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Hydrogenation of 2-Cyclopropyl-1- and -2-Alkenes. Isolation and Purification of 2-Cyclopropylalkanes[1]

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A barium-promoted copper chromite catalyst was found to be suitable for the selective hydrogenation of the carbon–carbon double bonds in some conjugated cyclopropylalkene hydrocarbons. 2-Cyclopropyl-1-alkenes were found to hydrogenate readily to give 2-cyclopropylalkanes. In contrast, the 2-cyclopropyl-2-alkenes hydrogenated sluggishly to give mixtures of 2-cyclopropylalkanes and methylalkanes. Azeotropic fractionation was employed to separate the cyclopropane–paraffin mixtures. 2-Cyclopropylpropane, -butane, -pentane and -hexane were obtained in high purity. The melting points, boiling points, refractive indices, densities and heats of combustion were determined. Further evidence was found to substantiate the proposal that systems in which a cyclopropyl ring is conjugated with a double bond can add hydrogen by either a 1,2- or a 1,4-mechanism.

The preparation of 2-cyclopropylalkenes in high yields from methylalkylcyclopropylcarbinols[2] suggested a method for preparing a series of cyclopropylalkanes not readily synthesized by other means. The method required the hydrogenation of the cyclopropylalkenes with a catalyst of sufficient selectivity to saturate the double bonds without attacking the cyclopropyl ring.

A search of the literature did not reveal any previous attempts to accomplish the selective hydrogenation of the double bonds in cyclopropylalkenes; however, the hydrogenation of a cyclopropyl ketone had been investigated previously by the authors.[3] Methyl cyclopropyl ketone was found to hydrogenate in the presence of a barium-promoted copper chromite catalyst to give exclusively methylcyclopropylcarbinol; in the presence of Raney nickel catalyst a mixture of methylcyclopropylcarbinol and pentanol-2 was obtained.

Although methyl cyclopropyl ketone and the 2-cyclopropylalkenes are of different molecular classes, certain structural similarities were noted which suggested that their reaction with hydrogen might be analogous. Both possessed a double bond capable of reacting with hydrogen, and in each case the unsaturation was in such a position that conjugation with the cyclopropyl ring was possible. Since in the presence of the copper–chromite catalyst the cyclopropyl ring remained intact during the hydrogenation of the carbonyl group of the ketone, the ring in the 2-cyclopropylalkenes might also be expected to be unchanged during the hydrogenation of the carbon–carbon double bond, especially when the hydrogenation of carbonyl and carbon–carbon double bonds require about the same conditions of temperature and pressure.[4] By similar reasoning, Raney nickel was considered unsatisfactory for the selective hydrogenation of the 2-cyclopropylalkenes; this was subsequently confirmed by Van Volkenburgh, *et al.*, who found in an investigation carried out concurrently with the present work that the Raney nickel hydrogenations of isopropenylcyclopropane (2-cyclopropylpropene) and vinylcyclopropane gave mixtures of 2-cyclopropylpropane and 2-methylpentane,[5] and ethylcyclopropane and *n*-pentane,[6] respectively. The present paper reports the results of the hydrogenations of 2-cyclopropyl-1- and -2-alkenes, from the propene to the hexenes, in the presence of the barium-promoted copper chromite catalyst.

Pronounced differences were found in the ease of hydrogenating the 2-cyclopropyl-1- and -2-alkenes. The 1-alkenes hydrogenated at 100°, and the reactions went to completion within 6 to 8 hours. In contrast, mixtures of the geometrical isomers of the 2-alkenes reacted sluggishly even at higher temperatures. For example, the hydrogenation of the isomeric 2-cyclopropyl-2-butenes required 16 times as long as the 2-cyclopropyl-1-butene under similar reaction conditions.

The composition of the hydrogenation products also differed; the 2-cyclopropyl-1-alkenes hydrogenated completely to give essentially a single product, the 2-cyclopropylalkanes, whereas the 2-cyclopropyl-2-alkenes did not completely hydrogenate and gave mixtures of unreacted olefin, 2-cyclopropylalkanes and paraffins.

The paraffin impurities in the 2-cyclopropyl-2-alkene hydrogenates were identified from their infrared spectra and found to be those which would form if the cyclopropyl ring were opened by the hydrogenation at the carbon atom adjacent to the side-chain. An approximation of the amount of paraffinic impurity present in the hydrogenates was made by assuming that the refractive index of mixtures of the paraffin and corresponding cyclopropylalkane varied linearly with composition on a volume %

TABLE I

ESTIMATED COMPOSITION OF PRODUCTS FROM HYDROGENATION REACTIONS

Olefin 2-Cyclopropyl-	Hydrogenation products 2-Cyclopropyl-	Hydrogenation products Paraffin	Wt. % hydrogenation products from 1-Alkene Cyclopropylalkane	1-Alkene Paraffin	2-Alkene[a] Cyclopropylalkane	2-Alkene[a] Paraffin
-propene	-propane	2-Methylpentane	98	2	..	..
-butene	-butane	3-Methylhexane	99	1	72	15
-pentene	-pentane	4-Methylheptane	99	1	71	17
-hexene	-hexane	4-Methyloctane	99	1	79	16

[a] Difference between these totals and 100% indicates amount of unhydrogenated olefin in products.

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

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

[3] V. A. Slabey and P. H. Wise, *ibid.*, **71**, 3252 (1949). Although the results were not published until 1949, the experimental work was completed in June, 1947.

[4] H. Adkins, "Reactions of Hydrogen with Organic Compounds Over Copper-Chromium Oxide and Nickel Catalysts," University of Wisconsin Press, Madison, Wisconsin, 1937, p. 51.

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

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

TABLE II

PHYSICAL PROPERTIES OF 2-CYCLOPROPYLALKANES

2-Cyclopropylalkane	M.p. (°C.)	M.p. for zero impurity (°C.[a])	ΔT/-mole % impurity (°C.)	Est. purity mole, %	B.p. °C. at 760 mm.	n^{20}D	d^{20}, g./ml.	Heat of comb., kcal./-mole	Analyses, % Carbon Calcd.	Analyses, % Carbon Found	Analyses, % Hydrogen Calcd.	Analyses, % Hydrogen Found
-propane	−112.97	−112.93	0.28[b]	99.9	58.31	1.3865	0.69858	900	85.62	85.58	14.38	14.33
-butane	Glass	......	...	..	90.98	1.4024	.72830	1045	85.63	85.55	14.37	14.33
-pentane	−118.46	......[c]	...	..	117.74	1.4111	.74294	1200	85.63	85.55	14.37	14.40
-hexane	− 98.04	− 97.99	0.20[d]	99.7	142.95	1.4178	.75438	1350	85.63	85.62	14.37	14.38

[a] Determined by the geometrical construction of Taylor and Rossini (W. J. Taylor and F. D. Rossini, *J. Research Natl. Bur. Standards*, **32**, 206 (1944)). [b] Determined by adding known amounts of 2-methylpentane. [c] Melting curves were not of sufficient duration to make calculation valid. [d] Determined by adding known amounts of 4-methyloctane.

basis. When the quantity of paraffin in each of the fractions from the initial fractionation of the hydrogenation products was totalled, the data presented in Table I were obtained.

That the paraffin impurities in the 2-cyclopropyl-2-alkene hydrogenates originated from diene impurities in the mixtures of geometrical isomers used for the hydrogenation experiments seemed unlikely, since the quantity of diene necessary to account for the amount of paraffin would have been detected in the stringent procedure used to isolate the pure 2-cyclopropyl-2-alkenes.[2] Ultraviolet spectra of the mixtures of geometrical isomers indicated that conjugated dienes were absent. Hydrogenolysis of the cyclopropane ring offered a possible explanation for the paraffin impurities; however, if the reaction conditions were sufficiently severe for hydrogenolysis of the ring, significant amounts of the impurities would have also been present in the hydrogenation products from the 2-cyclopropyl-1-alkenes. Since this was not the case (Table I), the results of the present work support the proposal[5] that systems in which a cyclopropyl ring is conjugated with a double bond can add hydrogen by either a 1,2- or a 1,4-mechanism.

Purification of the 2-cyclopropylalkanes was difficult in those experiments in which methylalkanes were formed, because in all cases the boiling points of the impurities were within 2° of the cyclopropanes. Azeotropic fractionations with appropriate entrainers were found to be effective for separating the close-boiling mixtures. Purifications were considered complete when (a) the melting curves of selected samples were interpreted to be indicative of purities of better than 99 mole per cent or (b) repeated fractionation and azeotropic distillation through columns rated at better than 150 theoretical plates gave no significant change in refractive index and density.

The physical properties of the 2-cyclopropylalkanes, determined by methods previously referenced,[7] are presented in Table II. The authors are indebted to Messrs. A. M. Busch for the heats of combustion, A. B. McKeown for the analyses, and J. F. Thompson for determination of physical constants.

Experimental

Hydrogenation of 2-Cyclopropylpropene.—Eight moles (658 g.) of 2-cyclopropylpropene (n^{20}D 1.4255), 66 g. of barium-promoted copper-chromite catalyst[8] and 500 ml. of ethanol were charged to a 3.4 l. rocker-type autoclave. Hydrogen was admitted to 1500 p.s.i., the rocker mechanism was started, and the autoclave heated to 100°. Hydrogenation began between 90 and 100°, and the heat of reaction increased the temperature to a maximum of 130°. The absorption of hydrogen was negligible after the first 8 hours, although the temperature was maintained at 120° for 20 hours. The total consumption of hydrogen was calculated to be 7.9 moles. The products were filtered through Celite to remove the catalyst, washed with water to extract the ethanol, dried over Drierite, and fractionated through a 6-ft. helix-packed column at 50-plate efficiency.

The distillate (Fig. 1) consisted of 417 g. of 2-cyclopropylpropane, n^{20}D 1.3863–1.3865, 132 g. which gradually decreased from n^{20}D 1.3862 to 1.3833, and 5 g. of residue.

Purification of 2-Cyclopropylpropane.—Product having n^{20}D 1.3864–1.3865 from several hydrogenations was refractionated through a 6-ft. Podbielniak column to obtain 1030 g. of distillate which was combined into 10 samples. Melting points of the 10 samples differed by less than 0.03°; that sample having the highest melting point was selected for determination of the other physical properties (Table II).

Hydrogenation of 2-Cyclopropyl-1-butene.—Forty grams of copper chromite catalyst and a solution of 4.1 moles (394 g.) of 2-cyclopropyl-1-butene (n^{20}D 1.4321) in 500 ml. of ethanol were charged to the hydrogenation vessel, and hydrogen was admitted to 1600 p.s.i. The hydrogenation was complete within 7 hours at 100–130°. The products were treated as previously described to remove catalyst and solvent. Fractionation (Fig. 1) gave 264 g. of 2-cyclopropylbutane, n^{20}D 1.4022–1.4024 and 43 g. of residue, n^{20}D 1.4039. The infrared spectrum of the residue showed the presence of a trace of olefin.

Hydrogenation of 2-Cyclopropyl-2-butenes.—The hydrogenation autoclave was charged with 4.8 moles (461 g.) of 2-cyclopropyl-2-butenes (a mixture of geometrical isomers, n^{20}D 1.4430–1.4468), 46 g. of catalyst, 500 ml. of ethanol and 1500 p.s.i. of hydrogen. At 110° hydrogenation was barely perceptible, so after 48 hours the temperature was increased to 130°. The total time required for consumption of the theoretical amount of hydrogen was 127 hours. Fractionation (Fig. 1) gave 246 g. of distillate which gradually decreased in index from n^{20}D 1.4004 to 1.3960, then 76 g. of distillate which increased in index from 1.3983 to 1.4425, and 42 g. of residue.

Purification of 2-Cyclopropylbutane.—The products from the described hydrogenations and the products from additional hydrogenations of 2-cyclopropyl-1- and -2-butenes were divided into two parts on the following basis: those fractions whose n^{20}D's were (a) less than 1.4000, and (b) greater than 1.4000. Each part was azeotropically fractionated with ethanol in a 6-ft. Podbielniak column, and the ethanol subsequently removed from each fraction by extraction with water. From 470 g of (a) there was obtained 136 g. of hydrocarbon, n^{20}D 1.3896–1.3912, which was found from the infrared spectrum to be principally 3-methylhexane, and 186 g. of 2-cyclopropylbutane, n^{20}D 1.4019–1.4024. From 909 g. of (b) there was obtained 222 g. of hydrocarbon, n^{20}D 1.3962–1.4017, and 644 g. of 2-cyclopropylbutane, n^{20}D 1.4022–1.4028. These data are shown in Fig. 2 (a) and (b), respectively.

Constant-index fractions from the azeotropic distillations (550 g., n^{20}D 1.4023) were refractionated through a 6-ft. Podbielniak column to give 387 g. of distillate which in

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

(8) E. I. du Pont de Nemours, Ammonia Division, Wilmington, Delaware.

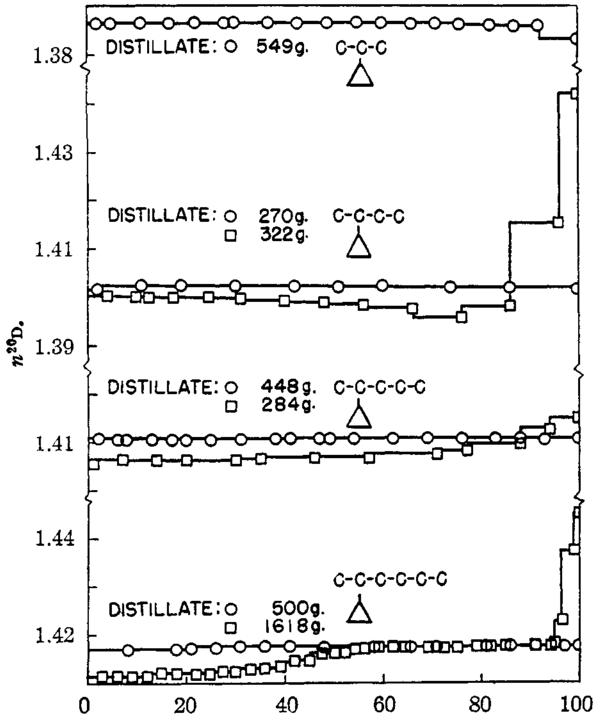

Fig. 1.—Distillation of products from the hydrogenations of 2-cyclopropyl-1-(○) and -2-alkenes (□).

ten fractions showed a variation in n^{20}D and d^{20} of only 0.0001. Physical properties (Table II) were determined on constant-index fractions which varied in density only 0.00002.

Hydrogenation of 2-Cyclopropyl-1-pentene.—A solution of 5 moles (555 g.) of 2-cyclopropyl-1-pentene (n^{20}D 1.4360–1.4362) in 500 ml. of ethanol and 55 g. of catalyst were charged to the autoclave, and hydrogen was admitted to 1500 p.s.i. The olefin was hydrogenated within 8 hours at 100–110°. Fractionation of the product (Fig. 1) gave 448 g. of 2-cyclopropylpentane, n^{20}D 1.4108–1.4110, and 23 g. of residue.

Hydrogenation of 2-Cyclopropyl-2-pentenes.—The autoclave was charged with 6.2 moles (684 g.) of 2-cyclopropyl-2-pentenes (a mixture of the geometrical isomers, n^{20}D 1.4442–1.4492), 800 ml. of ethanol, 140 g. of the catalyst (the weight of catalyst was increased in an attempt to increase the rate of hydrogenation) and 1750 p.s.i. of hydrogen. The hydrogenation was extremely sluggish; at 130° only 5 moles of hydrogen was consumed in 160 hours. Consequently, the reaction was stopped and the products were removed. Inspection of the exhaust lines from the autoclave showed that part of the charge had leaked into the exhaust system. The 344 g. of product obtained from the reaction was fractionated (Fig. 1) to give 284 g. of distillate increasing in index from n^{20}D 1.4057 to 1.4152, and 24 g. of residue.

Purification of 2-Cyclopropylpentane.—The products from the described hydrogenations were combined with the products from additional hydrogenations of 2-cyclopropyl-1- and -2-pentenes: those fractions whose n^{20}D's were (c) less than 1.4100, and (d) greater than 1.4100. Each of these combinations of distillate was azeotropically fractionated with propanol through a 6-ft. Podbielniak column. From 269 g. of (c) there was obtained 115 g. of distillate, n^{20}D 1.3980–1.3997, which was found from the infrared spectrum to be principally 4-methylheptane, and 72 g. of 2-cyclopropylpentane, n^{20}D 1.4108–1.4114. From 785 g. of (d), 138 g. of hydrocarbon, n^{20}D 1.4016–1.4109, and 596 g. of 2-cyclopropylpentane, n^{20}D 1.4110–1.4112, was obtained. These data are shown in Fig. 2 (c) and (d), respectively.

For the final purification 1028 g. of 2-cyclopropylpentane with constant refractive index (n^{20}D 1.4111) was fractionated through a 6-ft. Podbielniak column to give 952 g. of distillate which was combined into eight samples. Melting points of these samples differed by less than 0.05°. Physical properties (Table II) were determined on the sample having the highest melting point.

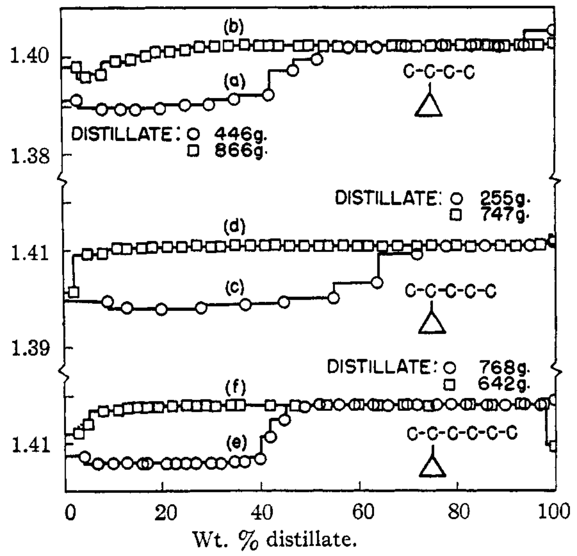

Fig. 2.—Hydrocarbon fractions from azeotropic distillations of the 2-cyclopropylalkane methylalkane mixtures.

Hydrogenation of 2-Cyclopropyl-1-hexene.—A solution of 4.8 moles (595 g.) of olefin (n^{20}D 1.4402–1.4405) in 500 ml. of ethanol and 60 g. of catalyst were charged to the hydrogenation vessel, and 1500 p.s.i. of hydrogen was admitted. The olefin was hydrogenated within 6 hours at 100–120°. The products were fractionated (Fig. 1) through a 6-ft. Podbielniak column to obtain 500 g. of 2-cyclopropylhexane, n^{20}D 1.4170–1.4179 (Fig. 1), and 46 g. of residue. Constant-index fractions (n^{20}D 1.4178) were combined into 4 samples for determinations of melting points. Properties of the last sample, which had the highest melting point, are given in Table II.

Hydrogenation of 2-Cyclopropyl-2-hexenes.—A total of 15.6 moles (1941 g.) of mixed geometrical isomers (n^{20}D 1.4453–1.4495) was hydrogenated in charges of approximately 400 g. of olefin, 40 g. of catalyst, and 500 ml. of ethanol at temperatures up to 175° and initial hydrogen pressures of 1600 p.s.i. The 1737 g. of products obtained in this way was combined and fractionated through a 6-ft. Podbielniak column to obtain 840 g. of hydrocarbon, n^{20}D 1.4114–1.4163, 697 g. of 2-cyclopropylhexane, n^{20}D 1.4170–1.4182, 165 g. of higher-index distillate and 84 g. of residue. These data are plotted in Fig. 1.

Purification of 2-Cyclopropylhexane.—The low-index products (830 g., n^{20}D less than 1.4170) from the hydrogenations of 2-cyclopropyl-2-hexenes were fractionated azeotropically with ethylene glycol monoethyl ether (Cellosolve) through a 6-ft. Podbielniak column to give (Fig. 2(e)) 262 g. of 4-methyloctane, n^{20}D 1.4061–1.4063, and 393 g. of 2-cyclopropylhexane, n^{20}D 1.4177–1.4181. The 4-methyloctane was identified by the infrared spectrum and properties of a selected sample: m.p. −113.2°, b.p. 142.3° (760 mm.), n^{20}D 1.4061, and d^{20} 0.71977 g./ml. (previously reported for 4-methyloctane[9]: m.p. −113.2°, b.p. 142.48° (760 mm.), n^{20}D 1.4061, and d^{20} 0.7199 g./ml.).

Fractions from the hydrogenation of 2-cyclopropyl-2-hexenes which were rich in 2-cyclopropylhexane (695 g., n^{20}D 1.4170–1.4182), were also azeotropically fractionated through a 6-ft. Podbielniak column, but with butanol instead of Cellosolve.[10] From this distillation (Fig. 2 (f)), 509 g. of 2-cyclopropylhexane, n^{20}D 1.4178, was obtained. The constant-index distillate was fractionated again azeotropically with butanol; from the melting points of the hydrocarbon fractions, about 75% of the distillate was calculated to be of better than 99.5 mole % purity.

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(9) "Selected Values of Properties of Hydrocarbons," Natl. Bur. of Standards Circular C461, Nov., 1947.

(10) The 2-cyclopropylhexane obtained from azeotropic fractionations with "Cellosolve" was found to be contaminated with an impurity which was believed to have originated from the "Cellosolve."