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

The Synthesis and Properties of 1,1,2-Trimethylcyclopropane[1]

BY ROBERT G. KELSO,[2] KENNETH W. GREENLEE, JOHN M. DERFER AND CECIL E. BOORD

The reaction between 2,4-dibromo-2-methylpentane and zinc in aqueous propanol at 0° was carried out on the enlarged laboratory scale. This permitted a rather thorough study of the reaction products. 1,1,2-Trimethylcyclopropane was found to comprise 68% of the hydrocarbon mixture obtained in 67% yield. 2-Methylpentane, 2-methyl-1-pentene and 2-methyl-2-pentene were identified as definite by-products, while 4-methyl-2-pentene was apparently present in minor amount. Other syntheses of 1,1,2-trimethylcyclopropane were investigated. Reaction mechanisms are proposed. The isolation of a substantial quantity of relatively pure 1,1,2-trimethylcyclopropane permitted accurate determination of its common physical properties and a study of its stability under certain conditions.

Several syntheses of 1,1,2-trimethylcyclopropane have been reported in the literature; a rather complete and critical summary of these has been published.[3] The hydrocarbon has been studied most recently by Lankelma and his coworkers,[3] who developed a modification of the Gustavson[4] synthesis (reaction of a 1,3-dibromide with zinc in a protonic solvent). The modified procedure was found general and gave higher yields and purities than previously reported for cyclopropanes from ring closure reactions involving secondary and/or tertiary bromine atoms. They found that by running such reactions in *n*-propanol at ice temperature (rather than at the reflux temperature of ethanol, as was customary), dehydrohalogenation of highly branched dibromides was kept to a minimum and cyclopropane formation was greatly encouraged. In their preparation of 1,1,2-trimethylcyclopropane, limited quantities of materials were involved, and, hence, a thorough study of the reaction and reaction products was not possible. Likewise, no cryoscopic studies were made.

In the present work, 1,1,2-trimethylcyclopropane was first prepared by the same general method used by Lankelma, *et al.*, but the synthesis was effected on the semi-pilot plant scale, higher efficiency distillation was employed, precision boiling point data were obtained, cryoscopic determinations of purity were made, and a thorough analysis of the reaction and reaction products was carried out; as a result, logical reaction mechanisms can now be proposed. Such are the benefits of an expanded scale of operations, not generally feasible in academic work.

The reaction of 2,4-dibromo-2-methylpentane with zinc dust in aqueous *n*-propanol at ice temperature gave a 67% (average) yield of hydrocarbon material.[5] This product (8.4 liters or 2.2 gallons) was first distilled at about 20-plate efficiency,[6] which separated it into semi-pure 1,1,2-trimethylcyclopropane (initial 64% of the distillate, b.p. 52.4° and $n^{20}\text{D}$ 1.3860) and higher boiling by-products (Fig. 1). The 36% latter portion showed two boiling plateaus, the first for a product with a low refractive index, indicating paraffinic material, and the second with a high index, indicating olefins of types[7] III, IV and/or V.

After treatment with sodium in liquid ammonia to destroy halogen containing impurities, the semi-pure cyclopropane fraction (5.4 liters) was re-

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[1] This paper was abstracted in part from a thesis submitted in 1949 by Robert G. Kelso to the Graduate School of The Ohio State University in partial fulfillment of the requirements for the degree of Doctor of Philosophy. The investigation was carried out under the auspices of the American Petroleum Institute Research Project 45 in coöperation with The Ohio State University Research Foundation. This work was presented before the Organic Division of the A. C. S. at its 113th and 117th Meetings.

[2] Carbide and Carbon Chemicals Division, Union Carbide and Carbon Corporation, South Charleston, W. Va.

[3] J. D. Bartleson, R. E. Burk and H. P. Lankelma, THIS JOURNAL, **68**, 2513 (1946).

[4] G. Gustavson, *J. prakt. Chem.*, (2) **26**, 367 (1882).

[5] This large scale preparation was carried out as a part of the work of the American Petroleum Institute Research Project 45 for the purpose of determining the combustion characteristics of 1,1,2-trimethylcyclopropane in the internal combustion engine and providing material from which "standard samples" could be prepared by the American Petroleum Institute Research Project 6, then at the National Bureau of Standards.

[6] This and subsequent column ratings represent estimates of efficiency under actual operating conditions.

[7] C. E. Boord, chapter in "The Science of Petroleum," Vol. II, Oxford Univ. Press, New York, N. Y., 1938, p. 1349 ff.

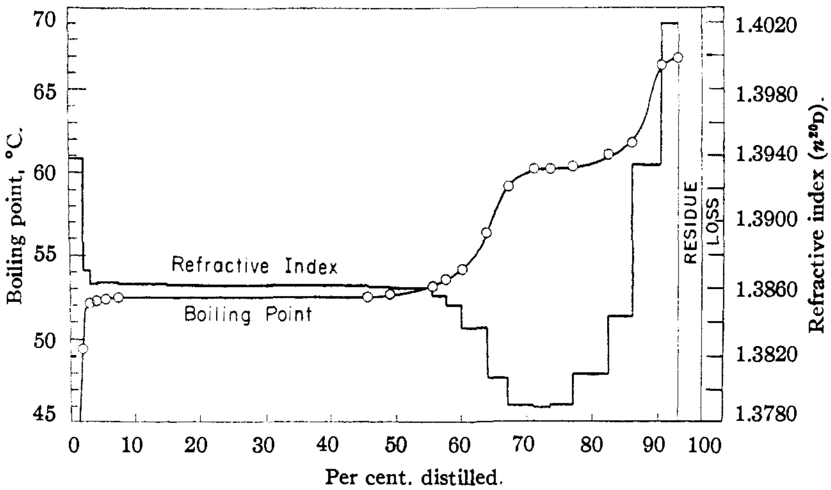

Fig. 1.—Preliminary distillation (20-plate efficiency) of 8.4 liters of crude 1,1,2-trimethylcyclopropane.

distilled at about 125-plate efficiency and fractions amounting to 77% of the charge had a narrow physical property range; this composite was determined cryoscopically to be 99.17 ± 0.15 mole per cent. pure.[8] The physical properties determined on this material are compared with those of Lankelma, *et al.*,[3] in Table I.

The higher boiling material (3.0 liters) from the 20-plate distillation of the crude product was also redistilled at 125-plate efficiency (Fig. 2); five boiling temperature plateaus were indicated. The first plateau showed the presence of about 4% of residual cyclopropane. The second, boiling in the range 58–60° and comprising about 8% of the charge, lay in the boiling point—refractive index region of 4-methyl-1-pentene and 4-methyl-2-pentene. Plateaus 3, 4 and 5 by their boiling points and refractive indices were identified as 2-methylpentane, 2-methyl-1-pentene and 2-methyl-2-pentene in the approximate ratios of 2:1:1.

In summary, 1,1,2-trimethylcyclopropane was found to comprise 68% of the crude hydrocarbon obtained (67% average yield) from 2,4-dibromo-2,2-methylpentane. 2-Methylpentane, 2-methyl-1-pentene and 2-methyl-2-pentene were definite by-products, comprising 14, 8 and 4%, respectively. 4-Methyl-2-pentene was apparently present in a smaller amount (about 2%); a residue of 3-4% was undoubtedly a mixture of condensation dimers. Only 2-methylpentane and 2-methyl-1-pentene were identified as by-products by Lankelma, *et al.*[3]

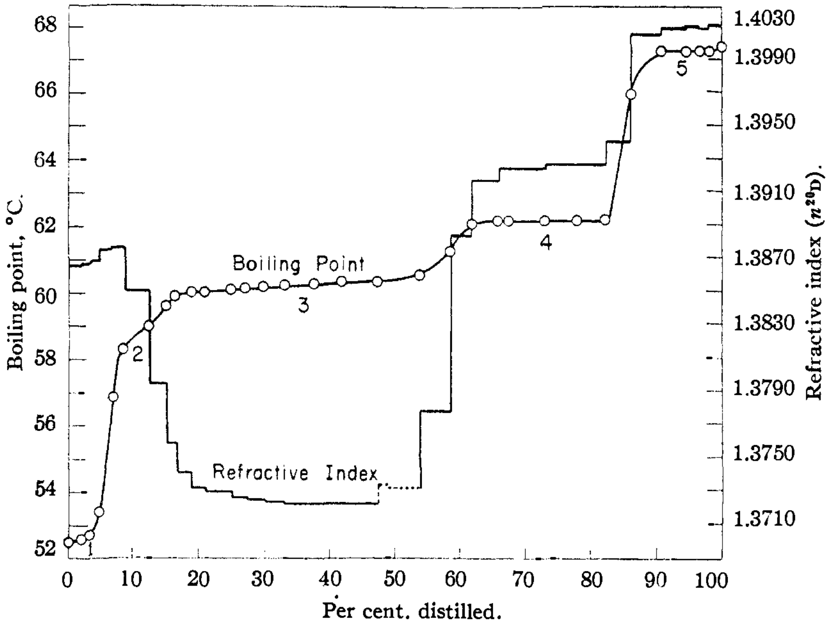

Fig. 2.—Redistillation (125-plate efficiency) of higher boiling material from preliminary distillation of crude 1,1,2-trimethylcyclopropane.

TABLE I

1,1,2-TRIMETHYLCYCLOPROPANE

	This work[a]	Lankelma, *et al.*[3]
F.p., °C.	−138.27	....
M.p., °C.	−138.30	....
Δ*t*/mole % impurity	0.23	....
Purity (mole %)	99.17	....
B.p., °C. (760 mm.)	52.55	52.3 to 53.5[b]
d*t*/d*p*, °C. (mm.)	0.039	....
d^{20}_4	0.6947	0.6853
n^{20}_D	1.3864	1.3850
d(n_D)/d*t*	0.00054	....

[a] The infrared absorption spectrogram of this material has already been published (J. M. Derfer, E. E. Pickett and C. E. Boord, THIS JOURNAL, 71, 2482 (1949)). [b] Corrected from 735 mm. by present authors.

Similar results were obtained whether the dibromide was prepared by the reaction of 2-methyl-2,4-pentanediol with phosphorus tribromide or from a mixture of 2-methyl- and 4-methyl-1,3-pentadiene with anhydrous hydrogen bromide.

Other Syntheses

The original dibromide, 2,4-dibromo-2-methylpentane, was also caused to react with zinc by various modifications of the usual low temperature procedure. There was no significant change in the reaction products when this dibromide was treated with zinc dust in (1) formamide at 0°, (2) 75% ethanol at 0°, and (3) 75% ethanol at 0° in the presence of sodium iodide and sodium carbonate. In the reaction in formamide, additional evidence for the character of the high-boiling by-products was obtained. After distillation of the easily

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(8) This value was determined by the American Petroleum Institute Research Project 6, at the National Bureau of Standards.

TABLE II

PHYSICAL PROPERTIES OF 1,1,2-TRIMETHYLCYCLOPROPANE AND ITS ISOMERIZATION PRODUCTS

	Experimental				Literature[a]	
Plateau	B.p., °C. (760 mm.)	n^{25}_D	Relative amount	Hydrocarbon	B.p., °C. (760 mm.)	n^{25}_D
1	52.6	1.3834	30	1,1,2-Trimethylcyclopropane	52.55[b]	1.3834[b]
2	55.6	1.3874	2.8	2,3-Dimethyl-1-butene	55.64	1.3874
3	61.0	1.3916	1.4	2-Methyl-1-pentene	60.64	1.3884
4	64.5–65.5	1.3987–1.3995	1.0	2-Methyl-2-pentene	67.25	1.3973
5[d]	73.3[c]	1.4070	1.6	2,3-Dimethyl-2-butene	73.21	1.4094

[a] "Selected Values of Properties of Hydrocarbons," Rossini, *et al.*, Circular C461 of the National Bureau of Standards, U. S. Government Printing Office, 1947. [b] Present work. [c] This boiling point taken in an ebulliometer. [d] Mixed melting point determination with authentic material showed no depression.

volatilized products from the reaction mixture, a small liquid layer remained atop the formamide. On distillation, this material boiled from 188–192° and had a refractive index 1.467–1.470; it was highly unsaturated to bromine in carbon tetrachloride. Hydrogenation gave a product boiling from 187 to 196° and having a refractive index n^{20}_D 1.435 to 1.453. No definite compound was isolated or identified, but the physical properties observed for the original and hydrogenated material lay in the range of known C_{12}-olefins and diolefins and paraffins, respectively. This would be the sort of products expected to originate from a Wurtz-type coupling of allylic bromides resulting from dehydrohalogenation of the dibromide (see Fig. 3) and would account for the fact that previous workers failed to account for 15 to 20% of the dibromide used in such cyclizations.

When the reaction was carried out in 90% methanol at Dry Ice temperature, no hydrocarbon was obtained by steam distillation and fractionation of the reaction mixture, but there was obtained a small amount of organic material (b.p. 130 to 170°, n^{20}_D 1.4495 to 1.4500) which was probably a mixture of monobromides formed by partial reduction. It appears that a more active metal than pure zinc is needed for successful reaction at this low temperature.

In order to verify the structure of the 1,1,2-trimethylcyclopropane prepared from 2,4-dibromo-2-methylpentane, the hydrocarbon was prepared from two other bromides, 1,3-dibromo-2,3-dimethylbutane (A) and 1,3-dibromo-2,2-dimethylbutane (B).

Reaction of (A) with zinc by the low temperature procedure gave an 85% yield of hydrocarbon material. A single distillation of this product at about 20-plate efficiency showed that virtually nothing except 1,1,2-trimethylcyclopropane was present. The purity of a center fraction was determined cryoscopically as 96.9 ± 0.1 mole % and indicated that the crude product was probably about 95% pure, as would be expected in the cyclization of a primary-tertiary dibromide by this procedure.

1,1,2-Trimethylcyclopropane was prepared from (B) in quantity sufficient for identification, but significant yield data were not obtained.

Reaction Mechanisms

With the delineation of the products of the Gustavson reaction as applied to 2,4-dibromo-2-methylpentane under low temperature conditions, it becomes possible to propose an adequate mechanism for the reaction. Figure 3 depicts such a series of integrated reactions consistent with generally accepted theories. The mechanism is thought to be of general application, although not all of the reactions indicated may be operative in an individual case.

2,4-Dibromo-2-methylpentane (I) reacts with metallic zinc to form two organozinc bromides (II and III). 1,1,2-Trimethylcyclopropane is formed by the elimination of zinc bromide intramolecularly from either (or both of) II and III.

II and III in the presence of a polar solvent (HQ) also may undergo alcoholysis to produce the alkyl bromides IV or V, respectively. These bromides may in turn form two new organozinc bromides (VI and VII), both of which upon alcoholysis will yield 2-methylpentane, the principal by-product.

It is well known that dibromoalkanes are prone to undergo dehydrohalogenation upon standing, more rapidly at higher temperatures. This action is accelerated by metals or metallic salts. In the dibromide (I) the bromine attached to the tertiary carbon atom is probably the more readily (though not exclusively) eliminated and Saytzeff's rule predicts that the hydrogen of the methylene group will be the one normally expelled. According to these principles, 4-bromo-2-methyl-2-pentene, and 5-bromo-5-methyl-2-pentene, both allylic-type bromides would be produced and would exist as the equilibrium mixture (XV). Both of these highly reactive dibromides can then form an organozinc bromide (XVI), which on alcoholysis will yield olefins (XVIII and XVII). Reactions of this type have been investigated by Young and his co-workers.[9,10] Saytzeff's rule, however, is not always followed. If one of the hydrogens of one of the three methyl groups is eliminated in the dehydrohalogenation, two non-allylic alkenyl bromides (X and XI) may form. These also can form organozinc bromides (XII and XX) which upon alcoholysis can give olefins (XIII and XIV).

The two allylic alkenyl bromides (XV) may condense with any of the several possible organozinc bromides to produce an alkylate or a condensation dimer. The 3 to 4% of high boiling residue could be accounted for in this way.

Isomerization and Hydrogenolysis

As a part of the coöperative effort of the American

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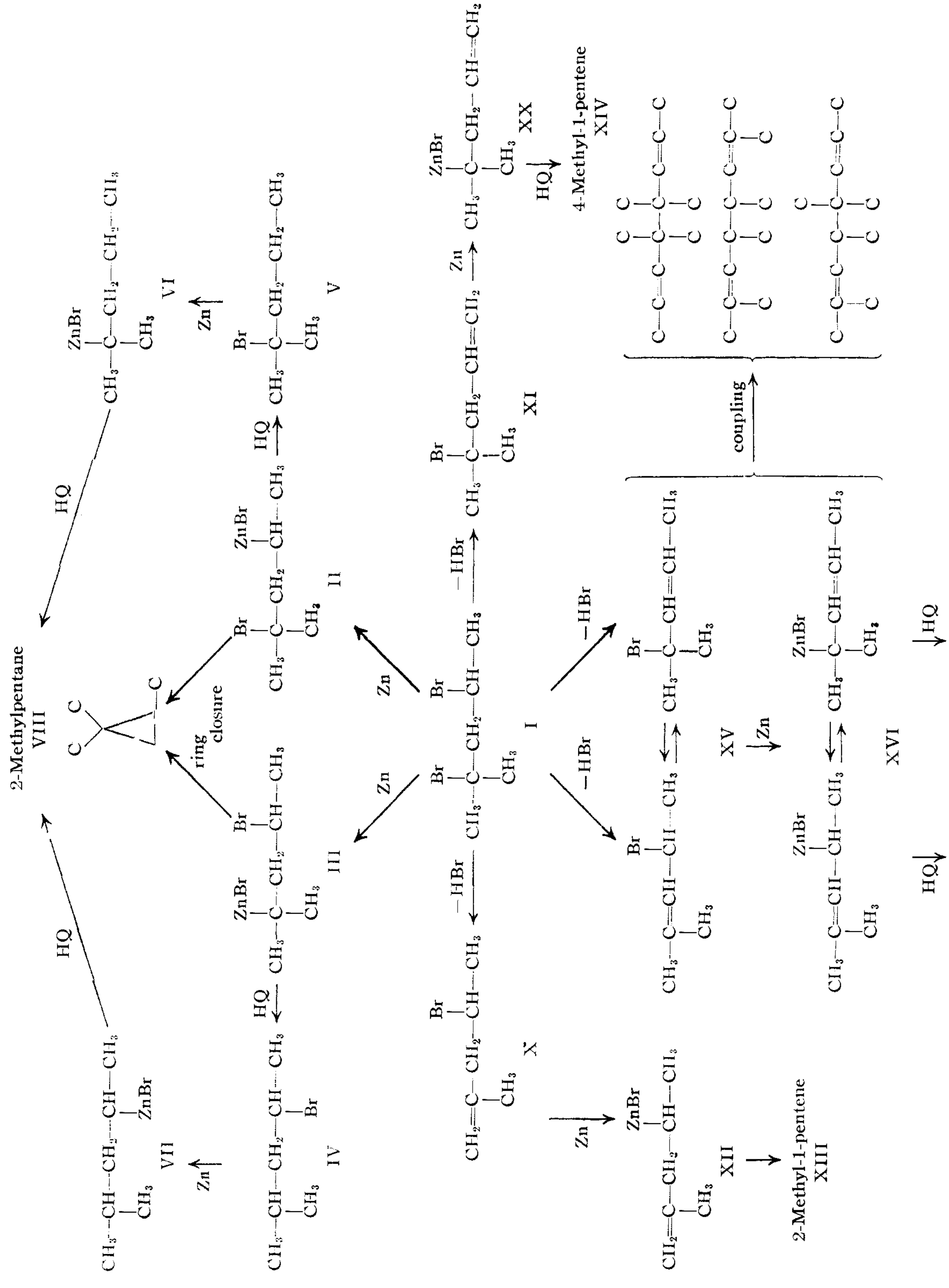
[9] W. G. Young and S. Winstein, THIS JOURNAL, **58**, 441 (1936).

[10] W. G. Young, N. Kaufman, A. Loshokoff and D. Pressman, *ibid.*, **60**, 900 (1938).



XVIII, 2-methyl-2-pentene XVII, 4-methyl-2-pentene

Fig. 3.—Proposed reaction mechanisms.

Petroleum Institute research projects, 3.68 liters of 1,1,2-trimethylcyclopropane (99.17 ± 0.14 mole % pure) was distilled on a metal helix packed column at 135-plate efficiency by API Research Project 6 under the supervision of Dr. F. D. Rossini at the National Bureau of Standards. The boiling point and refractive index curves (Fig. 4) both exhibited a very flat continuous plateau to a point where a little more than 80% of the product had distilled. Beyond this point, both the boiling point and the refractive index began to rise, the boiling point curve showing five plateaus, counting the residue as number five. Table II lists the data read from the curves in comparison with the properties of the hexenes most likely to be formed by isomerization.

The above isomerization can be understood on the basis of the following mechanism by which any

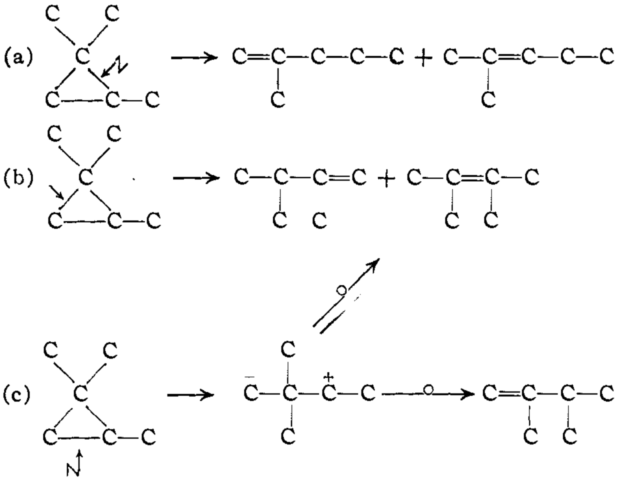
TABLE III

CATALYTIC ISOMERIZATION OF 1,1,2-TRIMETHYLCYCLOPROPANE

Catalyst	5 min.	2 hr.	7 hr.	1 day	3 days	7 days	14 days
	Refractive index (n^{20}D) after various time intervals						
SiO_2-gel[a]	1.3871	1.3923	1.3986	1.4060	1.4093	1.4098	1.4100
SiO_2-gel[b]	1.3863	1.3867	1.3873	1.3890	1.3929	1.3965	1.3993
Al_2O_3[a]	1.3863			No change			1.3863
Al_2O_3[b]	1.3863			No change			1.3863
$FeCl_3$	1.3885	1.3964	1.3995	1.4018	1.4038	1.4075	1.4037
$AlCl_3$	1.3912	1.3988	1.4047	1.4138	1.4183	1.4230	1.4470
Na_2SO_4	1.3863			No change			1.3863

[a] Neutral. [b] Acidic.

one of the C–C bonds of the cyclopropane ring may be ruptured.



No complete analysis can be made of the relative importance of these several modes of ring splitting, because of the overlapping between the products of (b) and (c). It is noteworthy, however, that the products of (b) and (c) predominate over those of (a) by a factor of two, possibly indicating steric hindrance to attack on the bond between the two substituted ring carbon atoms.

Since two of the products noted here, 2,3-dimethyl-1-butene and 2,3-dimethyl-2-butene, were entirely absent in the original rectification of this 1,1,2-trimethylcyclopropane (Figs. 1 and 2), it is clear that the original impurities were not due to isomerization but were actual by-products of the synthesis. It is also evident that the isomerization herein noted was not due to heat alone, *i.e.*, that some catalytic influence was operative before or during the redistillation just described.

Some simple experiments were performed to ascertain what sort of substances might catalyze the isomerization of 1,1,2-trimethylcyclopropane at ordinary temperatures. Small samples of the pure hydrocarbon (n^{20}D 1.3863) were allowed to stand in contact with about one-fourth their weight of several substances, including silica gel (40–200 mesh) and powdered alumina in the neutral condition, as well as these same substances rendered acidic by impregnation with nitric acid and dried at 80°. The effect of the exposure was followed by refractive index measurements over a period of 14 days—the expected olefins all have higher indices than 1,1,2-trimethylcyclopropane. Silica gel, anhydrous ferric chloride and anhydrous aluminum chloride produced large increases in refractive index which must have been due to both isomerization and polymerization; obviously, silica gel percolation should not be used indiscriminately in the purification of alkylcyclopropanes. The nature of the products obtained was not investigated.

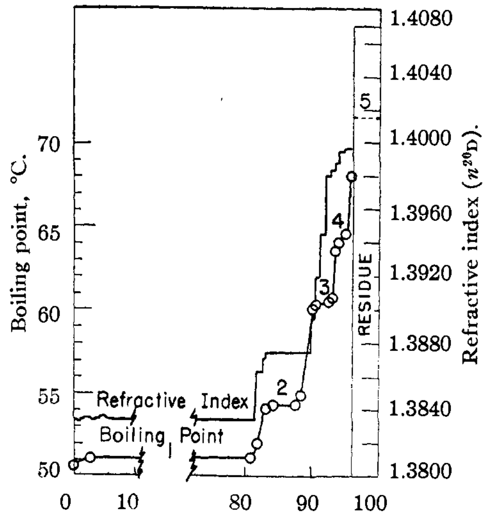


Fig. 4.—Redistillation (135-plate efficiency) of 99.2 mole % pure 1,1,2-trimethylcyclopropane, showing evidence of isomerization.

When 1,1,2-trimethylcyclopropane was subjected to hydrogenation over nickel-on-kieselguhr catalyst and 2800 p.s.i. hydrogen pressure, no absorption was noted until the temperature reached 320°. Then the temperature was lowered to 250°, and absorption continued until 60% of the theoretical amount had been absorbed. On distillation of the hydrogenate, 11% of the cyclopropane was recovered unchanged. The hydrogenolysis products consisted of 2,3-dimethylbutane (73%), 2-methylpentane (18%) and 2,2-dimethylbutane (9%).

Experimental

2,4-Dibromo-2-methylpentane.—This dibromide was prepared from commercial[11] 2-methyl-2,4-pentanediol and phosphorus tribromide by essentially the same procedure described by Lankelma, *et al.*[3] In a typical run, employing 18 moles of diol, there was obtained 4112 g. (93% yield) of crude (washed and dried) dibromide. Distillation of this product under reduced pressure, on a column regularly rated at 10 theoretical plates, gave 3020 g. (69% yield) of good 2,4-dibromo-2-methylpentane (b.p. 65 to 70° (5 mm.), n^{20}D 1.496 to 1.498). This distillation required close attention,

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(11) Purchased from Commercial Solvents Company.

as the dibromide is sensitive to heat and partially decomposes with the evolution of hydrogen bromide, even at temperatures less than 100°. In 14 runs, 53.4 kg. (93.2% average yield from diol) of the crude dibromide was obtained; distillation of 33.1 kg. of this product gave 14.1 kg. of purified dibromide (40% average yield). To eliminate losses inherent in the distillation, the remainder of the crude dibromide was used as such, since it was found to be essentially pure and its use gave rise to no undesirable by-products.

A small amount of this dibromide was prepared by the reaction of "2-methylpentadiene" (Shell Development Co.) with anhydrous hydrogen bromide. In a typical run about 200 ml. of the diene was placed in a 500-ml. 3-neck flask fitted with a stirrer, a gas inlet tube projecting beneath the liquid surface, and a gas outlet tube connected to a bubbler. When the flask and its contents had been cooled to about 0°, commercial hydrogen bromide gas was metered into the flask at such a rate that excess gas emerged occasionally at the exit bubbler. When the theoretical amount had been added, the dibromide was washed rapidly with ice-water to remove excess acid. The yields of the dibromide were practically quantitative and its physical properties checked closely with those of the same product prepared from the diol.

1,3-Dibromo-2,3-dimethylbutane.—Anhydrous hydrogen bromide was added to 2,3-dimethyl-1,3-butadiene by virtually the same procedure as described above. Two dibromides are produced by this reaction. One of the products, 2,3-dibromo-2,3-dimethylbutane (30% yield) is a solid melting at 160 to 164° and boiling at 78° (10 mm.). The other product, 1,3-dibromo-2,3-dimethylbutane (70% yield), is a liquid boiling at 76° (10 mm.). Thus it was easy to separate the desired product by chilling and removing most of the undesired 2,3-dibromide by filtration.

1,3-Dibromo-2,2-dimethylbutane.—The condensation product of acetaldehyde and isobutyraldehyde[12,13] was hydrogenated over Raney nickel at 70° and 1500 p.s.i. of hydrogen to produce 2,2-dimethyl-1,3-butanediol (b.p. 121° (20 mm.), $n^{20}\mathrm{D}$ 1.4408); the yield was 13% based on isobutyraldehyde. The glycol was treated with phosphorus tribromide at 0°, and the mixture was then heated to 50° (to complete reaction with the primary hydroxyl group). The reaction mixture was poured onto crushed ice, and the heavy dibromide layer which separated was used without further purification.

1,1,2-Trimethylcyclopropane.—The 2,4-dibromo-2-methylpentane (5 moles) was caused to react with zinc dust in aqueous *n*-propanol at 0° by the procedure of Lankelma, *et al.*[3] All material boiling up to 70° was removed from the reaction mixture by distillation through a small Vigreux column. In 18 runs, a total of 5610 g. (67% average yield from dibromide) of crude (dried) hydrocarbon was obtained.

The small quantities of 1,3-dibromo-2,3-dimethylbutane and 1,3-dibromo-2,2-dimethylbutane were debrominated by essentially the same procedure.

Hydrogenolysis of 1,1,2-Trimethylcyclopropane.—The catalyst used was $^1/_8$ inch pellets of 20% nickel-on-kieselguhr (Universal Oil Products Co.); 20 g. of it was triturated under the hydrocarbon sample (140 g., 99 mole % pure), and the mixture was placed in a 300 ml. high-pressure, rocking autoclave (American Instrument Company). Reaction with hydrogen was effected as described earlier in this paper. The hydrogenate was fractionated at about 35-plate efficiency, the individual hydrocarbons being identified by comparison of their boiling points and refractive indices, as read from the distillation curves, with reliable literature values.

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(12) V. Grignard and P. Abelman, *Bull. soc. chim.*, [4] **7**, 645 (1910).

(13) E. Swoboda and W. Fossek, *Monatsh.*, **11**, 389 (1890).

COLUMBUS, OHIO

RECEIVED JULY 2, 1951

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

The Synthesis, Purification and Properties of *t*-Amylbenzene[1]

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

Much confusion exists in the literature concerning the physical properties of *t*-amylbenzene. In the present research several methods for preparing the hydrocarbon were investigated, and the reaction of *t*-amyl chloride with benzene, catalyzed with anhydrous ferric chloride, was found best from the standpoint of yield and purity of the product. Aluminum chloride, the commonly used catalyst, gave a product containing a major portion of isomeric amylbenzenes. Accurate physical properties for *t*-amylbenzene and for the derived *t*-amylcyclohexane are given for the first time.

Syntheses (mostly Friedel–Crafts type reactions[2]) and physical properties of *t*-amylbenzene have been reported in the literature on numerous occasions,[3] but the reported properties showed such a wide range of variation that it was impossible to judge which product, if any, was authentic and pure. The present work was undertaken to investigate and evaluate several methods for preparing *t*-amylbenzene and to obtain accurate physical properties for the hydrocarbon.

From previous work done in this Laboratory, it was known that the aluminum chloride catalyzed reaction between *t*-butyl chloride and benzene gave a 65% yield of 99.8 mole per cent. pure *t*-butylbenzene after a single distillation of the reaction product at about 20-plate efficiency. Consequently, the preparation of pure *t*-amylbenzene was first attempted by the aluminum chloride catalyzed reaction between *t*-amyl chloride and benzene. The reaction was carried out on the enlarged laboratory scale, and the reaction product showed itself to be a mixture on distillation at about 30-plate efficiency; the best fractions (3980 g., corresponding to a 52% yield) boiled at 190 to 191°, uncor., and had a refractive index range ($n^{20}\mathrm{D}$) of 1.4930 to 1.4957. This product was then fractionated at better than 100-plate efficiency.[4] The observed boiling points described a curve (initial boiling point, 190.5°) which rose almost steadily throughout the first 74% of the distillation; the following 20% appeared on a plateau (b.p. 192.39 to 192.41°) (760 mm.); the residue, 6% of the charge, had

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(1) This paper was abstracted in part from a thesis submitted in 1949 by Masahiro Inatome to the Graduate School of The Ohio State University in partial fulfillment of the requirements for the degree Master of Science. The rest of the work described was carried out by the American Petroleum Institute Research Project 45 which is administered by The Ohio State University Research Foundation. This work was presented before the Organic Division of the A. C. S. at its 118th Meeting.

(2) For a review on this type of reaction see "Organic Reactions," Vol. III, by C. C. Price, John Wiley and Sons, Inc., N. Y., 1946, Chapter 1.

(3) A few of the key references to these works are: (a) G. F. Hennion and R. A. Kurtz, THIS JOURNAL, **65**, 1001 (1943); (b) V. N. Ipatieff and L. Schmerling, *ibid.*, **60**, 1476 (1938); (c) M. J. O'Conner and F. J. Sowa, *ibid.*, **60**, 125 (1938); (d) R. C. Huston, W. B. Fox and M. N. Binder, *J. Org. Chem.*, **3**, 251 (1938).

(4) This fractionation was performed at the National Bureau of Standards by the American Petroleum Institute Research Project 6, F. D. Rossini, Director.