Hydrogenolysis of Isopropylcyclopropane.—A sample of isopropylcyclopropane (b. p. 58.5 to 58.8°, $n^{20}\mathrm{D}$ 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.), $n^{20}\mathrm{D}$ 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).

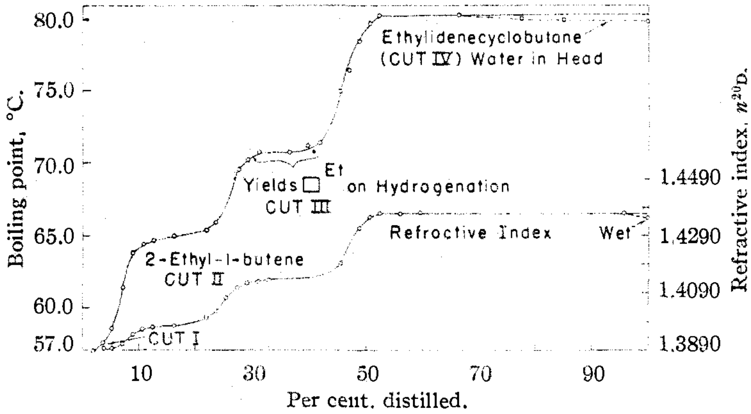

Fig. 1.—Curves describing the distillation of the crude product from the reduction of 1,1,1-tris-(bromomethyl)-propane.

40-plate efficiency[12] (Fig. 1) separated it into four cuts boiling at approximately 56, 64, 70 and 80°; these fractions constituted 3 (estm.) 12, 18, and 54% of the crude hydrocarbon mixture by weight, respectively and will be designated as Cut I, Cut II, Cut III and Cut IV.

The highest boiling and preponderant fraction (Cut IV) was shown to be a very pure individual compound by its time–temperature freezing curve and it was identified as ethylidenecyclobutane (not previously reported) by an ozonolysis experiment[13] from which both acetaldehyde and cyclobutanone were isolated and identified. Hydrogenation of ethylidenecyclobutane over Raney nickel at low pressures and temperatures gave ethylcyclobutane exclusively and quantitatively; the physical properties for this material were an improvement over those reported by Wibaut[14] for ethylcyclobutane prepared by another method.

Refractionation of Cut III at about 40-plate efficiency and determination of densities, refractive indices and standard boiling points on about every third fraction showed that this material was a mixture, and that it could not be separated by fractionation (Fig. 2) on the best column available (40-plates). The mixture gave ethylcyclobutane exclusively on hydrogenation, thus limiting the possible constituents to five substances: the two ethylcyclobutenes, ethylidenecyclobutane, vinylcyclobutane and ethylcyclobutane, itself. Oxidation of Cut III with chromic anhydride and glacial acetic acid failed to attack about 30% of it; the unoxidized material was identified as ethylcyclobutane on the basis of its physical properties and a mixed freezing point determination with an authentic sample of this hydrocarbon. By oxidation of Cut III with aqueous sodium dichromate–sulfuric acid solution, a small amount of material was isolated with physical properties in good agreement with those of cyclobutane carboxylic acid; esterification of this material with ethyl alcohol produced a substance which had approximately the same boiling point as the ethyl ester of cyclobutane carboxylic acid, and a carbon–hydrogen analysis gave values in fair agreement with the values calculated for this ester. Identification of this acid in the oxidation products indicated that a second component (about 70% of Cut III) was vinylcyclobutane; no evidence for the presence of either of the ethylcyclobutenes was found. The infrared absorption spectrogram of Cut III (Fig. 3) shows the characteristic absorption of an alpha olefin at 6.1 microns; vinylcyclobutane is the only olefin which would both exhibit this characteristic and hydrogenate to ethylcyclobutane.

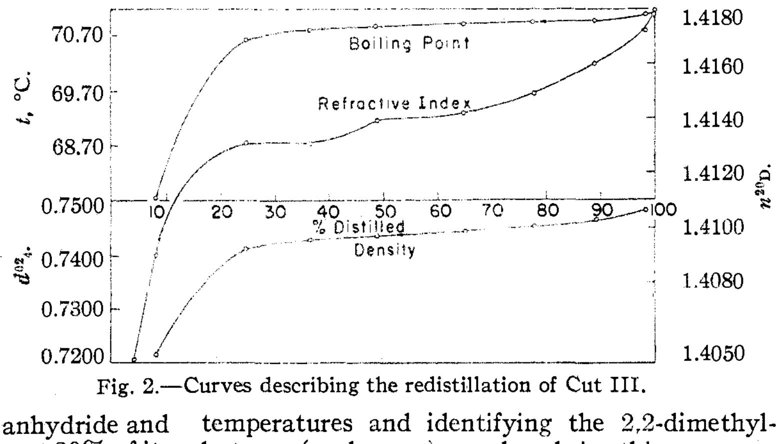

Fig. 2.—Curves describing the redistillation of Cut III.

Since both Cut III and Cut IV can be hydrogenated quantitatively to ethylcyclobutane, the over-all yield of ethylcyclobutane which can be produced by this reaction is about 65% of theory, based on the tribromide.

Cut II was identified as 2-ethyl-1-butene on the basis of its physical properties and by a mixed freezing point determination with an authentic sample of 2-ethyl-1-butene.

Cut I was shown conclusively to be 1-methyl-1-ethylcyclopropane (hitherto unreported) by subjecting it to hydrogenation at high pressures and temperatures and identifying the 2,2-dimethylbutane (neohexane) produced in this manner. (This type of hydrogenation is known to rupture the cyclopropane ring by splitting the bond opposite to the gem-substituted carbon atom.[7])

Reduction of 1,1,1-tris-(bromomethyl)-propane by zinc in 45–80% *aqueous ethanol* produced chiefly an ether, tentatively identified as ethyl 1-ethylcyclopropylcarbinyl ether. No apparent reaction

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[12] All plate ratings given in this paper represent estimates of column efficiency under actual operating conditions.

[13] Arnold, Master's Thesis, The Ohio State University, 1945.

[14] Wibaut, *Rec. trav. chim.*, 329 (1939).

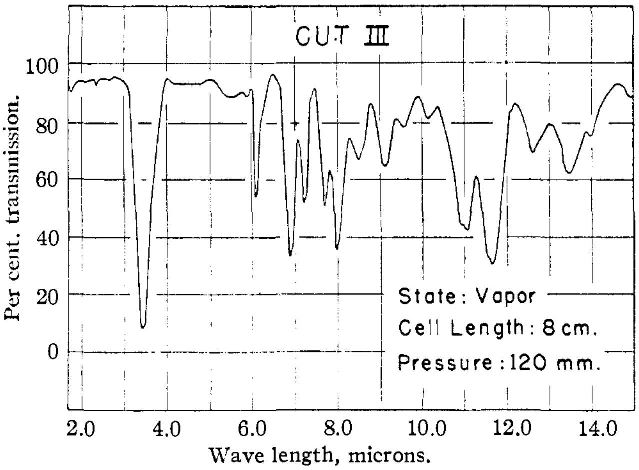

Fig. 3.—Infrared absorption spectrogram of Cut III.

took place between zinc and the tribromide in *anhydrous dioxane;* when a small amount of water was added to the mixture, reaction occurred, but no single product could be isolated.

Reduction of 1,1,1-tris-(Bromomethyl)-2-methylpropane.—The reaction of this tribromide with zinc by the Hass–McBee procedure produced a 97% yield of crude hydrocarbon material. Fractionation of this material at about 40-plate efficiency (Fig. 4) separated it into a forerun containing no constant refractive index or constant boiling fractions and a higher boiling cut (about 50% of the charge) which distilled at an essentially constant temperature (107°) and had a constant refractive index (1.4459).

The 107° material was shown to be a very pure individual compound by its time-temperature freezing curve, and was identified as isopropylidenecyclobutane (not previously reported) by an ozonolysis experiment from which both acetone and cyclobutanone were isolated and identified. Hydrogenation of isopropylidenecyclobutane over Raney nickel at low pressures and temperatures gave isopropylcyclobutane exclusively; physical properties determined on this material were an improvement over those reported for it by Kasansky.[15] The forerun was hydrogenated to saturation over Raney nickel at low pressures and temperatures; about 57% of the theoretical amount of hydrogen was absorbed, indicating that about this percentage of the forerun consisted of olefinic hydrocarbons. Fractionation of the hydrogenated material at about 40-plate efficiency separated it into two cuts boiling 81.7–83.2° and 88.8–92.1°. The lower boiling material was shown to be 1-methyl-1-isopropylcyclopropane (hitherto unreported) by a comparison of the infrared absorption spectrograms of its high pressure hydrogenation product (Fig. 5-A) with that of the expected product, 2,2,3-trimethylbutane (Fig. 5-B); these spectrograms are, for practical purposes, identical. The higher boiling material was found to be a mixture of 2,3-dimethylpentane and isopropylcyclobutane by a comparison of physical data (Table I), including infrared absorption spectrograms (Fig. 5-C-D-E). All characteristic bands of these two substances are present in the spectrogram of the mixture. By analogy with the corresponding study of the reaction producing ethylidenecyclobutane as the chief product, isopropylcyclobutane was undoubtedly a component of the unhydrogenated forerun; the 2,3-dimethylpentane identified in the hydrogenated material came from olefins with the same carbon skeleton, chief among which, by further analogy, was undoubtedly 3-methyl-2-ethyl-1-butene. Some isopropenylcyclobutane may also have been present, but the presence of one or both of the isopropylcyclobutenes seems improbable.

TABLE I

	2,3-Dimethylpentane	Isopropylcyclobutane	This material
B. p., °C. (760 mm.)	89.8	92.70	88.8–92.1
d^{20}_4	0.6951	0.7376	0.7213
$n^{20}\text{D}$	1.3920	1.4080	1.4013–1.4087

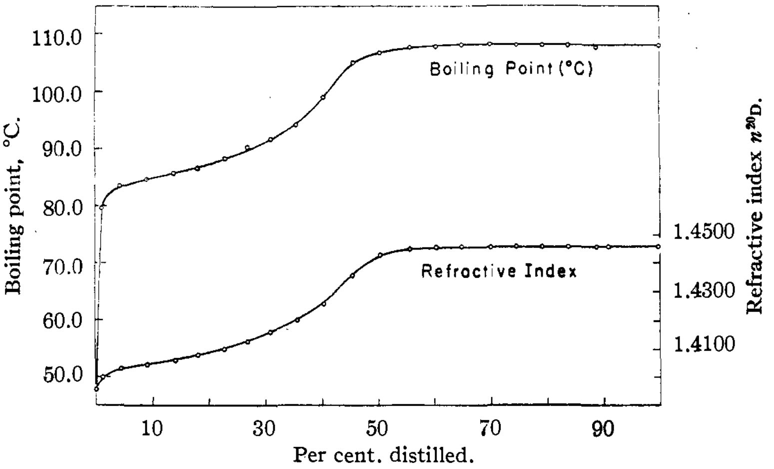

Fig. 4.—Curves describing the distillation of the crude product from the reduction of 1,1,1-tris-(bromomethyl)-2-methylpropane.

Reduction of 1,1,1-tris-(Bromomethyl)-ethane.—This tribromide was treated with zinc by the Hass–McBee procedure in the usual manner. The highest yield of hydrocarbon material obtained was 65%. Fractionation of this material at about 40-plate efficiency (Fig. 6) separated it into three cuts boiling at approximately 20, 31 and 37–43°; these fractions were

(15) Kasansky, *Ber.*, **69**, 950 (1936).

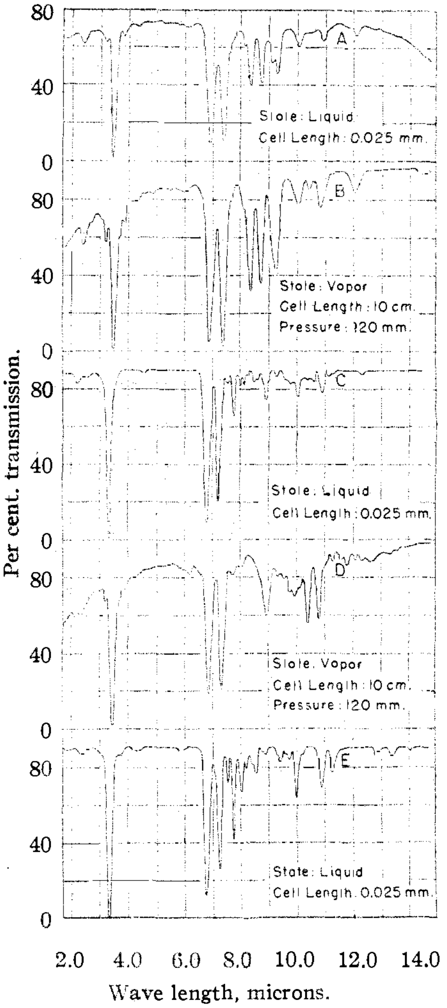

Fig. 5.—Infrared absorption spectrograms of: A, product formed by the hydrogenation of 1-methyl-1-isopropylcyclopropane; B, authentic sample of 2,2,3-trimethylbutane; C, 90° cut in the distillation of the hydrogenated forerun from the isopropylidenecyclobutane synthesis; D, authentic sample of 2,3-dimethylpentane; E, isopropylcyclobutane.

about 15, 38 and 47% of the crude hydrocarbon mixture by weight, respectively.

The 37–43° cut (expected to be relatively pure methylenecyclobutane) was a mixture (n^{20}D 1.3970–1.4203) which could not be separated into its components by redistillation at about 25-plate efficiency. About 78% of the theoretical amount of hydrogen was absorbed when this mixture was hydrogenated to saturation at low pressures and temperatures. Fractionation of the hydrogenate at about 20-plate efficiency produced no constant refractive index material (b. p. 34.6–36.6°, n^{20}D 1.3800–1.3880). An infrared absorption spectrogram of a cut soon after the obvious headings showed the material to be largely methylcyclobutane; no positive evidence as to the identity of the impurity could be obtained from the spectrogram. None of the fractions crystallized at liquid air temperature, but rather formed a viscous sirup. It is believed that methylcyclobutane of good purity could be obtained if the reaction were carried out on a large enough scale to permit the use of high-efficiency columns and other techniques not used in this work because of the small quantities of material involved. The original unhydrogenated material probably consisted of methylenecyclobutane (b. p. 42.2°, n^{20}D 1.4208), methylcyclobutane (b. p. 36.6°, n^{20}D 1.3875), and an unidentified impurity.

The 31 and 20° cuts were identified as 2-methyl-1-butene and 1,1-dimethylcyclopropane, respectively, as anticipated.

From the reaction residue were isolated two high-boiling by-products tentatively identified as 1-methylcyclopropylcarbinol and di-(1-methylcyclopropylmethyl) ether. Their formation was attributed to the reaction of 1-methyl-1-(bromomethyl)-cyclopropane with water produced by the interaction of protons with carbonate ions, carbonic acid thus being formed; evolution of carbon dioxide was noted during the reaction.

Reaction Mechanisms

Logical mechanisms have been proposed for the formation of all products from these reactions. These mechanisms will be demonstrated for the reaction which produced ethylidenecyclobutane as the chief product, since this reaction has been described the most completely.

The products identified from this reaction were ethylidenecyclobutane (I), vinylcyclobutane (II), 1-methyl-1-ethylcyclopropane (III), ethylcyclobutane (IV), and 2-ethyl-1-butene (V). It will be noted that the products from this reaction fall into two categories on the basis of their carbon-hydrogen ratios; I and II contain both a cycle and a double bond, whereas the other products contain *either* a cycle *or* a double bond. This suggests that two different mechanisms are involved simultaneously.

We believe that the first reaction to occur is the closing of a cyclopropane ring, as shown in Equation 1. Isolation of ethyl 1-ethylcyclopropylcarbinyl ether from the reaction of this tribromide with zinc in ethanol supports this belief. The intermediate monobromide (1-ethyl-1-bromomethylcyclopropane) could not be isolated when the tribromide was reacted with a limited amount of zinc (in various solvents); this is as would be expected, since the monobromide is somewhat allylic in nature due to the cyclopropane ring embracing the beta and gamma carbon atoms. Additional zinc would be expected to react with this "allylic type" bromide in preference to reaction with a new molecule of tribromide when both were present in the reaction mixture.

The formation of I and II is best explained by a Whitmore-type[16] mechanism. Zinc bromide acts

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[16] Whitmore, This Journal, **54**, 3274 (1932).

as the acid (electron seeking) reagent in much the same manner as it catalyzes the conversion of an alcohol to an alkyl halide in the presence of a hydrogen halide. The carbonium ion produced by Equation 2 undergoes rearrangement with ring expansion to form a new carbonium ion which stabilizes itself by expulsion of a proton to form I (Equation 3). In the formation of II, the same rearranged carbonium ion is formed, but migration of the alpha hydrogen atom with its bonding electrons (to the adjacent ring carbon atom) precedes the expulsion of a proton, as shown in Equation 4. It is possible that I rearranges to II in the presence of zinc bromide, but this seems less likely.

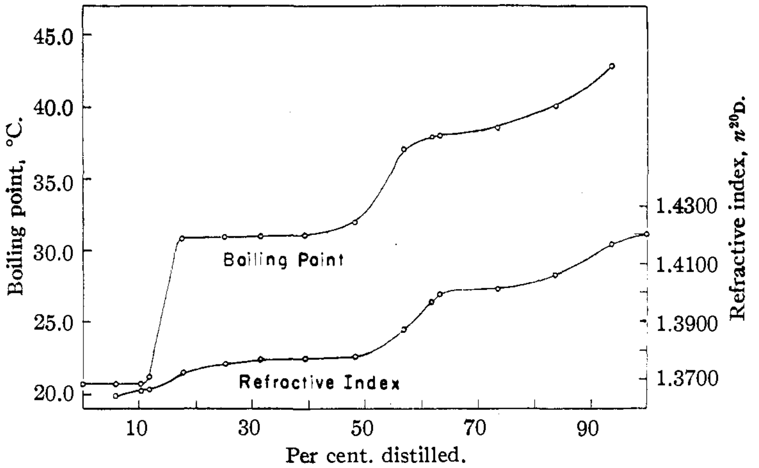

Fig. 6.—Curves describing the distillation of the crude product from the reduction of 1,1,1-tris-(bromomethyl)-ethane.

The formation of the other three products must involve an organozinc intermediate which can abstract an active hydrogen, probably by reaction with the enol form of the solvent, acetamide.

III is then formed without rearrangement, according to Equation 5 (HQ is acetamide or other molecule containing an active hydrogen).

IV results through a Whitmore-type rearrangement of the intermediate monobromide (as in the case of I), followed by the formation of an organozinc bromide which then reacts with an active hydrogen (Equation 6). It is not surprising that a bromide ion should combine with the rearranged carbonium ion as shown, since the concentration of bromide ions in the reaction mixture must be high, and since recombination with an original negative ion is one possibility suggested by Whitmore for rearrangements involving carbonium ions.

V is probably formed according to Equation 7. The initial electron shift is similar to that in Equation 3, except that the methylene group does not accompany the electron pair, but becomes positively charged. A methyl group is then formed by way of the organozinc intermediate, as shown. The similarity of this rearrangement to an allylic rearrangement will be noticed; other cases in which the cyclopropane ring appears to have some of the functions of a double bond have been noted.[17]

Experimental

Production of Trihydric Alcohols

1,1,1-tris-(Hydroxymethyl)-propane.—This triol was purchased from the Heyden Chemical Corporation, Garfield, New Jersey.

1,1,1-tris-(Hydroxymethyl)-2-methylpropane.

The procedure was developed by considerably modifying that of Von Marle and Tollens.[18] In a flask suitably equipped, were placed 172 g. (2 moles) of isovaleric aldehyde (Eastman Kodak Co.)and 650 g. (8 moles) of formalin (Merck, C.P.); stirring was started, and the slow addition of solid calcium hydroxide (1 mole) was begun from a side flask, the rate of addition being such that the temperature within the reaction flask remained at 55–65°. The reaction mixture was then heated (with stirring) for twelve hours at 32°, twenty-four hours at 50–60°, and six hours at 85°. The mixture was then filtered by suction, while hot, and evaporated to a volume of 600 ml. This residue was treated with about three times its volume of boiling 95% ethanol, and the solid calcium formate remaining was separated by filtration. The filtrate was stripped of alcohol and distilled at reduced pressure; 156 g. (53% yield, based on isovaleric aldehyde) of the desired triol boiling at 170–175° (6 mm.) was obtained. In subsequent runs, the reaction mixture was subjected to continuous ether extraction, and the triol concentrate obtained (after ether stripping) was treated, as such, with phosphorus tribromide, thus avoiding some decomposition during distillation.

The purified triol is hygroscopic, but a sample of the distilled triol, recrystallized five times from ether and dried for two days *in vacuo*, melted sharply at 82.0–82.1°.

Anal. Calcd. for $C_7H_{16}O_3$: C, 56.73; H, 10.88. Found: C, 56.74; H, 10.69.

1,1,1-tris-(Hydroxymethyl)-ethane.—This triol was prepared from propionaldehyde and formalin by the procedure of Brubaker and Jacobson[19] except that the solid sodium formate was removed by filtration of the acetone solution of the triol which was then purified by crystallization (yield from the aldehyde was 51%). After two recrystallizations from acetone solution this compound melted at 198.0–198.2°.

Anal. Calcd. for $C_5H_{12}O_3$: C, 49.98; H, 10.06. Found: C, 50.03; H, 10.21.

Production of Tribromides

1,1,1-tris-(Bromomethyl)-propane.—This compound was prepared from the corresponding triol and phosphorus tribromide by the same procedure as that described by Schurink[20] for the preparation of pentaerythrityl tetrabromide, except that the heating period was at 140°. The orange-red impurity (13% by weight) was removed by filtration from the hot alcohol solution of the tribromide which was then purified by crystallization (59% yield from triol). After two recrystallizations from alcohol solution, the tribromide melted at 94.3°. Separation of the colored impurity was found unnecessary for the present purpose.

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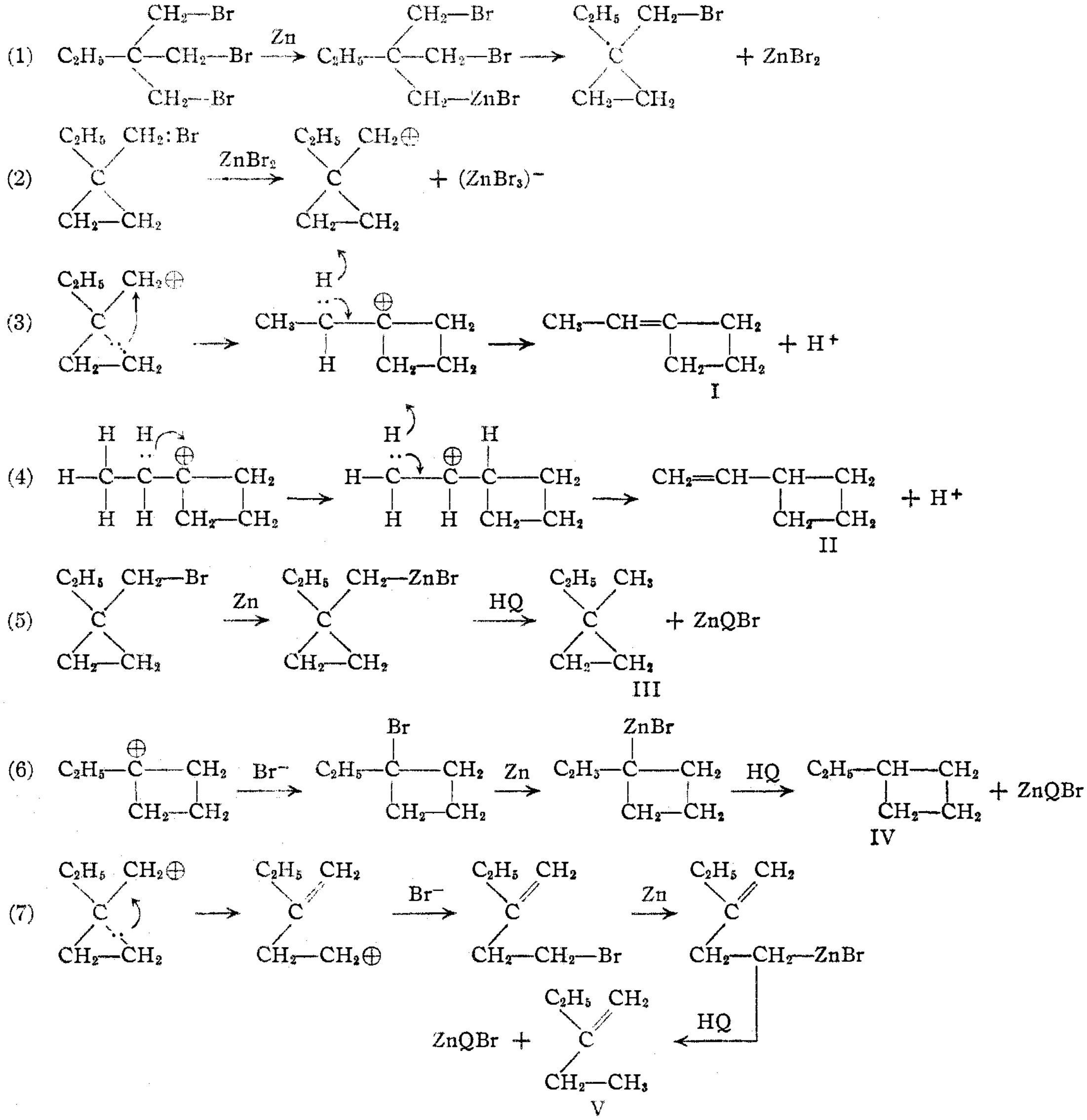
[17] Van Volkenburgh, Greenlee, Derfer and Boord, THIS JOURNAL, **70**, 172 (1948).

[18] Von Marle and Tollens, *Ber.*, **36**, 1342 (1903).

[19] Brubaker and Jacobson, U. S. Patent 2,292,926.

[20] "Organic Syntheses," Coll. Vol. II, Editor A. H. Blatt, John Wiley and Sons, Inc., New York, N. Y., 1946, p. 476.

Equations Demonstrating Reaction Mechanisms



Anal. Calcd. for $C_6H_{11}Br_3$: C, 22.35; H, 3.42. Found: C, 22.38; H, 3.49.

1,1,1-tris-(Bromomethyl)-2-methylpropane.—This tribromide was prepared from the corresponding triol in the same way as the one above, except that the temperature was 145–150° during the heating period. This compound was a liquid and (after washing) was separated from the usual red impurity by suction filtration; after drying it was purified by vacuum distillation (yield 48%, based on triol). Physical properties were determined on a center fraction: f. p. +1.8°; b. p. 106° (3 mm.); $n^{20}\text{D}$ 1.5568; d^{20}_4 1.9122.

Anal. Calcd. for $C_7H_{13}Br_3$: C, 24.99; H, 3.89. Found: C, 25.36; H, 3.93.

1,1,1-tris-(Bromomethyl)-ethane.—This tribromide (also a liquid) was prepared from the corresponding triol by the same procedure used in preparing 1,1,1-tris-(bromomethyl)-2-methylpropane; it was purified by vacuum distillation (68% yield, based on triol). Physical properties determined were: f. p. +9.2°; b. p. 108° (6 mm.); $n^{20}\text{D}$ 1.5593; d^{20}_4 2.0917.

Anal. Calcd. for $C_5H_9Br_3$: Br, 77.67: Found: Br, 77.5.

Production and Identification of Hydrocarbons

FROM 1,1,1-TRIS-(BROMOMETHYL)-PROPANE.—In a flask, suitably equipped and surrounded by an oil-bath, were placed 1062 g. (18 moles) of acetamide (Merck C.P.), 636 g. (6 moles) of sodium carbonate, 27.0 g. (0.18 mole) of sodium iodide, and 392 g. (6 gram atoms) of powdered zinc. The mixture was heated to 110°, and stirring was started as soon as the contents of the flask had softened sufficiently. Crude red tribromide (1431 g., corresponding to 3.17 moles of pure tribromide) was added in small chunks through a side flask. As the hydrocarbon formed, it distilled from the reaction mixture through a 1 × 25 cm. Vigreux column into a series of two traps surrounded by a Dry Ice–acetone-bath. The yield was 244 g. or 93%, based on pure tribromide and the empirical formula C_6H_{10}; no significant difference in yield was noted when pure tribromide was used. The crude product was dried by passage through a column of silica gel and was fractionated at about 40-plate efficiency.

Ethylidenecyclobutane (Cut IV, Fig. 1).—The details of the ozonolysis of this substance are found elsewhere.[13] Acetaldehyde was identified through its 2,4-dinitrophenylhydrazone, m. p. 156–162° after five recrystallizations.

An authentic sample of this derivative also melted at 156–162°, and the mixed melting point was identical; a mixed melting point with the corresponding derivative of formaldehyde showed a 20° depression. A second ozonolysis product boiling at 100° was identified as cyclobutanone (b. p. 99°) and gave a 2,4-dinitrophenylhydrazone which melted (after two recrystallizations) at 140–142°; this derivative was not further purified, since it already melted higher than the literature value, which has since been shown to be erroneous (see under **Isopropylidenecyclobutane**). Physical properties: b. p. 80.26° (760 mm.), f. p. −105.37°; d^{20}_4 0.7678; $n^{20}_{\rm D}$ 1.4370; dt/dp 0.0505°/mm.

Anal. Calcd. for C_8H_{10}: C, 87.22; H, 12.27. Found: C, 87.25; H, 12.61.

Ethylcyclobutane.—This compound was produced by hydrogenation of ethylidenecyclobutane (1.0 mole) over Raney nickel (5 g.) at temperatures up to 90° on a Burgess–Parr low pressure hydrogenator (pressures up to 50 p. s. i.); the theoretical amount of hydrogen was absorbed. The hydrogenated material was distilled at about 25-plate efficiency to give ethylcyclobutane exclusively; physical properties determined on a center cut were (the values in brackets are those of Wibaut[14]): b. p. 70.64° (760 mm.) (70.7); f. p. −142.85°.[21] (−143.2); d^{20}_4 0.7280 (0.7279); $n^{20}_{\rm D}$ 1.4020 (1.4021).

Vinylcyclobutane–Ethylcyclobutane (Cut III, Fig. 1).—Part of Cut III (335 g.) was hydrogenated to saturation over 15 g. of Raney nickel suspended in 20 cc. of ethylcyclohexane; an Aminco high pressure hydrogenation outfit was used, and the temperature was not allowed to exceed 100° (pressure, *ca.* 1000 p. s. i.). Fractionation of this material at about 40-plate efficiency produced (except for a very small amout of "heads") only ethylcyclobutane; physical properties of a center cut were: b. p. 70.64° (760 mm.); f. p. −143.16°; d^{20}_4 0.7278, $n^{20}_{\rm D}$ 1.4021. This material was mixed with about $^1/_3$ its weight of authentic ethylcyclobutane (f. p., −143.11°) and the mixed freezing point determined as −143.17° (no depression).

A portion of Cut III (20 g.) was subjected to oxidation by chromic anhydride in glacial acetic acid, according to the procedure of Chavanne and Becker.[22] About 30% (6.9 g.) of the hydrocarbon material remained unoxidized. Isolated by steam distillation, washed with 5% sodium bicarbonate and water, and dried over a chip of metallic sodium, this product (b. p. 71.8° (760 mm.), $n^{20}_{\rm D}$ 1.4058) exhibited a slight residual unsaturation to bromine. Therefore, the material (7 cc.) was treated exhaustively with permanganate, distilled, and dried over a chip of sodium ($n^{20}_{\rm D}$ 1.4021, the same as ethylcyclobutane). This sample (5 cc.) was mixed with 40 cc. of authentic ethylcyclobutane (f. p. −143.16°); the freezing point of the mixture was −143.17° (no depression). Distillation of the ether extract of the acidified (sulfuric acid) reaction residue produced acetic acid, largely; however, about 7 cc. of material thought to be cyclobutanecarboxylic acid was isolated: b. p. 190–192° (uncor.); $n^{20}_{\rm D}$ 1.4405; $n^{25}_{\rm D}$ 1.4394 (cyclobutanecarboxylic acid b. p. 195°; $n^{25}_{\rm D}$ 1.4403).[23]

Another oxidation of Cut III (90 g.) was carried out according to the procedure of Whitmore, *et al.*[24] Distillation of the lighter-than-water layer (50 g.) at about 10-plate efficiency gave 36.1 g. of ethylcyclobutane, 3.9 g. of intermediates, and 7.4 g. of cyclobutanecarboxylic acid which was then esterified in the usual manner.

Anal. Calcd. for ethyl ester ($C_7H_{12}O_2$): C, 65.7; H, 9.5. Found: C, 67.0; H, 10.4. (The material analyzed was distilled directly from the esterification mixture and was insufficient for further purification, hence the noticeable discrepancy between the C–H analysis and theory).

TABLE II

		Cyclobutanecarboxylic acid	
	This material	Perkin[25]	Other sources
B. p.	190–192 (749 mm.)	191 (720 mm.)	189–191[26]
$n^{25}_{\rm D}$	1.4411	....	1.4403[23]
B. p. of Et ester	152–154 (749 mm.)	151 (720 mm.)	159–162[27]
$n^{20}_{\rm D}$ of Et ester	1.425	....	......

2-Ethyl-1-butene (Cut II, Fig. 1).—Cut II was redistilled at about 35-plate efficiency; physical properties determined on a center fraction were (values in parentheses are those listed by Rossini, *et al.*[28]): b. p. 64.69° (760 mm.) (64.95); f. p. −132.02° (−131.92); d^{20}_4 0.6899 (0.6894); $n^{20}_{\rm D}$ 1.3969 (1.3969).

This material was mixed with an equal volume of authentic 2-ethyl-1-butene (f. p., −132.11°), and the mixed freezing point determined as −132.04° (no depression).

1-Methyl-1-ethylcyclopropane (Cut I, Fig. 1).—This material was treated exhaustively with permanganate, steam distilled, and refractionated at about 35-plate efficiency. Physical properties were determined on a center cut: b. p. 56.79° (760 mm.), f. p. −130.23°, $n^{20}_{\rm D}$ 1.3888, d^{20}_4 0.7015.

Cut I was then hydrogenated at high temperature (250°) and pressure (2600 p. s. i.). Neohexane was the exclusive product; its physical properties were (values in brackets from Footnote 28 for comparison): b. p. 49.65° (760 mm.) (49.74); $n^{20}_{\rm D}$ 1.3688 (1.3688); d^{20}_4 0.6491 (0.6491).

1,1,1-tris-(Bromomethyl)-propane also reacted with zinc in ethanol by the Gustavson[5a] procedure. The reaction mixture was distilled (1-plate) at atmospheric pressure, and the distillate (clear homogeneous liquid) boiling up to 90° was collected. Dilution of the distillate with about four times its volume of water caused it to separate into two layers. The organic layer (40% yield, based on tribromide and the empirical formula ($C_8H_{16}O$) was treated with sodium in liquid ammonia to remove any residual halide and was fractionated at about 35-plate efficiency. This material was probably ethyl 1-ethylcyclopropylcarbinyl ether (a new compound). Physical properties determined on a center cut were: b. p. 135° (760 mm.) d^{20}_4 0.8352; $n^{20}_{\rm D}$ 1.4209. Mol. refraction: Calcd. for ethyl 1-ethylcyclopropylcarbinyl ether: 39.28; observed: 38.92. *Anal.* Calcd. for $C_8H_{16}O$: C, 74.95; H, 12.58. Found: C, 74.94; H, 12.66.

The infrared absorption spectrogram of this compound appeared to substantiate both the ether linkage (evidenced by a band at about 9 μ) and the cyclopropane ring.[29] The material peroxidized extensively on standing.

FROM 1,1,1-TRIS-(BROMOMETHYL)-2-METHYLPROPANE.—This tribromide was treated with zinc in molten acetamide in the same manner as was 1,1,1-tris-(bromomethyl)-propane, the only difference being that a slightly higher reaction temperature (135–140°) was maintained; the yield of crude hydrocarbon material was 97% of theory, based on tribromide and the empirical formula C_7H_{12}. The crude hydrocarbon mixture was dried over metallic sodium and fractionated at about 40-plate efficiency (Fig. 4).

Isopropylidenecyclobutane.—A part of the 107° cut (Fig. 4) was ozonized and the ozonide decomposed by low pressure hydrogenation according to the procedure of Henne and Perilstein.[30] Acetone was identified by the

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[21] This corresponds to a purity of 99.6 mole % as calculated from cryoscopic data.

[22] Chavanne and Becker, *Bull. soc. chim. Belg.*, **36**, 594 (1927).

[23] Heilbron, "Dictionary of Organic Compounds," Oxford University Press, New York, N. Y., 1943.

[24] Whitmore, Homeyer and Trent, U. S. Patent 2,004,066 (1935).

[25] Perkin, *J. Chem. Soc.*, **51**, 12 (1887).

[26] Perkin, *ibid.*, **61**, 40 (1892).

[27] Freund and Gudeman, *Ber.*, **21**, 2696 (1888).

[28] Rossini, *et al.*, "Selected Values of Properties of Hydrocarbons," U. S. Government Printing Office, 1947.

[29] A study of the infrared absorption spectra of a considerable number of cyclopropane and cyclobutane hydrocarbons has been carried out in this Laboratory and a paper on this subject is in preparation.

[30] Henne and Perilstein, THIS JOURNAL, **65**, 2183 (1943).

melting points of its 2,4-dinitrophenylhydrazone (125.7–125.8°) and semicarbazone (187.0–187.3°); mixed melting point determinations with authentic samples of these derivatives showed no depression. Cyclobutanone ($n^{16}\text{D}$ 1.4221, literature[23] $n^{16}\text{D}$ 1.4220) was identified through its semicarbazone (m. p. 202.6–203.0°, lit. 204°); the 2,4-dinitrophenylhydrazone of this material melted 146.3–146.7°; the literature gives a value of 132.3° for this derivative and must be considered in error.

Physical properties were determined on a center cut from the 40-plate refractionation of the 107° material: b. p. 107.26° (760 mm.); f. p. −58.33°, d^{20}_4 0.7823, $n^{20}\text{D}$ 1.4459.

Isopropylcyclobutane.—Hydrogenation of isopropylidenecyclobutane over Raney nickel at 50–60 p. s. i. and 80–100° gave isopropylcyclobutane exclusively; the hydrogenation proceeded less readily than in the case of ethylidenecyclobutane. Physical properties were determined on a center cut from a 40-plate fractionation of the hydrogenated material (values in brackets are those of Kasansky[15]): b. p. 92.70° (760 mm.) (90.5–91.5 (750)); f. p. −106.43°; d^{20}_4 0.7376 (0.7464 at 14.5°); $n^{20}\text{D}$ 1.4080 (1.4096 at 19°).

Anal. Calcd. for C_7H_{14}: C, 85.62; H, 14.38. Found: C, 85.44; H, 14.46.

Purification and Identification of Forerun.—The material boiling at 79.5–98.1° (Fig. 4) was refractionated at about 40-plate efficiency; no further separation was effected. All fractions were recombined and hydrogenated to saturation in the same way as was isopropylidenecyclobutane. The hydrogenated material was fractionated at about 40-plate efficiency.

The 82° cut (1-methyl-1-isopropylcyclopropane) made up about 15% of the distillate and had the following physical properties: b. p. 82.1° (760 mm.), d^{20}_4 0.722$_7$, $n^{20}\text{D}$ 1.399$_8$; there was insufficient material for a freezing point determination. This material was hydrogenated under the same conditions as was 1-methyl-1-ethylcyclopropane.

The 88.8–92.1° cut had the following physical properties: d^{20}_4 0.7213; $n^{20}\text{D}$ 1.4013–1.4087.

FROM 1,1,1-TRIS-(BROMOMETHYL)-ETHANE.—The reaction of this tribromide with zinc in molten acetamide was carried out in exactly the same manner as in the case of 1,1,1-tris-(bromomethyl)-propane. The major portion of the tribromide used was purified only to the extent of filtering out the solid red impurity; further purification seemed unnecessary, since a batch of crude, assayed by fractionation, was found to be about 97% pure. In three runs the yields of hydrocarbon material obtained ranged from 45–65%. The crude hydrocarbon mixture (214 g.) was dried and distilled at about 40-plate effiiciency (Fig. 6).

Methylcyclobutane.—Hydrogenation of the later fractions (66 g., b. p. 38.6–43.0°, $n^{20}\text{D}$ 1.4014–1.4203) from the redistillation of the 37–43° cut was carried out over Raney nickel at 50 p. s. i. and 55°.

2-Methyl-1-butene.—The 31° cut (Fig. 6) was refluxed over metallic sodium and redistilled at about 40-plate efficiency. Physical properties determined on a center fraction were (the values in parentheses are those listed by Rossini, *et al.*[28]): b. p. 30.9° (760 mm.) (31.10); f. p. −138.06° (−137.58); d^{20}_4 0.6508 (0.6504); $n^{20}\text{D}$ 1.3778 (1.3778).

1,1-Dimethylcyclopropane.—The best fraction from the 20° cut (Fig. 6) (b. p. 20.67° (760 mm.); $n^{20}\text{D}$ 1.3662) was essentially saturated; 3-methyl-1-butene (b. p. 20.06° (760 mm.) $n^{15}\text{D}$ 1.3675)[28] is the only other hydrocarbon having physical properties in this range, and it is unsaturated. Shortridge, *et al.*,[7] give the following properties for 1,1-dimethylcyclopropane: b. p. 20.63° (760 mm.); $n^{20}\text{D}$ 1.3668.

High Boiling By-products.—Steam distillation of the reaction residues produced a lighter than water layer; distillation at 25-plate efficiency separated the material into two fractions boiling at about120 and 174° in the ratio of 2:1.

1-Methylcyclopropylcarbinol.—Physical properties of the 120° cut were: b. p. 120–121° (760 mm.); f. p. (approx.) −15°, d^{20}_4 0.9033, $n^{20}\text{D}$ 1.4333. Mol. ref.: Calcd. for 1-methylcyclopropylcarbinol, 25.3; obs., 24.8.

This substance reacted slowly with metallic sodium; its 3,5-dinitrobenzoate melted sharply at 133.3–133.4° after five crystallizations from a water–ethanol mixture.

Anal. Calcd. for $C_5H_{10}O$: C, 69.7; H, 11.7. Found: C, 69.4; H, 11.7.

Di-(1-methylcyclopropylmethyl) Ether.—The 174° material was refluxed two days over metallic sodium and redistilled at about 5-plate efficiency. Its physical properties were: b. p. 174° (760 mm.), d^{20}_4 0.8892, $n^{20}\text{D}$ 1.4501. Mol. ref.: Calcd. for di-(1-methylcyclopropylmethyl) ether, 47.0; obs., 46.6.

Anal. Calcd. for $C_{10}H_{18}O$: C, 78.0; H, 11.7. Found: C, 78.05; H, 11.76.

Infrared absorption spectrograms of the two compounds above seem to substantiate the identities tentatively assigned to them.

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Summary

Three neopentyl-type tribromides have been prepared for the first time, and their reactions with zinc in molten acetamide have been carefully studied. The hydrocarbon mixtures obtained were separated by distillation insofar as possible and the components were identified, four of them being new compounds. This reduction has been shown to constitute a general and practical method for synthesizing monoalkylidene and monalkyl cyclobutanes.

Reaction mechanisms, based on well recognized theories, have been proposed to account for all of the products identified.

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