reaction mixture. The addition of an equivalent of sodium hydride had no effect on the course of the reaction.

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Synthesis and Purification of 2-Cyclopropyl-3-methyl-1-butene and 2-Cyclopropyl-3-methylbutane

BY VERNON A. SLABEY

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The preparation of a series of cyclopropylalkenes[1] and cyclopropylalkanes,[2] in which the cyclopropyl ring was located in the 2-position of C_3, C_4, C_5 and C_6 straight chains, was recently reported. Similar reactions are described herein for the preparation of a cyclopropylalkene and a cyclopropylalkane in which the cyclopropyl ring was located in the 2-position of a branched C_4 chain.

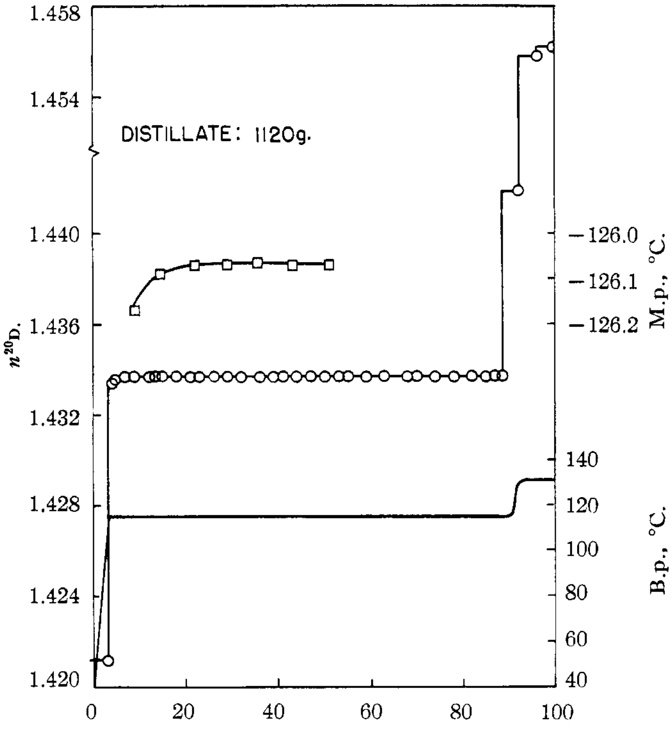

Fig. 1.—Distillation of products from the dehydration of methyl isopropylcyclopropylcarbinol over alumina.

The Grignard reagent of isopropyl bromide reacted with methyl cyclopropyl ketone to give methylisopropylcyclopropylcarbinol. The purified carbinol was dehydrated over alumina at 200–250°. Fractionation of the products (Fig. 1) gave principally 2-cyclopropyl-3-methyl-1-butene. A small amount of product which boiled considerably higher than anticipated for the other position isomer, 2-cyclopropyl-3-methyl-2-butene, and a large amount of viscous residue were also obtained.

The formation of 2-cyclopropyl-3-methyl-1-butene in high yield from the dehydration reaction was unexpected. If the formation of either of the position isomers were to be favored, removal of the tertiary hydrogen adjacent to the hydroxyl group was expected to predominate with 2-cyclopropyl-3-methyl-2-butene the resultant product. Although the 2-butene may have been produced in the dehydration reaction and subsequently polymerized during the fractionation process to give the viscous residue, the high yield of 2-cyclopropyl-3-methyl-1-butene (64%) indicated that the removal of primary hydrogen was favored in the dehydration process.

The hydrogenation of 2-cyclopropyl-3-methyl-1-butene in the presence of a barium-promoted copper chromite catalyst gave principally 2-cyclopropyl-3-methylbutane. Although the hydrogenation product was fractionated through a 6-ft. Podbielniak column at better than 150-plate efficiency, all the distillate had the same refractive index and none of the fractions could be crystallized. Small changes in density from fraction to fraction indicated that the distillate contained an impurity boiling too close to the cyclopropane hydrocarbon to be separated. From the results of previous hydrogenations of other 2-cyclopropyl-1-alkenes,[2] the hydrogenation of 2-cyclopropyl-3-methyl-1-butene was expected to give small amounts (<2% of the product) of 2,3-dimethylhexane. Since azeotropic fractionations had previously proved useful in separating close-boiling paraffin–cyclopropane mixtures,[2] the distillate was refractionated azeotropically with propanol. Although the hydrocarbon purified in this way still could not be crystallized, the densities of successive fractions of the hydrocarbon portion of the distillate from the points of 20 to 80% distilled (Fig. 2) were identical within the limits of the accuracy of measurement (0.00005 unit). While the purity of the hydrocarbon could not be established, it was believed to be near that of the other 2-cyclopropylalkanes already reported,[2] *i.e.*, better than 99 mole %.

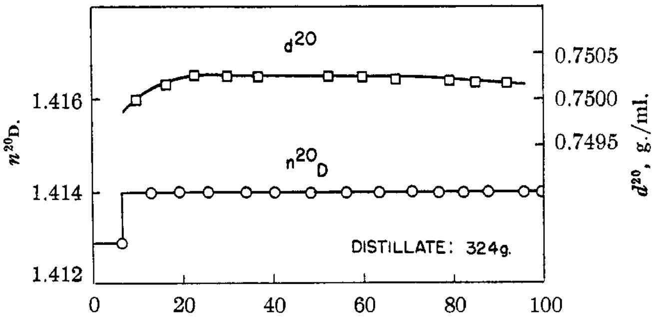

Fig. 2.—2-Cyclopropyl-3-methylbutane from azeotropic distillation with propanol.

The physical properties of the hydrocarbons, determined by methods previously referenced,[3] are presented in Table I. The author is indebted to

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

[2] V. A. Slabey and P. H. Wise, *ibid.*, **74**, 3887 (1952).

[3] I. A. Goodman and P. H. Wise, *ibid.*, **72**, 3076 (1950).

Messrs. A. M. Busch for the heats of combustion, A. B. McKeown for the analyses, and J. F. Thompson for the determinations of physical constants.

TABLE I

PHYSICAL PROPERTIES OF 2-CYCLOPROPYL-3-METHYL-1-BUTENE AND 2-CYCLOPROPYL-3-METHYLBUTANE

		2-Cyclopropyl-3-methyl-1-butene	2-Cyclopropyl-3-methylbutane
M.p., °C.		−126.06	Glass
M.p., °C. for zero impurity		−125.98[a]	
B.p., °C. at 760 mm.		116.81	115.49
$n^{20}\text{D}$		1.4337	1.4140
d^{20}, g./ml.		0.77395	0.75026
Net heat of combustion, kcal./mole		1160	1200
Carbon, %	Calcd.	87.20	85.63
	Found	87.14	85.63
Hydrogen, %	Calcd.	12.80	14.37
	Found	12.84	14.40

[a] Determined by the geometrical construction method of W. J. Taylor and F. D. Rossini, *J. Research Natl. Bur. Standards*, **32**, 197 (1944). By assuming that for 2-cyclopropyl-3-methyl-1-butene the depression in the melting point per mole % impurity is between 0.2 and 0.3° (see footnote 12, reference 1), the purity of the hydrocarbon is better than 99.5 mole %.

Experimental

Methylisopropylcyclopropylcarbinol.—Methyl cyclopropyl ketone (120 moles, 10,100 g.) reacted with Grignard reagent from 135 moles (3280 g.) of magnesium turnings and 130 moles (15,990 g.) of isopropyl bromide in a 30-gal. glass-lined reactor to yield 7767 g. (51% yield) of crude methylisopropylcyclopropylcarbinol. The crude carbinol was refluxed with alcoholic sodium hydroxide[1] to obtain 3500 g. of halide-free product. A sample of the purified carbinol had the following properties: b.p. 160.3° (760 mm.), $n^{20}\text{D}$ 1.4465, d^{20} 0.8856 g./ml.

2-Cyclopropyl-3-methyl-1-butene.—The halide-free carbinol (13.5 moles, 1734 g.) was passed at a rate of 5 ml./min. through a 2.5- by 90-cm. Pyrex column which was packed with 8 to 14 mesh alumina and heated to 200–250°. The organic products were separated from the water layer (12 moles), dried over calcium chloride, and fractionated through a 22-mm. by 7-ft. column which was packed with $^1/_8$-in. glass helices. The distillate consisted of 956 g. (64% yield) of 2-cyclopropyl-3-methyl-1-butene, b.p. 115–116°, $n^{20}\text{D}$ 1.4337, 130 g. of products boiling from 130–131°, $n^{20}\text{D}$ 1.4558–1.4562, and 345 g. of viscous residue.

Seven samples of the constant index distillate were selected for determination of melting points (Fig. 1). Physical properties of that sample having the highest melting point are presented in Table I.

The distillate boiling from 130–131° was not identified; the infrared spectrum of the distillate showed negligible absorption for C=C between 6.0–6.2 μ, and only moderate absorption between 9.7–9.9 μ, the region in which cyclopropane derivatives are known to absorb.[4] Strong absorption between 9.1 and 9.5 μ, observed in some tetrahydrofurans,[4a] was not present in the spectrum; the high refractive index also indicated that the unidentified distillate was not a tetrahydrofuran derivative.

Ozonolysis of 2-Cyclopropyl-3-methyl-1-butene.—A solution of 0.3 mole (33 g.) of the olefin in 100 ml. of ethanol was ozonized[5] and the products fractionated to give formaldehyde (detected only by odor and the presence of a white solid, presumably paraformaldehyde, which sublimed into the still-head) and 14 g. (42% yield) of isopropyl cyclopropyl ketone: b.p. 139–140° (atm.), $n^{20}\text{D}$ 1.4290 (lit.[6] b.p. 141.0–141.4° (761 mm.), $n^{20}\text{D}$ 1.42986). The 2,4-dinitrophenylhydrazone of the ketone was prepared, m.p. 187.5–188.0°.

Anal. Calcd. for $C_{13}H_{16}N_4O_4$: N, 19.17. Found: N, 19.29.

2-Cyclopropyl-3-methylbutane.—A solution of 6.6 moles (727 g.) of 2-cyclopropyl-3-methyl-1-butene ($n^{20}\text{D}$ 1.4337) in 500 ml. of ethanol and 73 g. of barium-promoted copper chromite catalyst[7] were charged to a 4.4-l. rocker-type autoclave under an initial hydrogen pressure of 1850 p.s.i. The rocking mechanism was started and the temperature gradually increased to 100°; hydrogenation began within 30 min., and was completed within 6 hours. Maximum temperature and pressure reached were 140° and 2480 p.s.i., respectively. The products were removed from the autoclave when cooled to room temperature, filtered through Celite to remove the catalyst, washed with water to remove the ethanol, dried over calcium chloride, and then fractionated through a 6-ft. Podbielniak column. Part of the product was lost midway through the distillation because of insufficient cooling water in the still head; however, the 487 g. of distillate that was obtained had a constant refractive index, $n^{20}\text{D}$ 1.4138, and, omitting the first and last fractions, varied in density from 0.7498 to 0.7501. Fractions taken near the end of the distillation varied in density only 0.00005 unit, so these fractions were combined and the physical properties of the sample were determined: m.p., glass; b.p. 115.45° (760 mm.), $n^{20}\text{D}$ 1.4140, d^{20} 0.75001.

In order to obtain the hydrocarbon in higher purity, the constant index fractions were combined and azeotropically fractionated with propanol through a 6-ft. Podbielniak column. Each fraction of distillate was washed with water to remove the propanol and the hydrocarbon layer was dried over calcium chloride. The refractive index and density of the hydrocarbon portions of the distillate are plotted in Fig. 2. The distillate collected between the points of 20 to 80% distilled was of constant refractive index and density within the limits of accuracy of measurement, 0.0002 and 0.00005 unit, respectively. Since none of the fractions could be induced to crystallize and methods of determining purity based on melting points could not be applied, the distillate between the points of 25 to 50% distilled was selected for the determination of physical properties (Table I).

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[4] (a) Unpublished work from this Laboratory and (b) J. M. Derfer, E. E. Pickett and C. E. Boord, THIS JOURNAL, **71**, 2482 (1949).

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

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

[7] Purchased from E. I. du Pont de Nemours and Co., Ammonia Division, Wilmington, Delaware.

The Vapor Pressures of Rhenium Heptoxide and Perrhenic Acid

BY WM. T. SMITH, JR., LLOYD E. LINE, JR.,[1] AND W. A. BELL

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Although the vapor pressure of rhenium heptoxide has been reported[2] a check on the work seemed desirable since the data are essential to the calculation of the thermodynamic properties of perrhenic acid.

Experimental

Since the heptoxide vapor reacts with mercury and also with stopcock lubricants, but not with glass, it was decided to make the measurements in an all-glass container. A sickle gage of the type designed by Jackson[3] was used as a null instrument. The air pressure necessary to counterbalance the pressure of the system within the sickle was measured to ±0.05 mm. with a cathetometer on a closed mercury manometer. The temperatures from 30 to 70° used in measurements on perrhenic acid were controlled to within ±0.1° using a water-bath. The higher temperatures, 220 to 350°, necessary for measuring the vapor pressures of solid and liquid rhenium heptoxide were controlled to within ±0.5° in a molten salt-bath containing 53% potassium nitrate,

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[1] This paper is based in part on a thesis presented by Lloyd E. Line, Jr., to the University of Tennessee as a part of the requirements for the M.S. degree, August, 1941.

[2] E. Ogawa, *Bull. Chem. Soc. Japan*, **7**, 265 (1932).

[3] C. G. Jackson, *J. Chem. Soc.*, **99**, 1066 (1911).