans*), causing a gradual rise in refractive index.

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[5] Hydrogenolysis of the cyclopropane ring in such pseudoconjugated systems can apparently be avoided by the use of a barium-promoted copper chromite catalyst. See Slabey, Wise and Gibbons, THIS JOURNAL, **71**, 1518 (1949).

[6] (a) Van Volkenburgh, Greenlee, Derfer and Boord, *ibid.*, **71**, 172 (1949). (b) Derfer, Greenlee and Boord, *ibid.*, **71**, 175 (1949). (c) Mariella, Peterson and Ferris, *ibid.*, **70**, 1494 (1948). (d) Rogers, *ibid.*, **69**, 2544 (1947). (e) Allen and Boyer, *Can. J. Research*, **9**, 159 (1933). (f) Carr and Burt, THIS JOURNAL, **40**, 1590 (1918). (g) Kishner, *J. Russ. Phys.-Chem. Soc.*, 1163 (1911).

[7] Derfer, Pickett and Boord, THIS JOURNAL, **71**, 2482 (1949).

[8] U. S. Industrial Chemicals, Inc.

[9] Wilds, "Organic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1944, Chapter 5, p. 200. The procedure given was patterned after that of Young, Hartung and Crossley [THIS JOURNAL, **58**, 100 (1936)].

[10] Nystrom and Brown, THIS JOURNAL, **69**, 1197 (1947).

[11] Henry, *Bull. soc. chim. Belg.*, **40**, 647–656 (1931).

[12] Shriner and Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1940, p. 136.

The good fractions from the distillation described above (Fig. 1) were combined with similar material from an identical run, and the composite was redistilled at about 20-plate efficiency to obtain the 16 g. of material on which the physical properties in Table I were determined.

Ozonolysis.—Vinylcyclopropane, 3.6 g. (0.053 mole), was ozonized in the apparatus described by Henne and Perilstein.[13] *n*-Pentane was used as the solvent, and the solution was immersed in a Dry Ice-cooled medium.

The ozonide solution was decomposed by the method of Cook and Whitmore[14] in which the ozonide solution is added dropwise to Raney nickel in *n*-pentane with stirring. The pentane was stripped off through a short Vigreux column, and the residue, after heating one and one-half hours on a steam-bath to assure complete decomposition of the ozonide, was extracted with *n*-pentane. The filtered extract was fractionated to remove the pentane but the residue failed to give a derivative with 2,4-dinitrophenylhydrazine, though it should have contained the bulk of the expected cyclopropanecarboxaldehyde. Presumably the aldehyde was hydrogenated or decarbonylated by contact with the hot Raney nickel.

The pentane stripped from the ozonide decomposition was fractionated at about 20-plate efficiency giving a distillate rich in formaldehyde and a residue from which cyclopropanecarboxaldehyde was isolated as the 2,4-dinitrophenylhydrazone (8% yield). This derivative, after recrystallization, melted at 182–185°, and there was no depression when it was mixed with an authentic sample.[15]

Formaldehyde was identified by extracting it from the pentane distillates with small amounts of water, and preparing the dimedone derivative. The crude derivative (3.3 g. or 21% yield) was leached with 10 ml. of hot methyl alcohol, filtered and dried to yield 2.8 g. of crystals with a melting point of 187.5–189.5° (cor.). A mixed melting point with an authentic sample (m. p. 188–189°) showed no depression.

Hydrogenation.—A portion (7.3 g., 0.11 mole) of the vinylcyclopropane on which physical properties were determined was hydrogenated over 0.5 g. of Raney nickel in absolute ethanol at 65 p. s. i. g. and 10 to 20°. Absorption of hydrogen ceased after about six hours. The hydrogenate was steam distilled, washed thoroughly with water and dried by percolation through a small column of silica gel to obtain a 64% yield of material with a refractive index of 1.3724. The infrared absorption spectrum of this product corresponded closely to that of an authentic sample of ethylcyclopropane,[7] but showed minor bands indicating the presence of *n*-pentane (about 30% on the basis of refractive index). Similar results had been obtained in the hydrogenation of isopropenylcyclopropane.[6a]

Infrared Absorption Spectra.—The spectra determined in the course of this work were measured on the Beckman IR-2 Spectrophotometer of the Department of Chemistry at The Ohio State University.

Summary

Vinylcyclopropane has been prepared from methyl cyclopropyl ketone. Additional evidence for the double bond character of the cyclopropane ring has been presented.

COLUMBUS, OHIO RECEIVED APRIL 30, 1949

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[13] Henne and Perilstein, THIS JOURNAL, **65**, 2183 (1943).

[14] Cook and Whitmore, *ibid.*, **63**, 3540 (1941).

[15] Kindly furnished by Christopher L. Wilson, The Ohio State University.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF CARSON-NEWMAN COLLEGE]

Polynitro Paraffins

BY CARL T. BAHNER AND HARVEY T. KITE[1]

Dinitro paraffins in which the nitro groups are in a 1,3-position to each other and the middle carbon atom carries no hydrogen atom have been prepared by Fraser and Kon,[2] Hass and Bourland,[3] and Larrison and Hass[4] by reaction of nitromethane with ketones. Hass[5] has found evidence that the reaction of nitromethane with acetone takes place through the formation of 1-nitro-2-methylpropene which adds nitromethane to form dinitroneopentane. Lambert and Piggott[6] have reported the preparation of dinitro compounds by "heating a primary or secondary nitroparaffin or nitroether or nitrothioether.... with a Δ^{α}-nitro-olefin.... in the presence of a basic substance." Prior to the publications by Hass and Lambert and their associates we had undertaken the preparation of polynitro paraffins by the addition of alkali salts of nitro paraffins to nitro olefins. Our experiments throw light on matters not investigated by them.

Using nitro olefins of the type $R^1C(NO_2)=CHR^2$, where R^1 and R^2 represent H or an alkyl radical, and nitro paraffins containing two or more carbon atoms we have succeeded in obtaining a type of compound which it is inherently impossible to prepare from ketones by the methods of Fraser and Kon, Hass, Larrison and Bourland. We have found that the alkali metal salts of the nitro paraffins give much better results than the use of nitro paraffins together with a basic catalyst. For example, the gradual addition of 2-nitro-1-butene to an alcoholic solution of an equivalent quantity of potassium salt of *aci*-2-nitropropane gave about 90% of the theoretical yield of crude potassium salt of 3,5-dinitro-3-methylhexane, from which the free dinitro compound was recovered readily by treatment with acetic acid. On the other hand, no 3,5-dinitro-3-methylhexane was isolated from a reaction mixture of equimolecular quantities of 2-nitropropane, diethylamine and 2-nitro-1-butene. The use of a quantity of potassium hydroxide sufficient to convert only one-fourth of the 2-nitropropane into the potassium salt resulted in the formation of a viscous high molecular weight product instead of the dinitro paraffin, while the use of a large excess of so-

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[1] Present address: Carbide and Carbon Chemicals Corporation, Oak Ridge, Tennessee.

[2] Fraser and Kon, *J. Chem. Soc.*, 604–610 (1934).

[3] Hass and Bourland, U. S. Patent 2,343,256, March 7, 1944.

[4] Larrison and Hass, U. S. Patent 2,383,603, Aug. 28, 1945.

[5] Hass, *Ind. Eng. Chem.*, **35**, 1151 (1943).

[6] Lambert and Piggott, *J. Chem. Soc.*, 1489–1492 (1947); British Patent 584,789, July 24, 1944.