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

The Synthesis of Some Cyclopropane Hydrocarbons from Methyl Cyclopropyl Ketone[1]

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

This paper describes the synthesis of three cyclopropane hydrocarbons from methyl cyclopropyl ketone obtained from a commercial source.[2]

Ethylcyclopropane was prepared by a Wolff–Kishner reduction of the ketone at atmospheric pressure, the method used being a modification of that of Herr, Whitmore and Schiessler[3] who first described a practical procedure for carrying out this reaction without the use of pressure equipment. These workers decomposed the hydrazone of methyl cyclopropyl ketone with sodium methylate in triethylene glycol by heating the mixture to a maximum temperature of 200°; the yield of ethylcyclopropane was about 60%. In the present work the reaction was carried out in diethylene glycol and the cheaper and more easily handled sodium hydroxide was used in place of sodium methylate; the yield of purified ethylcyclopropane was 72%, and the physical properties obtained were an improvement over the best previously reported (Table II).

Isopropenylcyclopropane was produced by dehydration of dimethylcyclopropylcarbinol, this product being obtained from the reaction of methyl cyclopropyl ketone and the Grignard reagent from methyl chloride. Four methods of dehydration were investigated: catalytically over (A) activated alumina, (B) oxalic acid, (C) sulfuric acid, and chemically (D) by the Tschugaeff xanthate method. Table I summarizes the products and yields (from the carbinol) obtained by fractional distillation (25 plates) of the organic material resulting by each method; headings, tailings and residues (largely polymerization products) are not shown in the table because of the inherent difficulty of calculating yields on these mixtures.

TABLE I

	Method A	B	C	D
Isopropenylcyclopropane, %	12	57	80	24
Methylpentadiene, %	20	..	..	..
2,2-Dimethyltetrahydrofuran, %	10	15	..	..

It will be noted that of the first three methods, the one employing the strongest acid (sulfuric) gave the highest yield of isopropenylcyclopropane. The formation of this hydrocarbon is best explained by a Whitmore-type[4] mechanism involving a carbonium ion, this ion (cyclopropyldimethylcarbonium) apparently being most easily stabilized without rearrangement by expulsion of a proton from one of the methyl groups, rather than by ring rupture or expansion. It is noteworthy that the tertiary hydrogen atom on the cyclopropane ring is not expelled to produce isopropylidenecyclopropane. An explanation of this behavior is possible if it is recalled that the cyclopropane group sometimes appears to have many of the attributes of a double bond and the structure of isopropenylcyclopropane may thus be considered as somewhat analogous to that of isoprene. This would account for the failure in the present case of hydrogen to be expelled according to Saytzeff's rule (since its nature would be somewhat vinylic) and for the consequent expulsion of a hydrogen atom from a methyl group normally low in reactivity, to form the pseudoconjugate isopropenylcyclopropane, stabilized to some extent by resonance. Further, the strain of a double bond attached to a three membered ring may also be a factor. Since more than one mechanism is apparently involved in methods (A) and (B), it appears that as the acid strength of the catalyst is increased, the reaction proceeds through the carbonium ion to a greater extent. Inasmuch as nothing except isopropenylcyclopropane was found when method C was used, the dehydration over sulfuric acid must have proceeded almost exclusively through the carbonium ion mechanism.

The structure of isopropenylcyclopropane was proved by an ozonolysis experiment (on a sample prepared by method C) from which methyl cyclopropyl ketone was isolated and identified through its semicarbazone; a mixed melting point with the corresponding derivative of an authentic sample of the ketone showed no depression. The physical properties of a sample of isopropenylcyclopropane of 99.4 mole per cent. purity are given in Table II. In order to verify the identity of the isopropenylcyclopropane prepared by the other three methods, a series of mixed melting points were determined with a portion of the hydrocarbon whose structure had been proved by ozonolysis; no significant depression occurred with any of the samples.

The preparation of isopropylcyclopropane by the hydrogenation of isopropenylcyclopropane under mild conditions was investigated. In the

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(2) U. S. Industrial Chemicals, Inc., 60 E. 42nd Street, New York, N. Y.

(3) Herr, Whitmore and Schiessler, THIS JOURNAL, **67**, 2061 (1945).

(4) Whitmore, *ibid.*, **54**, 3274 (1932).

TABLE II

	B. p., °C. (760 mm.)	F. p., °C.	d^{20}_4	n^{20}_D	Estimated purity[a]
Ethylcyclopropane (this work)	35.94	−149.41	0.6839	1.3786	99%
Ethylcyclopropane (Whitmore)[3]	36.0	......	....	1.3784	..
Isopropenylcyclopropane (this work)	70.41	−102.36	.7514	1.4254	99.4
Isopropenylcyclopropane (Van Keersbilck[7])	69.5 to 70.0/751	......	.74999	1.42524	..
Isopropylcyclopropane (this work)	58.7	−118.3	.6889	1.3833	85
2-Methylpentane[8]	60.27	−153.68	.6532	1.3715	..
2,3-Dimethylbutane[8]	57.99	−128.41	.6616	1.3750	..

[a] These values were calculated from cryoscopic data. For isopropenylcyclopropane the Δt/mole per cent. impurity was determined as 0.25°, and by use of this datum and analysis of the freezing curve the "100% pure" freezing point for this hydrocarbon was calculated to be −102.20°. Likewise for isopropylcyclopropane the Δt/mole per cent. impurity was 0.20° and the "100% pure" freezing point was −115.24°.

three trials, the best sample of isopropylcyclopropane[5] obtained (see Table II) was only 85 mole per cent. pure as calculated from cryoscopic data. The chief impurity appeared to be 2-methylpentane formed by rupture of the cyclopropane ring at the bond adjacent to the side chain; 2,3-dimethylbutane (the other possible product formed by ring rupture) was not detected.

While the completely preferential hydrogenation of a double bond in the presence of a cyclopropane ring would seem feasible in consideration of the severity of conditions required for rupturing the cyclopropane ring,[6] the present case appears to be an exception. This may be explained if, as before, isopropenylcyclopropane is considered to be pseudoconjugated. It may then be proposed that some addition of hydrogen proceeded "1,4-," as in the case of a truly conjugated diene, leading to rupture of a ring C–C bond adjacent to the side chain, with the intermediate formation of 2-methyl-2-pentene and finally 2-methylpentane.

When a sample of about 80% pure isopropylcyclopropane was hydrogenated under conditions vigorous enough to cause hydrogenolysis, 2,3-dimethylbutane was the major component of the resulting mixture.[5] 2-Methylpentane (the impurity in the isopropylcyclopropane hydrogenated) was detected as only a minor component, and an unidentified paraffin was also present in very small amount. No unchanged isopropylcyclopropane was found. This study seems to indicate that in the hydrogenation of isopropenylcyclopropane under mild conditions, the 2-methylpentane impurity was not formed by hydrogenolysis of the newly formed isopropylcyclopropane, but by some mechanism such as that proposed above.

Striking evidence for conjugation is found in the boiling point of isopropenylcyclopropane which is 11.7° higher than that of isopropylcyclopropane. This suggests that isopropenylcyclopropane is comparable to 2,3-dimethyl-1,3-butadiene which, due to conjugation, boils about 13.3° higher than 2,3-dimethyl-1-butene; the latter, by contrast, actually boils 2.4° lower than the saturated analog, 2,3-dimethylbutane. Similarly, the refractive index of isopropenylcyclopropane shows an exaltation of 0.0267 (at 20°) which approaches the exaltation of 0.0332 exhibited by 2,3-dimethyl-1,3-butadiene.

Experimental

Methyl Cyclopropyl Ketone.—The commercial product[2] was distilled at about 25-plate efficiency, 78% of the charge being obtained as good product with the following physical properties: b. p. 111.2° (760 mm.), f. p. −68.3°, d^{20}_4 0.8991, n^{20}_D 1.4250.

Ethylcyclopropane.—The apparatus and general procedure described by Whitmore and his co-workers[3] were used with the following exceptions: The hydrazone from 74 g. (0.879 mole) of methyl cyclopropyl ketone was prepared using 122 g. (2.06 moles) of hydrazine hydrate,[9] 200 ml. of diethylene glycol, and 5 ml. of acetic acid. The hydrazone was cooled and dropped slowly into a solution of 60 g. (1.5 moles) of sodium hydroxide in 200 ml. of diethylene glycol at a temperature of 180–200°. The hydrocarbon collected weighed 47.0 g. (76% yield from the ketone) and had a refractive index of 1.3786 at 20°. Distillation of this material at about 15-plate efficiency gave 44.2 g. of constant index material (n^{20}_D 1.3786), a 72% yield. The physical properties of ethylcyclopropane (Table II) were determined on a center cut from the redistillation of the constant index fractions. The product did not absorb bromine from a carbon tetrachloride solution in the cold.

Dimethylcyclopropylcarbinol.—Methyl chloride was added as a gas below the liquid surface to 267 g. (11.0 moles) of magnesium turnings in 4 liters of ether in a 5-gallon copper-lined reactor provided with a steel stirrer. Addition was continued until all of the magnesium turnings were used up, after which the mixture was refluxed about an hour before the slow addition of 841 g. (10.0 moles) of methyl cyclopropyl ketone in 2 liters of dry ether was begun. When the last of the ketone had been added and reflux had been maintained for a period of two days, the reaction mixture was hydrolyzed with 1 liter of saturated ammonium chloride solution. (A large excess of ammonium chloride is undesirable as it apparently converts significant quantities of the newly formed carbinol to a chloride which appears as "tailings" when the product is distilled.) The mixture was then washed, stripped of ether, and distilled at about 20-plate efficiency to obtain 679 g. (68% yield from ketone) of good dimethylcyclopropylcarbinol, 146 g. (15% yield) of material

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[5] This sample was examined spectroscopically (infrared) by F. P. Hochgesang of the Socony-Vacuum Laboratories, Paulsboro, N. J.

[6] Shortridge, Craig, Greenlee, Derfer and Boord, THIS JOURNAL, **70**, 946 (1948).

[7] Van Keersbilck, *Bull. soc. chim. Belg.*, **38**, 205 (1929).

[8] "Selected Values of Properties of Hydrocarbons," N. B. S. Circular C461, Rossini, *et al.*, U. S. Gov. Printing Office, Washington, D. C., p. 38.

[9] Purchased from the Edwal Laboratories.

worth redistillation and 50 g. of a high boiling residue. In a subsequent run of 5-mole proportions over twice as much of the high boiling material was obtained and had the following physical properties: b.p. *ca.* 73° (50 mm.), n^{20}_D 1.443 to 1.495; this material contained chloride (or chlorides), the probable genesis of which has been explained. The physical properties determined for the carbinol follow, the values in brackets are those of Bruylants[10] given for comparison: b.p. 123.4° (760 mm.) (123.4 to 123.6° (752 mm.)), d^{20}_4 0.8842 (0.88063), n^{20}_D 1.4337 (1.43257), f. p. −43.0°.

Isopropenylcyclopropane.—Dimethylcyclopropylcarbinol was dehydrated in four different ways:

A. **Over Activated Alumina.**—A 2.4 (i.d.) × 120.0 cm. pyrex tube was placed in a vertical furnace and packed with 4–8 mesh, Grade F-1, Alorco alumina which was activated by heating to 300° and passing air through the tube overnight. The tube and its contents were cooled to 250° and the carbinol (154 g., 1.54 moles) was passed through at a rate of one drop per three seconds at this temperature. The conversion based on the water collected was 49%, and the yield of organic material was 95 g. This was distilled at about 30-plate efficiency with the results shown in Table I. No evidence was found for the presence of unchanged carbinol, and a subsequent run at 300° showed that the yield of isopropenylcyclopropane was decreased at the higher temperature, more of the other products being formed.

B. **Over Oxalic Acid.**—The carbinol (197 g., 1.97 moles) was dehydrated by boiling it with 10% its weight of oxalic acid and distilling off the low boiling products as they formed. After washing and drying, the product weighed 145 g. and was distilled at about 30-plate efficiency. The analysis of this distillation is shown in Table I.

C. **Over Sulfuric Acid.**—Twelve drops of concentrated sulfuric acid were added to 152 g. (1.52 moles) of the carbinol in a half-liter flask attached to a glass packed distilling column. The mixture was heated to a gentle boil, and the hydrocarbon was distilled through the column and collected as the carbinol was dehydrated. The crude product, washed and dried, weighed 104 g. and was distilled at about 20-plate efficiency (see Table I).

D. **By the Tschugaeff Xanthate Method.**[11]—Two liters of reagent grade "xylene" were dried by percolation through a column of silica gel and placed in a 5-liter flask equipped with a stirrer, dropping funnel and reflux condenser. Sixty-nine grams (1.76 moles) of metallic potassium, scraped free of oxide, were added, and the flask was heated until the potassium melted. The addition of 176 g. (1.76 moles) of dimethylcyclopropylcarbinol was begun dropwise and continued until complete (one and one-half hours). Carbon disulfide (151 g., 1.98 moles) was added slowly to the cooled mixture, after which 286 g. (2.02 moles) of methyl iodide was added over a period of one and one-half hours. After standing overnight, the mixture was refluxed at 65° for about ten hours and then was allowed to cool and stand for several days at room temperature. The solid potassium iodide was removed by filtration and the organic material adhering to it was leached with xylene. The bulked xylene solution of the xanthate was placed in a flask attached to a column packed with glass helices, and the xanthate was decomposed by heating at 130–135° for about eight hours, the hydrocarbon being distilled from the mixture as it formed. The distillate was washed with 25% sodium hydroxide, steam distilled, and fractionated at about 20-plate efficiency to obtain 80 g. of material (b.p. 53–80°) which smelled strongly of organic sulfur compounds. This product was washed again with 25% sodium hydroxide, then with water, and was dried over anhydrous sodium sulfate before being treated with sodium in liquid ammonia. The treated material still had a strong odor so it was shaken with saturated mercuric chloride solution and water, and, after steam distillation, was washed with dilute hydrochloric acid and dried over sodium sulfate. By distillation of this product at about 30-plate efficiency nothing except isopropenylcyclopropane was detected, but the yield was low (Table I).

Proof of Structure of Isopropenylcyclopropane by Ozonolysis.—A portion (11.79 g.) of the isopropenylcyclopropane obtained from the sulfuric acid dehydration of dimethylcyclopropylcarbinol was ozonized by the procedure and in the apparatus described by Henne and Perilstein,[12] acetic acid being used as the solvent. The solution of the ozonide was poured into 25 ml. of water, 5 g. of zinc dust was added, and, after standing overnight, the mixture was heated on a steam-bath for one-half hour. After decantation from the zinc, the organic material was distilled at about 20-plate efficiency, that portion boiling under 100° being collected. This water–ketone fraction was treated with 10 g. of semicarbazide hydrochloride, 15 g. of sodium acetate, and sufficient water to make a total volume of 100 ml. The mixture was heated on a steam-bath for a few minutes, and, on cooling, 6.3 g. (32% yield) of the crude semicarbazone crystallized. After 4 recrystallizations from absolute alcohol 3.2 g. (16% yield) of the semicarbazone remained and had a melting point of 121.4 to 122.5°. The semicarbazone prepared from an authentic sample of methyl cyclopropyl ketone in the same manner melted at 121.7 to 122.4°, and a mixed melting point showed no depression.

Isopropylcyclopropane.—A sample (56 g., 0.68 mole) of isopropenylcyclopropane was hydrogenated in a glass liner over Raney nickel at 40° and a pressure of 900 p.s.i. Fractionation of the hydrogenate indicated that the reduction was only about 40% complete, and that some 2-methylpentane (ring fission product) was present. A "best" fraction from this distillation had the following properties: b. p. 58.2 to 58.6° (uncor.), n^{20}_D 1.3850 to 1.3851.

A second hydrogenation was carried out as before using 70 g. (0.86 mole) of isopropenylcyclopropane (known purity 98.7 mole per cent.); the maximum temperature reached was 97°, and the maximum pressure 800 p.s.i. The product, separated from the nickel catalyst, was washed with 10% permanganate solution several times, but after steam distillation it still showed unsaturation. Instead of further permanganate treatment, the material was distilled at 20-plate efficiency. The main portion boiled at 58.5 to 58.8°, but the refractive index after rising to a maximum of 1.3842 for the second fraction dropped off gradually to 1.3774 toward the end of the distillation. It was evident that far more 2-methylpentane was present than that contained in the sample hydrogenated. The amount of impurity present in the hydrogenate, assuming the impurity to be 2-methylpentane, was calculated to be 12 to 13 g., or about 17 mole per cent. of the charge.

In a third attempt, 80 g. of isopropenylcyclopropane were hydrogenated over Raney nickel catalyst, at 35–40° and 1100 p.s.i., with 90% of the theoretical amount of hydrogen absorbed. The hydrocarbon recovered by washing the crude hydrogenate with water, steam distilling, and drying over anhydrous sodium sulfate was 82% of theory; it was distilled at about 30-plate efficiency. The first 6% of the distillate boiled from 57.9 to 58.6° and may have contained a little 2,3-dimethylbutane, but the refractive index, 1.3834 at 20°, was only slightly lower than the maximum which followed immediately on the curve. The next 45% boiled from 58.6 to 58.8° while the refractive index slowly dropped from 1.3836 to 1.3829; the physical properties listed in Table II were determined on this portion. Distillation was continued until a temperature of 59.0° was reached; meanwhile the refractive index dropped to 1.3811, presumably due to 2-methylpentane which would be expected to appear in the tailings. By a study of infrared absorption spectra,[5] 2-methylpentane was identified as an impurity in the portion of the distillate used in determining physical properties; 2,3-dimethylbutane was not detected and was judged to comprise less than 6% of the sample, if present at all.

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(10) Bruylants, *Bull. soc. chim. Belg.*, **36**, 153 (1927).

(11) Tschugaeff, *Ber.*, **32** 3332 (1899).

(12) Henne and Perilstein, THIS JOURNAL, **65**, 2183 (1943).

Hydrogenolysis of Isopropylcyclopropane.—A sample of isopropylcyclopropane (b. p. 58.5 to 58.8°, $n^{20}{}_{D}$ 1.3823–1.3841) was hydrogenated over 10% its weight of nickel-on-kieselguhr catalyst. Absorption of hydrogen began at 150° and 1250 p. s. i. When absorption had ceased, the temperature was raised to 200°, whereupon further absorption occurred (from 1220 p. s. i.). Further increase in temperature did not cause additional reaction. The hydrogenate was washed with water and dried over anhydrous sodium sulfate; this material (b. p. 53–61° (760 mm.), $n^{20}{}_{D}$ 1.3740) was sent for infrared analysis.

Acknowledgment.—Sincere appreciation is expressed to Dr. F. P. Hochgesang for his determination and interpretation of the infrared absorption spectra of some of the hydrocarbon samples described herein.

Summary

Ethylcyclopropane, isopropenylcyclopropane and isopropylcyclopropane have been synthesized from methyl cyclopropyl ketone. Evidence for the behavior of isopropenylcyclopropane as a pseudoconjugated system has been presented.

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A New Synthesis of Monoalkylcyclobutanes: Reduction of Neopentyl Type Tribromides[1]

BY JOHN M. DERFER, KENNETH W. GREENLEE AND CECIL E. BOORD

Introduction

Hydrocarbons of the cyclopropane or cyclobutane series have been produced by the dehalogenation (or dehydrohalogenation) of mono-, di- and tetrahalo derivatives of neopentane.

Whitmore[2,3,4] and his co-workers have shown that the reaction of neopentyl chloride with an equivalent amount of metallic sodium gives a 25% yield of 1,1-dimethylcyclopropane; the overall yield of this hydrocarbon is increased to 51% when a four-fold excess of the chloride is employed. When propyl sodium is used instead of metallic sodium, the cyclopropane hydrocarbon is formed in 75% yield.

The debromation of *sym*-dibromoneopentane by either the Gustavson[5a] or the Hass–McBee[6] method gives good yields of 1,1-dimethylcyclopropane.[3,5b,7]

The products from the reduction of pentaerythrityl tetrabromide by the Gustavson method have been identified by Whitmore and Williams[8] as 2-methyl-1-butene and methylenecyclobutane in the ratio of about 1:11, respectively; Murray and Stevenson,[9] using Raman spectra, found traces of spiropentane also to be present. Slabey[10] found that when sodium iodide and sodium carbonate are added to the reaction mixture, the hydrocarbon product (obtained in 79–89% yield) consists of spiropentane (25%), methylenecyclobutane (56%), 2-methyl-1-butene (15%) and traces of 1,1-dimethylcyclopropane. When the Hass–McBee procedure is employed in the reduction of pentaerythrityl tetrabromide, a 38% yield of hydrocarbon material is obtained; this consists of 47–60% of spiropentane and smaller amounts of methylenecyclobutane and 2-methyl-1-butene.[10,11]

There is no indication in the literature that any investigation has ever been made concerning the debromination (or dehydrobromination) of tribromides containing the neopentyl structure, or even that such halides have ever been prepared. The present work not only closes this gap, but also appears to furnish a general and practical method for the preparation of monoalkylcyclobutanes with the possible exception of methylcyclobutane.

The general scheme employed in this work has been to prepare neopentyl type tribromides from the corresponding trihydric alcohols and to treat them with zinc by the Hass–McBee[6] procedure. Alkylidenecyclobutanes are formed in about 50% yield and can be hydrogenated to the corresponding alkylcyclobutanes. The method has been applied to three tribromides: 1,1,1-tris-(bromomethyl)-propane, 1,1,1-tris-(bromomethyl)-2-methylpropane and 1,1,1-tris-(bromomethyl)-ethane.

Discussion

Reduction of 1,1,1-tris-(Bromomethyl)-propane.—The reaction of this tribromide with zinc by the Hass–McBee procedure[6] produced a mixture of hydrocarbons in yields of 90–93% of theory. Fractionation of this material at about

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[1] The material in this paper was abstracted from the dissertation submitted by John M. Derfer to the Graduate School of the Ohio State University in partial fulfillment of the requirements for the Degree of Doctor of Philosophy in 1946. Parts of this work were presented before the Organic Division at the 109th and 111th meetings of the American Chemical Society; see also THIS JOURNAL, **67**, 1863 (1945).

[2] Whitmore, Popkin and Pfister, *ibid.*, **61**, 1616 (1939).

[3] Whitmore, Popkin, Bernstein and Wilkens, *ibid.*, **63**, 124 (1941).

[4] Whitmore and Zook, *ibid.*, **64**, 1783 (1942).

[5] (a) Gustavson, *J. prakt. Chem.*, **36**, 300 (1887); (b) Gustavson and Popper, *ibid.*, **58**, 458 (1898).

[6] Hass, McBee, Hinds and Glusenkamp, *Ind. Eng. Chem.*, **28**, 1178 (1936).

[7] Shortridge, Craig, Greenlee, Derfer and Boord, THIS JOURNAL, **70**, 946 (1948).

[8] See footnote to article by Bauer and Beach, *ibid.*, **64**, 1142 (1942).

[9] Murray and Stevenson, *ibid.*, **66**, 314 (1944).

[10] Slabey, *ibid.*, **68**, 1335 (1946).

[11] Murray and Stevenson, *ibid.*, **66**, 812 (1944).