The mixture was then hydrolyzed by the cautious addition of water. The volatile products were removed by steam distillation, dried over Drierite, and then fractionated through a 22-mm. by 7-ft. column which was packed with $^1/_8$-inch glass helices. The distillate after the ether was removed consisted of 321 g. of unreacted cyclopropyl chloride, 110 g. of hydrocarbon, b.p. 70–75°, n^{20}D 1.4225–1.4242 (98 g., b.p. 74–75°, n^{20}D 1.4237–1.4239), and 100 g. of tar. In addition to these products, a total of 272 g. of cyclopropane was collected during the course of the reaction, and another 86 g. during hydrolysis of the reaction mixture.

The disposition of the cyclopropyl chloride was calculated to be 21% recovered, 32% used in the formation of cyclopropane during the reaction and 10% during the hydrolysis, and 14% used in the formation of liquid products; the remaining 23% was presumed to have been lost through volatilization and polymer and tar formation.

Purification of the Hydrocarbon.—A quantity of the hydrocarbon (93 g., n^{20}D 1.4237–1.4239) was chilled to 0° and extracted in a separatory funnel first with six 80-ml. portions of an ice-cold saturated solution of silver nitrate and then with two 100-ml. portions of distilled water. Loss of hydrocarbon during the extraction process was 4 g. The extracted hydrocarbon was dried over calcium chloride and the physical properties then determined: m.p. −82.74°, b.p. 76.07° at 760 mm., n^{20}D 1.4340, d^{20} 0.78969 g./ml. This material plus additional hydrocarbon treated in the same manner (total quantity, 167 g.) was passed through a 6-ft. water-cooled column of "through 200 mesh" silica gel to obtain 155 g. of constant n^{20}D fractions. Azeotropic fractionation of 144 g. of the constant index hydrocarbon with ethanol through a 6-ft. Podbielniak column gave the following *hydrocarbon* fractions: first fraction, n^{20}D 1.4235 (5.5 g.), next eight fractions, n^{20}D 1.4239 (106 g.), last fraction, n^{20}D 1.4246 (9.0 g.). The six middle fractions were combined for determination of physical properties (Table I). The purified hydrocarbon did not decolorize one drop of either 5% bromine in carbon tetrachloride or 2% potassium permanganate in acetone.[9]

Anal. Calcd. for C_6H_{10}: C, 87.73; H, 12.27. Found: C, 87.65; H, 12.32.

Separation of Impurities with Silica Gel.—A 50-g. sample of the crude liquid reaction product was absorbed in a water-cooled column (ASTM designation D-936-49T) of "through 200 mesh" silica gel. Ethanol was used to elutriate the hydrocarbon from the gel, and the hydrocarbon was collected in 20 fractions: the first fraction (2.2 g.), n^{20}D 1.4235; the next 13 fractions (35.6 g.), n^{20}D 1.4239; two fractions (4.4 g.), n^{20}D 1.4227 and 1.4214, respectively; two fractions (1.2 g.), n^{20}D 1.4246; and the last two fractions (1 g. each), n^{20}D 1.4250 and 1.4258, respectively. Infrared spectra were determined for all fractions; the first 14 were essentially identical and showed all the bands of the major constituent of the reaction product, and no absorption at 3μ (C≡C) or at 6.1 μ (C=C), while the last 6 showed acetylenic and olefinic impurities were present. The olefinic impurity appeared in higher concentration in the last 6 fractions with each successive fraction, while the acetylenic impurity remained at approximately the same concentration. The infrared spectrum of fraction 19 (Fig. 1(e)) shows the major absorption bands of the impurities, and is presented to substantiate their proposed identification.

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[9] R. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," John Wiley and Sons, Inc., New York, N. Y., 1940, pp. 36, 38.

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[CONTRIBUTION FROM THE LEWIS FLIGHT PROPULSION LABORATORY OF THE NATIONAL ADVISORY COMMITTEE FOR AERONAUTICS]

Dehydration of Methylcyclopropylcarbinol over Alumina. A Synthesis of Vinylcyclopropane

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The dehydration of methylcyclopropylcarbinol over alumina at temperatures between 265 and 300° gave vinylcyclopropane in yields as high as 54%. Other identified products of the reaction were propene, isoprene, 1,3-pentadienes and 2-methyltetrahydrofuran. Vinylcyclopropane of high purity (99.9 mole %) was obtained by fractionating the hydrocarbon azeotropically with ethanol. Some physical properties of vinylcyclopropane (m.p., b.p., n^{20}D, d^{20}, heat of combustion and $\Delta T_{\text{m.p.}}$/mole % impurity) were measured and the liquid phase infrared spectrum of the hydrocarbon was determined.

The preparation of several cyclopropylalkenes by the dehydration of tertiary alkylcyclopropylcarbinols over alumina[1] suggested that vinylcyclopropane could be prepared from methylcyclopropylcarbinol in the same way, although Dojarenko[2] had already investigated the reaction at temperatures varying from 240 to 365° and had concluded that the products were propene, divinylmethane, piperylene and methylcyclobutene. The results of the previous work were questioned, because (1) only very small quantities of carbinol were used in the investigation, (2) the identification of products by reaction with bromine would obscure the presence of cyclopropane derivatives, and (3) vinylcyclopropane was apparently not considered to be a possible product of the reaction. Recently, Van Volkenburgh, *et al.*,[3] reported that methylcyclopropylcarbinol was dehydrated very slowly by sulfuric acid to give a mixture which contained approximately equal amounts of vinylcyclopropane and other unsaturated hydrocarbons (presumably isoprene, 1,4-pentadiene and 1,3-pentadienes); the yield of vinylcyclopropane was 39%. Vinylcyclopropane has also been prepared by the exhaustive methylation of methylcyclopropylcarbinylamine.[4]

Contrary to the previous report,[2] vinylcyclopropane has now been found to be the principal product when methylcyclopropylcarbinol, dissolved in toluene, is passed over an alumina catalyst at temperatures from 265 to 300°. Other distillable products of the reaction were propene, isoprene, 1,3-pentadienes and 2-methyltetrahydrofuran. The process was less time consuming than previously reported methods of preparing vinylcyclopropane, and is convenient for preparations on either large or small scale.

The effect of temperature, over the limited range investigated (265–300°), on the yield of vinylcyclopropane was not so nearly pronounced as

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[1] V. A. Slabey and P. H. Wise, THIS JOURNAL, **74**, 1473 (1952).

[2] M. Dojarenko, *Ber.*, **60B**, 1536 (1927).

[3] R. Van Volkenburgh, K. W. Greenlee, J. M. Derfer and C. E. Boord, THIS JOURNAL, **71**, 3595 (1949).

[4] N. J. Demjanov and M. Dojarenko, *Ber.*, **55B**, 2718 (1922).

TABLE I

YIELDS OF PRODUCTS FROM THE DEHYDRATION OF METHYLCYCLOPROPYLCARBINOL OVER ALUMINA

Product	Temperature, °C.		
	265–280[a]	285–300[a]	285–300[b]
Propene	<1	4	6
Isoprene	<1	3	3
Vinylcyclopropane	52	54	38
1,3-Pentadienes	2	5	8
2-Methyltetrahydrofuran	4	4	3

[a] Liquid rate, 10 ml./min. [b] Liquid rate, 5 ml./min.

the effect of the rate at which the carbinol solution was introduced into the column (Table I). While an increase in the reaction temperature (from 265–280° to 285–300°) increased the yields of all products, the effect on the yield of vinylcyclopropane was negligible. Decreasing the rate at which the carbinol solution was passed through the dehydration column, however, increased the total yield of by-products, and significantly decreased the yield of vinylcyclopropane.

Typical distillation data for the product obtained at the lower reaction temperature (265–280°) are shown in Fig. 1. The low boiling points and refractive indices of the first 7% of the distillate were caused by the presence of propene, isoprene and oxygenated impurities. The next 70% was found to be vinylcyclopropane of higher purity than previously reported; the distillate of maximum purity, indicated by the melting points of four successive samples (Fig. 1), occurred between the points of 30 and 50% distilled. Small amounts of the *cis*- and *trans*-1,3-pentadienes were found to be responsible for the rise in index after removal of the vinylcyclopropane, and the appearance of 2-methyltetrahydrofuran in the distillate corresponded with the sudden increase in boiling point and decrease in index of refraction. The last 10% of the distillate contained the reaction solvent, toluene, in increasing amounts.

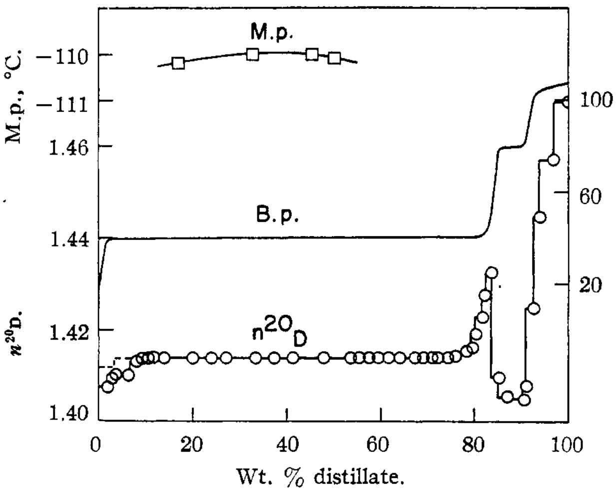

Fig. 1.—Distillation of products from the dehydration of methylcyclopropylcarbinol over alumina at 265–280°.

Vinylcyclopropane of high purity (99.9 mole %) was obtained by refractionating the hydrocarbon azeotropically with ethanol through a 6-ft. Podbielniak column at an efficiency better than 150 theoretical plates. The distillation data presented in Fig. 2 were determined after the ethanol had been removed and the fractions dried. Measurement of the refractive index did not resolve changes in the composition of the distillate; consequently, density and melting point measurements were made to determine that distillate of maximum purity. The purest samples of vinylcyclopropane were obtained between the points of 50 and 75% distilled. Physical properties of that sample of vinylcyclopropane having the highest purity (based on constancy of index, density and melting point) are given in Table II.[5] A comparison of these properties with those recently reported indicates that the product of ref. 3 was contaminated with 8 to 10% of higher-boiling impurity, most probably *cis*- and *trans*-1,3-pentadienes.

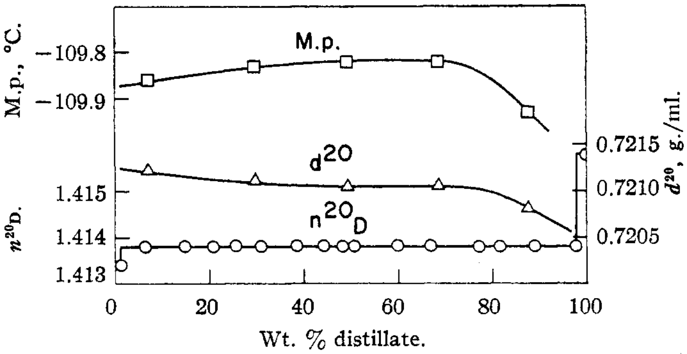

Fig. 2.—Vinylcyclopropane from azeotropic distillation with ethanol.

The liquid phase infrared spectrum of vinylcyclopropane is shown in Fig. 3. Typical absorption for olefins of type I structure is observed at 6.1μ (C═C stretching) and at 10.13 and 10.68 μ (hydrogen bending). Strong absorption at 9.77 μ appears to be that band in the spectrum of vinylcyclopropane indicative of the presence of the cyclopropyl ring.[6] A Baird double-beam recording spectrophotometer was used in determining the infrared spectrum.

Experimental

Methylcyclopropylcarbinol.—The carbinol was prepared by the previously described[7] hydrogenation of methyl cyclopropyl ketone in the presence of a barium-promoted copper chromite catalyst.

Vinylcyclopropane.—A solution of 19.5 moles (1680 g.) of methylcyclopropylcarbinol, $n^{20}D$ 1.4317–1.4319, in 2 liters of toluene was passed at a rate of 10 ml./min. into a 2.5- by 90-cm. Pyrex column which was packed with 8 to 14 mesh alumina and heated to 270°. The temperature of the column was kept between 265 and 280° during the course of the dehydration. Liquid products were collected in a chilled receiver and gaseous products were condensed in a solid CO_2-acetone trap. The quantity of water collected, 264 g., indicated that a 75% conversion of carbinol to olefin was accomplished. The or-

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(5) Methods of determining these properties are referenced in an article by I. A. Goodman and P. H. Wise, THIS JOURNAL, **72**, 3076 (1950).

(6) Unpublished work from this Laboratory and J. M. Derfer, E. E. Pickett and C. E. Boord, *ibid.*, **71**, 2482 (1949).

(7) V. A. Slabey and P. H. Wise, *ibid.*, **71**, 3252 (1949).

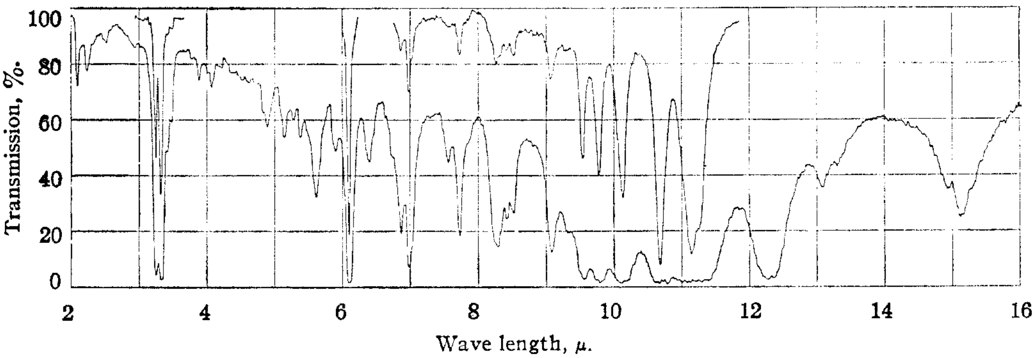

Fig. 3.—Infrared spectrum of vinylcyclopropane. Liquid phase, undiluted (lower trace) and diluted 1:10 with CCl_4 (upper trace); cell width 0.1 mm.

ganic layer was dried over Drierite, and then fractionated through a 22-mm. by 6-ft. column packed with $^1/_8$-inch glass helices. The identified products all boiled below toluene; when the toluene was removed by distillation, 306 g. of sirupy residue, boiling above 150°, remained.

Infrared spectra of the first few fractions indicated the presence of oxygenated materials which were removed by extraction with water. (The dotted line in Fig. 1 shows the change in refractive index which occurred.) The quantities of products, estimated from the distillation data, and their identities, determined from infrared spectra, were: propene, isoprene and oxygenated products, <1% each; vinylcyclopropane, 686 g. (52% yield); 1,3-pentadienes, 29 g. (2%); and 2-methyltetrahydrofuran, 66 g. (4%). The distillation curve is shown in Fig. 1.

TABLE II

PHYSICAL PROPERTIES OF VINYLCYCLOPROPANE

	This work	Ref. 3
M.p., °C.	−109.82	−112.6
M.p. for zero impurity, °C.[a]	−109.81	
ΔT/mole % impurity, °C.[b]	0.28	
Estimated purity, mole %	99.9	
B.p., °C. at 760 mm.	40.19	40.41
n^{20}_D	1.4138	1.4156
d^{20}, g./ml.	0.72105	0.7160
Net heat of combustion, kcal./mole	720	
Analyses:		
Carbon, % Calcd. for C_5H_8	88.16	
Found	88.05	
Hydrogen, % Calcd. for C_5H_8	11.84	
Found	11.96	

[a] Determined by the geometrical construction method of W. J. Taylor and F. D. Rossini, *J. Research Natl. Bur. Standards*, **32**, 197 (1944). [b] Determined by adding known amounts of 1-*trans*-3-pentadiene.

In another reaction 6.5 moles (556 g.) of carbinol, dissolved in 660 ml. of toluene, was passed through the dehydration column at a rate of 10 ml./min. with the temperature increased to 285 to 300°. The water obtained from the reaction was 80% of the theoretical quantity. The yields of products are given in Table I.

A third dehydration of 10.7 moles (920 g.) of carbinol dissolved in 670 ml. of toluene, at the same temperature (285–300°) but at a rate of 5 ml./min., gave 84% of the theoretical quantity of water; the yields of other products are shown in Table I.

Purification of Vinylcyclopropane.—Azeotropic distillation of 561 g. of vinylcyclopropane (n^{20}_D 1.4137–1.4138) with ethanol through a 6-ft. Podbielniak column gave 17 fractions which were washed with water to remove the ethanol and dried over calcium chloride. The recovered hydrocarbon, which weighed 400 g. (losses are high because of the volatile nature of both the azeotrope and the hydrocarbon), had a constant refractive index over 97% of the distillation. The constant index fractions were combined into 5 samples, and the melting points and densities were determined for each. The index, density and melting point data are plotted in Fig. 2. The physical constants of the purest sample of vinylcyclopropane are given in Table II.

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