In view of the symmetrical structure of this peroxide, the infrared spectrum (Fig. 1B) failed to show the presence of an acetylene bond. However, the peroxide absorbed 4.76 moles of hydrogen per mole when catalytically hydrogenated in glacial acetic acid using platinum oxide as catalyst, a value which is in close agreement with the theoretical of 4.00. The higher experimental value indicates some hydrogenolysis of the glycol formed. When 2 g. of the dihydroperoxide was hydrogenated in absolute alcohol, about 2 g. of a crude product was obtained; m.p. 77–78°. This was recrystallized from *n*-pentane into long, colorless needles; m.p. 88–89°. 2,5-Dimethylhexanediol-2,5 is reported to melt at 88.5–89 °.[8]

1,1'-Dihydroperoxy-1,1'-dicyclohexylacetylene.—This dihydroperoxide was prepared in exactly the same manner as the previous dihydroperoxide. 1,1'-Dihydroxy-1,1'-dicyclohexylacetylene[9] (10 g.) was slowly added in small portions with rapid stirring to a cold (0°) mixture of hydrogen peroxide (9.6 g. of 50%) and sulfuric acid (14 g. of 95.5%). After five hours of stirring the product was recovered as before; yield 9 g. (79%). This titrated 85% as dihydroperoxide. It was recrystallized from cyclohexane, m.p. 95° (dec.).

Anal. Calcd. for $C_{14}H_{22}O_4$: C, 66.11; H, 8.72; (O), 12.6. Found: C, 66.25; H, 8.87; (O) ,11.8.

The infrared spectrum of this dihydroperoxide is shown in Fig. 1C.

Di-(3-methylbutynyl)-3-peroxide.—To 12.7 g. of 70% cold (−3 to 0°) sulfuric acid was added dropwise with stirring a mixture of 6.05 g. of 3-methyl-3-hydroperoxybutyne-1 and 5.07 g. of 3-methyl-3-hydroxybutyne-1 in the course of one-half hour. Stirring was continued at 0 to +5° for 4.5 hours; then the mixture diluted with two volumes of water and extracted with *n*-pentane. The pentane solution was extracted twice with 10% sodium hydroxide solution, washed with water and dried. Finally, the pentane was removed and the residue distilled under reduced pressure and the portion boiling at 60° (76 mm.) collected and analyzed; yield of the pure product, 23%.

Anal. Calcd. for $C_{10}H_{14}O_2$: C, 72.25; H, 8.49. Found: C, 71.63; H. 8.61.

This peroxide is a very sweet smelling liquid and the presence of the acetylene groups was shown by a copious precipitate formed with ammoniacal alcoholic silver nitrate solution. Because of its reactivity with hydrogen iodide to form black solutions our present methods of analysis for peroxidic oxygen are not satisfactory for analysis of this peroxide as well as those that follow.

Di-(3-methylpentynyl)-3-peroxide.—This dialkynyl peroxide was prepared in exactly the same manner as its lower homolog. A yield of 34% of a sweet smelling liquid was obtained boiling at 53–55° (2 mm.); n^{25}_D 1.4390; d^{25}_4 0.903; MR_D(calcd.), 57.47; MR_D(obsd.), 56.65.

Anal. Calcd. for $C_{12}H_{18}O_2$: C, 74.19; H, 9.34. Found: C, 70.83; H, 9.25.

This peroxide also gives a copious precipitate with ammoniacal alcoholic silver nitrate solution.

2,5-Dimethyl-2,5-di-(*t*-butylperoxy)-hexyne-3.—To a cold mixture (0°) of 6 g. of *t*-butyl alcohol and 11.2 g. of 70% sulfuric acid was slowly added with stirring 4.7 g. of 2,5-dimethyl-2,5-dihydroperoxyhexyne-3 in the course of 15 minutes. Stirring was continued at room temperature for five hours longer, then the mixture diluted with two volumes of water and extracted with ether; the ethereal solution dried and the ether removed under reduced pressure. A yield of 6.8 g. (88.3%) was obtained. This was distilled under reduced pressure and the fraction boiling at 65–67° (2 mm.) collected and analyzed; n^{25}_D 1.4219; d^{25}_4 0.881; MR_D (calcd.), 81.78; MR_D(obsd.), 82.61.

Anal. Calcd. for $C_{16}H_{30}O_4$: C, 67.10; H, 10.56. Found: C, 67.02; H, 10.71.

The infrared spectrum of this peroxide is shown in Fig. 1D.

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[8] "Beilstein," Vol. I, p. 256, 1928.

[9] A. W. Johnson, "The Chemistry of the Acetylenic Compounds," Vol. 1, Edward Arnold and Co., London, 1946, p. 138.

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

The Dehydration of Methylalkylcyclopropylcarbinols. Isolation and Purification of 2-Cyclopropylalkenes[1]

BY VERNON A. SLABEY AND PAUL H. WISE

Ten 2-cyclopropyl-1- and -2-alkenes have been prepared from methyl cyclopropyl ketone by condensing the ketone with various Grignard reagents and dehydrating the resultant methylalkylcyclopropylcarbinols. Both alumina at 200 to 250° and sulfuric acid were found to be satisfactory dehydrating agents. Isolation of both the position and geometrical 2-cyclopropylalkene isomers in high purity was accomplished by fractional and azeotropic distillations. Melting points, boiling points, refractive indices, densities and heats of combustion are reported for the ten cyclopropylolefins. Methyl, ethyl, propyl and butyl cyclopropyl ketones were isolated as ozonolysis fragments of the cyclopropylolefins, and the melting points of their 2,4-dinitrophenylhydrazones are given.

The preparation and purification of a series of cyclopropylalkenes was undertaken in order to provide pure hydrocarbon samples for an investigation of the effect of molecular structure on physical and chemical properties. The reaction of various Grignard reagents with methyl cyclopropyl ketone[2] and dehydration of the resultant methylalkylcyclopropylcarbinols offered a possible method of synthesizing the cyclopropylalkenes. The previous work of Bruylants[3] and Henry[4] showed that Grignard reactions of the type proposed were suitable for preparing the methylalkylcyclopropylcarbinols.

The practicability of the dehydration of cyclopropylcarbinols as a synthetic method, however, had not been established when this research was begun, although dehydrations of dimethyl[5-8] and methylethylcyclopropylcarbinol[5,9] with sulfuric acid,[5] oxalic acid[6] or acetic anhydride[7-9] were reported. In an investigation which occurred concurrently with the present work, Van Volkenburgh, *et al.*,[10] found that of three catalytic methods for dehydrating dimethylcyclopropylcarbinol, the

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[1] Presented before the Organic Division of the American Chemical Society, Chicago, Ill., September 3-8, 1950.

[2] Commercially available from U. S. Industrial Chemicals Inc., 60 E. 42nd Street, New York, N. Y., at the time this research was begun.

[3] P. Bruylants, *Bull. soc. chim. Belg.*, **36**, 153 (1927).

[4] J. Henry, *ibid.*, **40**, 647 (1931).

[5] N. van Keersbilck, *ibid.*, **38**, 208 (1929).

[6] N. Zelinsky, *Ber.*, **40**, 4743 (1907).

[7] N. Kizhner and V. Klavikordov, *J. Russ. Phys. Chem. Soc.*, **43**, 597 (1910).

[8] D. Alexejew, *ibid.*, **37**, 419 (1905).

[9] P. Bruylants, *Rec. trav. chim.*, **28**, 224 (1908).

[10] R. Van Volkenburgh, K. W. Greenlee, J. M. Derfer and C. E. Boord, THIS JOURNAL, **71**, 172 (1949).

one employing the strongest acid (sulfuric) gave the highest yield of 2-cyclopropylpropene (80%), whereas the weakest acid (alumina) gave a poor yield of 2-cyclopropylpropene (12%) and appreciable amounts of methylpentadienes (20%) and 2,2-dimethyltetrahydrofuran (10%). Since alumina dehydrations had already been found to be practicable in the present work, the scope of the investigation was enlarged to include comparisons of the alumina and sulfuric acid methods of dehydrating dimethyl-, methylethyl-, methylpropyl- and methylbutylcyclopropylcarbinol. During the investigation ten 2-cyclopropylalkenes were isolated from the dehydration products, nine of which were purified and characterized for the first time.

The preparations of the methylalkylcyclopropylcarbinols were performed in ether solution in glass-lined reactors and the hydrolyses of the Grignard complexes were accomplished with ammonium chloride solution to avoid dehydration. Halogenated impurities were found in all the carbinols after an initial fractionation to separate the carbinols from any by-products. It has been suggested[10] that excesses of ammonium chloride during the hydrolysis reaction are responsible for the halogenated by-products. Although ammonium chloride may affect the extent of the side reaction, the present work indicated that a simple metathesis does not occur. For example, in the preparation of methylethylcyclopropylcarbinol from ethylmagnesium bromide the halogenated by-product was isolated and the elemental analysis corresponded to a bromide, $C_7H_{13}Br$. The infrared spectrum of the compound indicated the basic structure to be that of a Type IV olefin (RRC=CHR) rather than a cyclopropane derivative. The by-product was presumed to be 1-bromo-4-methyl-3-hexene; Bruylants and Dewael[11] obtained halides of similar structure when dimethylcyclopropylcarbinol was treated with hydrogen halides.

Removal of the halogenated impurities from the carbinols was accomplished by refluxing with alcoholic sodium hydroxide prior to final fractionation at reduced pressure. Dehydration of the carbinols during the final fractionation occurred to a slight extent, but infrared spectra indicated the presence of less than 1% olefins in the samples used for determinations of physical properties.

The dehydration of the carbinols was accomplished by the use of (a) alumina at 200 to 250° and (b) concentrated sulfuric acid. The products and yields summarized in Table I were estimated from fractional distillation curves. For all but the dimethylcyclopropylcarbinol the total yield by either method was identical within experimental error, but alumina was found to give significantly higher yields of the 1-olefins. No distillable products other than the 2-cyclopropyl-1- and -2-alkenes were found in the dehydration products.

TABLE I

YIELDS OF PRODUCTS FROM THE DEHYDRATION OF METHYLALKYLCYCLOPROPYLCARBINOLS

	Alumina, % yield of			Sulfuric acid, % yield of		
Cyclopropylcarbinol	1-olefin	2-olefin	Total	1-olefin	2-olefin	Total
Dimethyl	..	..	57[a]	..	..	69
Methylethyl	32	47	79	23	56	79
Methylpropyl	39	38	77	19	56	75
Methylbutyl	41	37	78	21	57	78

[a] The carbinol was dissolved in toluene.

In the case of dimethylcyclopropylcarbinol, sulfuric acid gave a higher yield of 2-cyclopropylpropene and only that product, whereas alumina gave a lesser yield of the olefin and small amounts of diolefin (probably methylpentadienes) and 2,2-dimethyltetrahydrofuran. The significant improvement in the yield of 2-cyclopropylpropene from the alumina dehydration, when compared to that previously reported,[10] appeared to have resulted from the use of a solvent which, in essence, would reduce local temperatures and contact time.

Purification of the olefins was accomplished by fractional and azeotropic distillations in 22-mm. by 6-ft. columns which were packed with 1/8-inch glass helices. Separation of geometrical isomers required, in addition, azeotropic fractionations through 6-ft. Podbielniak columns which were operated at efficiencies in excess of 150 theoretical plates. Examination of time–temperature melting curves indicated that all the olefins but the 2-cyclopropyl-2-hexenes were obtained in purities of better than 99 mole per cent.[12] The unexpectedly high densities of the 2-cyclopropyl-2-hexene isomers, the fact that the lower-boiling isomer would not crystallize, and the quality of the melting curve of the higher-boiling isomer indicated that these hydrocarbons contained a greater amount of impurity than the others.

A pronounced tendency to oxidize was observed for several of the 2-cyclopropylalkenes. The oxidation manifested itself generally in marked changes in the density and the infrared spectrum of the hydrocarbon. Over relatively long periods of time (1 to 10 months) a wide absorption band at 2.8 to 3.0 microns, not observed in the spectrum of freshly distilled olefin, became more pronounced with increasing time. This change was accompanied by an increase in absorption at 5.8 to 6.0 microns. Hydroxyl hydrogen-bonding is known to occur in the 2.8 to 3.0 microns region, and the band observed in the "aged" olefin samples may have been caused by the presence of hydroperoxides. The band at 5.8 to 6.0 microns was probably caused by carbonyl compounds resulting from the degradation of the hydroperoxides.

The identity of the olefins was proved by ozonolysis.[13] The fragments from the ozonolyses were characterized by physical properties, and analyses and mixed melting points of their 2,4-dinitrophenylhydrazones.

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(11) P. Bruylants and A. Dewael, *Bull. sci. acad. roy. Belg.*, **14**, 140 (1928).

(12) Estimation of purity was based on the difference between the actual melting point and that for zero impurity [determined according to the geometrical method of Taylor and Rossini, *J. Research Natl. Bur. Standards*, **32**, 206 (1944)], and on the assumption that the melting point depressions for all the cyclopropylalkenes would fall within the limits 0.2 to 0.3°/mole % impurity. Although the melting point depressions of 2-cyclopropylpropene, 2-cyclopropylpropane and 2-cyclopropylhexane are within these limits, it should be recognized that actual measurement of the depressions for each of the cyclopropylalkenes is necessary to prove the validity of this assumption.

(13) A. L. Henne and W. L. Perilstein, THIS JOURNAL, **65**, 2183 (1943).

The physical properties listed in Table III were determined by methods previously referenced.[14] The authors are indebted to Mr. A. M. Busch for the heats of combustion, Mr. A. B. McKeown for the analyses, and Mr. J. F. Thompson for the determination of physical constants.

Experimental

Methylalkylcyclopropylcarbinols.—The preparations of the carbinols were similar to that already described for dimethylcyclopropylcarbinol.[10] Halogenated impurities which were not completely removed by an initial fractionation of the reaction products were eliminated by refluxing 2-kg. quantities of the carbinols for 4 hours with 200 g. of sodium hydroxide in one liter of ethanol, washing the refluxed mixture with water until neutral to litmus, drying and refractionating at 60 mm. pressure. Yields and physical properties of the carbinols are summarized in Table II.

TABLE II

YIELDS AND PROPERTIES OF CARBINOLS

Cyclopropylcarbinol	Reaction size, moles	Yield, %	B.p., °C. at 760 mm.	$n^{20}\text{D}$	d^{20}, g./ml.
Dimethyl-	150	64	123.7	1.4335	0.8789
Methylethyl-	20	77	142.3	1.4412	.88068
Methylpropyl-	150	51	163.5	1.4438	.87632
Methylbutyl-	97	52	183.7	1.4466	.77348

TABLE III

PHYSICAL PROPERTIES OF 2-CYCLOPROPYLALKENES

Hydrocarbon	M.p., °C.	B.p., °C. at 760 mm.	$n^{20}\text{D}$	d^{20} g./ml.	Heat of combn., kcal./mole	Analyses, % Carbon Calcd.	Carbon Found	Hydrogen Calcd.	Hydrogen Found
2-Cyclopropylpropene	−102.34	70.33	1.4255	0.75153	865	87.73	87.55	12.27	12.20
2-Cyclopropyl-1-butene	−119.55[a] −121.94	98.57	1.4319	.76820	1025	87.42	87.49	12.58	12.54
2-Cyclopropyl-2-butene, l.b.[b]	− 97.83	106.55	1.4428	.78100	1020		87.41		12.56
2-Cyclopropyl-2-butene, h.b.	− 74.07	107.46	1.4474	.78745	..		87.31		12.56
2-Cyclopropyl-1-pentene	−113.87	123.94	1.4362	.77660	1150	87.20	87.27	12.80	12.90
2-Cyclopropyl-2-pentene, l.b.	−113.65	128.61	1.4458	.78402	1155		87.16		12.80
2-Cyclopropyl-2-pentene, h.b.	−107.61	129.98	1.4502	.79077	..		87.14		12.73
2-Cyclopropyl-1-hexene	−106.16	148.89	1.4403	.78447	1320	87.04	86.94	12.96	12.98
2-Cyclopropyl-2-hexene, l.b.	Glass	152.08	1.4486	.79051	..		86.90		12.97
2-Cyclopropyl-2-hexene, h.b.	− 97.40	153.08	1.4529	.79666	1305		86.86		12.73

[a] Two crystalline modifications were observed. [b] L.b. and h.b. designate the lower-boiling and higher-boiling isomers, respectively.

In the case of methylethylcyclopropylcarbinol, the high-boiling residue which remained after the initial fractionation of the Grignard products was investigated. A halogenated by-product (approx. 5 wt. % of the reaction products) was isolated: b.p. 91–92° (54 mm.), $n^{20}\text{D}$ 1.4775, d^{20} 1.1873 g./ml.

Anal. Calcd. for $C_7H_{13}Br$: C, 47.47; H, 7.40; Br, 45.13. Found: C, 47.61; H, 7.39; Br, 44.89.

The infrared spectrum of the by-product showed medium absorption at 6.03 μ (typical position and intensity for internal carbon–carbon double bond), only weak absorption between 9.5 and 10 μ, and strong absorption between 11.6 and 12.2 μ. Characteristic absorption between 9.7 and 10 μ for cyclopropane systems[15] was absent; of those absorption bands previously reported for olefins[16] only the band for Type IV (11.9 to 12.7 μ) was present.

2-Cyclopropylpropene.—The two methods of dehydrating dimethylcyclopropylcarbinol were:

A. **With Alumina.**—A solution of 2.6 moles (260 g.) of carbinol in 350 ml. of toluene was passed at a rate of 5 ml./min. through a 2.5- by 120-cm. column packed with 8 to 14 mesh alumina and heated to 200 to 250°. The quantity of water collected (40 g.) indicated that the conversion of carbinol to olefin was 85% of theory. The organic products were dried over Drierite and fractionated through a 22-mm. by 6-ft. column packed with $^1/_4$-inch glass helices to give 121 g. (57% yield) of 2-cyclopropylpropene, b.p. 70°, $n^{20}\text{D}$ 1.4255, and smaller amounts of conjugated diolefins (probably methylpentadienes) and 2,2-dimethyltetrahydrofuran. The diolefins and 2,2-dimethyltetrahydrofuran were not isolated, but were detected from infrared spectra of distillate boiling from 70 to 93°; less than 10% yield of each was obtained in the dehydration reaction.

B. **With Sulfuric Acid.**—The procedure was similar to that already described.[10] Six moles (602 g.) of carbinol and 0.4 ml. of concentrated sulfuric acid were heated in a flask attached to a 4-ft. helix-packed column, and the dehydration products collected as they formed. The distillate was washed with water, dried and fractionated through the described 6-ft. column to give 340 g. (69% yield) of 2-cyclopropylpropene, b.p. 70°, $n^{20}\text{D}$ 1.4255; no other distillable products were obtained. The physical properties (Table III) were determined on a portion of the constant-index distillate.

Ozonolysis of 2-Cyclopropylpropene.—Three-tenths mole (25 g.) of 2-cyclopropylpropene in 150 ml. of ethanol was ozonized. The products were fractionated to obtain formaldehyde (detected only by its odor and the appearance of a white amorphous solid that sublimed into the stillhead above 85° (presumably paraformaldehyde)), and methyl cyclopropyl ketone. The ketone was identified by preparing the 2,4-dinitrophenylhydrazone (m.p. 148.6–149.2°); no depression was observed when the unknown derivative was mixed with an authentic sample.

2-Cyclopropylbutenes.—Typical dehydration reactions of methylethylcyclopropylcarbinol are described.

A. **With Alumina.**—The alumina dehydration of 14.7 moles (1685 g.) of carbinol (no solvent) at 200 to 250° gave 13.1 moles of water in addition to the organic products. Fractionation of the dried organic layer through the 6-ft. column gave 452 g. of 2-cyclopropyl-1-butene (32% yield) and 664 g. of 2-cyclopropyl-2-butene (47% yield)

B. **With Sulfuric Acid.**—Eight moles (912 g.) of carbinol and 0.8 ml. of concentrated sulfuric acid, refluxed as previously described for dimethylcyclopropylcarbinol, gave 7 moles of water, 177 g. (23% yield) of 2-cyclopropyl-1-butene and 430 g. (56% yield) of 2-cyclopropyl-2-butene.

Purification of 2-Cyclopropylbutenes.—Fractionation of 739 g. of a concentrate of 2-cyclopropyl-1-butene ($n^{20}\text{D}$ 1.4300 to 1.4400) through the 6-ft. helix-packed column gave 422 g. of distillate which had a constant $n^{20}\text{D}$ 1.4321. While physical constants of selected samples were being determined, the densities were observed to increase about 0.0001 unit every 24 hours, presumably because of rapid oxidation. Consequently, a small portion (110 g.) of the constant-index distillate was azeotropically fractionated with ethanol to re-establish the purity, and the physical constants (Table III) were determined immediately after the distillate was removed from the column, washed with water and dried.

2-Cyclopropyl-2-butene (1500 g., $n^{20}\text{D}$ 1.4400–1.4500) was refractionated into two parts: $n^{20}\text{D}$ 1.4437–1.4449 and

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(14) I. A. Goodman and P. H. Wise, THIS JOURNAL, **72**, 3076 (1950).

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

(16) R. B. Barnes, R. C. Gore, R. W. Stafford and V. Z. Williams, *Anal. Chem.*, **20**, 402 (1948).

1.4451–1.4478. The lower-index distillate (868 g.) was azeotropically fractionated with ethanol to obtain 490 g. of a higher concentrate of the lower-boiling (lower-index) isomer, $n^{20}\text{D}$ 1.4428–1.4433. A second azeotropic fractionation gave 225 g. of distillate, $n^{20}\text{D}$ 1.4428, which was azeotropically fractionated a third time through a 6-ft. Podbielniak column to give 115 g. of the lower-boiling isomer of 2-cyclopropyl-2-butene for the determination of physical properties (Table III).

The higher-index portion of the 2-cyclopropyl-2-butene (300 g.) was azeotropically fractionated with ethanol in a 6-ft. Podbielniak column to obtain 131 g. of the higher-boiling isomer of 2-cyclopropyl-2-butene for the determination of physical properties (Table III).

Ozonolysis of 2-Cyclopropylbutenes.—2-Cyclopropyl-1-butene (0.28 mole, 27 g.) gave formaldehyde (detected as before) and 11 g. (39% yield) of ethyl cyclopropyl ketone: b.p. 130° (atm.), $n^{20}\text{D}$ 1.4284 (lit.[17]: b.p. 131.8° (769 mm.), $n^{20}\text{D}$ 1.42986). The 2,4-dinitrophenylhydrazone was prepared, m.p. 160.4–160.5°.

Anal. Calcd. for $C_{12}H_{14}N_4O_4$: N, 20.13. Found: N, 20.17.

The lower-boiling isomer of 2-cyclopropyl-2-butene (0.42 mole, 41 g.) gave 6.3 g. (34% yield) of acetaldehyde and 14.3 g. (40% yield) of methyl cyclopropyl ketone. The 2,4-dinitrophenylhydrazone of each of the fragments was prepared; mixed melting points with authentic derivatives showed no depression.

The higher-boiling isomer of 2-cyclopropyl-2-butene (0.38 mole, 37 g.) gave 5.5 g. (33% yield) of acetaldehyde and 13 g. (40% yield) of methyl cyclopropyl ketone. Mixed melting points of the 2,4-dinitrophenylhydrazone derivatives of each of the fragments with known derivatives showed no depression.

2-Cyclopropylpentenes.—Dehydration of methylpropylcyclopropylcarbinol gave the 2-cyclopropylpentenes in the following manner:

A. **With Alumina.**—The carbinol (14.3 moles, 1831 g.) was passed through the alumina column at 225 to 250°; 12.2 moles of water was obtained. The organic layer was dried and fractionated through the 6-ft. helix-packed column to give 614 g. (39% yield) of 2-cyclopropyl-1-pentene and 602 g. (38% yield) of 2-cyclopropyl-2-pentene.

B. **With Sulfuric Acid.**—Ten moles (1282 g.) of carbinol and 0.4 ml. of concentrated sulfuric acid were refluxed as previously described to give 8 moles of water, 207 g. (19% yield) of 2-cyclopropyl-1-pentene and 621 g. (56% yield) of 2-cyclopropyl-2-pentene.

Purification of 2-Cyclopropylpentenes.—2-Cyclopropyl-1-pentene (1382 g., $n^{20}\text{D}$ 1.4360–1.4364) was fractionated in the 6-ft. helix-packed column to give 774 g. of distillate, $n^{20}\text{D}$ 1.4361, which was combined into 5 samples. The melting points of the 5 samples differed by less than 0.1°; that sample having the highest melting point was used to determine the other properties (Table III).

2-Cyclopropyl-2-pentene (1400 g., $n^{20}\text{D}$ 1.4459–1.4487) was azeotropically fractionated with propyl alcohol to give concentrates of each of the geometrical isomers. The concentrate of the lower-boiling isomer (538 g., $n^{20}\text{D}$ 1.4461–1.4468) was azeotropically fractionated with propyl alcohol in a 6-ft. Podbielniak column to yield 398 g. of distillate, $n^{20}\text{D}$ 1.4458. Peroxidation of the distillate occurred before the physical properties could be determined; consequently, a third azeotropic fractionation was performed to obtain the sample used for the determination of physical properties (Table III).

The concentrate of the higher-boiling isomer (318 g., $n^{20}\text{D}$ 1.4481–1.4504) was fractionated with propyl alcohol in a 6-ft. Podbielniak column to obtain 182 g. of distillate, $n^{20}\text{D}$ 1.4496–1.4501. A second azeotropic fractionation with propyl alcohol gave the sample which was used for the determination of physical properties (Table III).

Ozonolysis of 2-Cyclopropylpentenes.—2-Cyclopropyl-1-pentene (0.48 mole, 53 g.) gave formaldehyde (detected as previously described) and 23 g. (43% yield) of propyl cyclopropyl ketone, b.p. 148° (atm.), $n^{20}\text{D}$ 1.4324, d^{20} 0.8795 g./ml. (lit.,[16] b.p. 151.0–151.4° (754 mm.), $n^{20}\text{D}$ 1.43247, d^{20} 0.88078 g./ml.). The 2,4-dinitrophenylhydrazone of the ketone was prepared, m.p. 165.0—165.5°.

Anal. Calcd. for $C_{13}H_{16}N_4O_4$: N, 19.17. Found: N, 19.19.

The lower-boiling isomer of 2-cyclopropyl-2-pentene (0.3 mole, 33 g.) gave 3 g. (17% yield) of propionaldehyde and 11 g. (43% yield) of methyl cyclopropyl ketone. Mixed melting points of the 2,4-dinitrophenylhydrazones with known derivatives showed no depressions.

The higher-boiling isomer of 2-cyclopropyl-2-pentene (0.3 mole, 33 g.) gave 10.5 g. (60% yield) of propionaldehyde and 18.5 g. (73% yield) of methyl cyclopropyl ketone. No depressions in melting points were observed when the 2,4-dinitrophenylhydrazones of the fragments were mixed with the corresponding derivatives of known materials.

2-Cyclopropylhexenes.—Methylbutylcyclopropylcarbinol was dehydrated to give the 2-cyclopropylhexenes.

A. **With Alumina.**—The carbinol (8.3 moles, 1180 g.) was passed through the alumina column at 225 to 250° to give 7.6 moles of water in addition to the organic products. Fractionation of the organic layer yielded 422 g. (41% yield) of 2-cyclopropyl-1-hexene and 383 g. (37% yield) of 2-cyclopropyl-2-hexene.

B. **With Sulfuric Acid.**—Ten moles (1422 g.) of the carbinol and 0.8 ml. of sulfuric acid were refluxed as previously described to obtain 9.4 moles of water, 260 g. (21% yield) of 2-cyclopropyl-1-hexene and 709 g. (57% yield) of 2-cyclopropyl-2-hexene.

Purification of 2-Cyclopropylhexenes.—2-Cyclopropyl-1-hexene (1740 g., $n^{20}\text{D}$ 1.4385–1.4450) was azeotropically fractionated with ethylene glycol monoethyl ether (Cellosolve) to give 536 g. of distillate, $n^{20}\text{D}$ 1.4403. Melting points of selected samples were determined and that sample having the higher melting point was used for the determination of the other constants (Table III).

2-Cyclopropyl-2-hexene (1320 g., $n^{20}\text{D}$ 1.4459–1.4517) was azeotropically fractionated with Cellosolve in the helix-packed column to obtain concentrates of the geometrical isomers. The concentrate of the lower-boiling isomer (764 g., $n^{20}\text{D}$ 1.4446–1.4503) was refractionated with Cellosolve in a 6-ft. Podbielniak column to give 304 g. of distillate, $n^{20}\text{D}$ 1.4487. The physical properties reported in Table III were determined on a selected sample of this distillate; however, further purification was attempted because the density appeared to be abnormally high and the sample could not be crystallized. An attempt to fractionate the olefin through a Podbielniak column without the benefit of azeotropy resulted in the isomerization and polymerization of the charge.

Azeotropic fractionation of the concentrate of the higher-boiling 2-cyclopropyl-2-hexene isomer (362 g., $n^{20}\text{D}$ 1.4506–1.4531) through a 6-ft. Podbielniak column gave only 94 g. of distillate in the index range $n^{20}\text{D}$ 1.4525–1.4530; infrared spectra of samples of the distillate from the fractionation indicated that isomerization had occurred during the distillation. The physical properties for the higher-boiling isomer reported in Table III were determined with 69 g. of constant-index material which was isolated near the end of the azeotropic fractionation of the concentrate of the lower-boiling isomer.

Ozonolysis of 2-Cyclopropylhexenes.—From 0.3 mole (37 g.) of 2-cyclopropyl-1-hexene there was obtained formaldehyde (detected as before) and 28.5 g. (75% yield) of butyl cyclopropyl ketone, b.p. 170–171° (atm.), $n^{20}\text{D}$ 1.4369, d^{20} 0.8805 g./ml. (lit.,[16] b.p. 173.8–174° (757 mm.), $n^{20}\text{D}$ 1.43710, d^{20} 0.87878 g./ml.). The 2,4-dinitrophenylhydrazone of the ketone was prepared, m.p. 114.5–115°.

Anal. Calcd. for $C_{14}H_{18}N_4O_4$: N, 18.29. Found: N, 18.41.

The lower-boiling isomer of 2-cyclopropyl-2-hexene (0.29 mole, 36 g.) gave butyraldehyde, which distilled with the solvent and 12 g. (49% yield) of methyl cyclopropyl ketone. The 2,4-dinitrophenylhydrazones of the fragments showed no depression in melting points when mixed with known derivatives.

The higher-boiling isomer of 2-cyclopropyl-2-hexene (0.2 mole, 25 g.) gave butyraldehyde and 13 g. (77% yield) of methyl cyclopropyl ketone. The fragments again were identified from mixed melting points of their 2,4-dinitrophenylhydrazone derivatives.

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[17] P. Bruylants, *Bull. soc. chim. Belg.*, **36**, 519 (1927).