as that described was heated three-quarters of an hour and then poured into 200 ml. of water. Sodium bicarbonate was added to excess. After reaction ceased, the solution was extracted twice with chloroform and the combined, dried extracts were concentrated under reduced pressure to a residual oil which was dissolved without delay in about 70–100 ml. of water and assayed spectrophotometrically. Under the conditions described, 30% was a typical yield. Addition of a few crystals of hydroquinone is advisable. Solutions without antioxidant deposit anemonin in various degrees of purity quite rapidly. The mixed m. p. of a purified sample with anemonin from natural protanemonin was not depressed.

Variations in the amount of sulfuric acid used affected the rate at which the maximum yield of protoanemonin was reached, but not the yield itself. The conversion of acetylacrylic acid to protoanemonin was also achieved in solvents other than acetic acid, such as dioxane (peroxide-free), and with other catalysts, such as *p*-toluene sulfonic acid.

3-Bromopentene-2-olide-1,4 (VII).—The attempted dehydrobromination of the bromoacetoxy lactone (VI) with anhydrous sodium acetate in dry ether[3] gave a neutral fraction which, even after fifteen hours of reflux, contained a very high bromine content. Fractionation gave material b. p. 60-64° (1 mm.) which crystallized in a Dry Ice–alcohol-bath. Rapid filtration left a colorless solid, m. p. 49–53°, which, after recrystallization from ethyl acetate, reached a constant m. p. 51–53°.

Anal. Calcd. for $C_5H_5O_2Br$: C, 33.91; H, 2.83; Br, 45.24. Found: C, 33.25; H, 3.08; Br, 44.73.

The molecular weight in camphor was 365 in comparison with a calculated 177 for the monomeric lactone. Dimerization may have taken place during the heating in camphor. The volatility (b. p. 80° (5 mm.)), molecular extinction of 12,000 at 220 mμ (ether), and ease of formation directly from β-bromolevulinic acid with acetic anhydride are best explained by the simple structure given. The bromine atom is inert to boiling alcoholic silver nitrate. The lactone is probably formed by isomerization of an intermediate Δ^3-lactone.

Acknowledgment.—The author is indebted to Mr. W. A. Lott for his interest and encouragement. The assistance of Dr. Nettie H. Coy of the Biological Laboratories, E. R. Squibb & Sons, in the spectroscopic work is gratefully acknowledged. Microanalyses were performed by Mr. J. F. Alicino.

Summary

Protoanemonin is formed by the action of acetic anhydride on acetylacrylic acid in the presence of an acid catalyst.

Spectroscopic data on the ring-chain tautomerism of acetylacrylic acid and of penicillic acid are given.

NEW BRUNSWICK, N. J. RECEIVED JULY 15, 1946

[CONTRIBUTION FROM THE MORLEY CHEMICAL LABORATORY OF WESTERN RESERVE UNIVERSITY]

The Preparation and Identification of Alkylcyclopropanes: 1,1,2-Trimethylcyclopropane and 1,2-Dimethyl-3-ethylcyclopropane

BY JOHN D. BARTLESON, ROBERT E. BURK[1] AND HERMAN P. LANKELMA

The Freund reaction[1a,2] for the preparation of cyclopropane by the action of zinc on 1,3-dibromopropane has been employed for the preparation of several of its homologs. Although the reaction appears to be generally applicable to the preparation of hydrocarbons of this type the yields obtained have in certain cases been unsatisfactory due largely to the formation of olefins as the principal product. Shortridge and Boord[3] have pointed out that the type of dibromide employed determines the yield of cyclopropane hydrocarbon obtained. They state that, in general, primary-primary 1,3-dibromides give high yields, primary-secondary dibromides give good yields. Secondary-secondary dibromides give fair yields but all condensations involving a tertiary bromide give products containing an olefin as the principal or sole product.

The present work deals with the preparation by the Freund reaction of 1,1,2-trimethylcyclopropane from 2-methyl-2,4-dibromopentane and 1,2-dimethyl-3-ethylcyclopropane from 3-methyl-2,4-dibromohexane, secondary-tertiary and secondary-secondary dibromides, respectively. Both hydrocarbons were obtained in excellent yield and in a high degree of purity. Infrared absorption spectra were applied as a guide to purity and to the identification of by-product hydrocarbons formed in the ring closure reaction.

Results

1,1,2-Trimethylcyclopropane has been prepared by the Freund reaction from 2-methyl-2,4-dibromopentane by Zelinsky and Zelikow,[4] by Oestling,[5] by Whitmore and Carney[6] and by Shortridge and Boord.[3] It has also been prepared by Kishner[7] by the pyrolysis of 3,5,5-trimethylpyrazoline and by Whitmore and Carney[6] by the action of sodium on 1-chloro-2,2-dimethylbutane. Zelinsky and Zelikow carried out the ring closure reaction at the temperature of a steam-bath. The product was purified by distillation and by prolonged treatment with aqueous potassium permanganate. Oestling did not describe the reaction condition employed in his work. Although the physical constants of his product checked quite closely with those reported by Zelinsky and Zeli-

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[1] Present address: E. I. du Pont de Nemours and Co., Wilmington, Del.

[1a] Freund, *J. prakt. Chem.*, [2] **26**, 367 (1882).

[2] Gustavson, *ibid.*, [2] **36**, 300 (1887).

[3] Shortridge and Boord, "The Preparation of Three 1,1-Dialkylcyclopropanes," Cleveland Meeting of Am. Chem. Soc., April, 1944.

[4] Zelinsky and Zelikow, *Ber.*, **34**, 2656 (1901).

[5] Oestling, *J. Chem. Soc.*, **101**, 457 (1912).

[6] Whitmore and Carney, THIS JOURNAL, **63**, 2633 (1941).

[7] Kishner, *J. Russ. Phys.-Chem. Soc.*, **44**, 165 (1912).

kow he felt that the constitution of his product was doubtful since it decolorized permanganate instantly and exhibited a value for molecular dispersion 20% higher than that expected for a cyclopropane homolog. He also observed that Ipatieff[8] in a parallel reaction had obtained trimethylethylene from 2-methyl-2,4-dibromobutane instead of dimethylcyclopropane. Whitmore and Carney employed a modification of the Freund reaction.[9] The product was purified by distillation in a column with an efficiency of 25 theoretical plates. The purified product decolorized very dilute aqueous potassium permanganate rapidly at first, then only slowly. This was explained by assuming the presence of a small amount of olefin. They showed that a possible isomeric hexene, 4-methyl-1-pentene decolorized the permanganate rapidly and in large volume. They concluded that their product was the desired 1,1,2-trimethylcyclopropane. Shortridge and Boord[3] reported that the hydrocarbon obtained by the action of zinc on 2-methyl-2,4-dibromopentane contained a negligible amount of 1,1,2-trimethylcyclopropane. The work of Shortridge and Boord appears to be a repetition of the work of Zelinsky and Zelikow. Whitmore used a higher temperature, 155°, to effect ring closure of the dibromide. Work in this Laboratory has shown that this dibromide decomposes even at 100° with a copious evolution of hydrogen bromide. At the higher temperature used by Whitmore, olefins from the decomposition of the dibromide must have been formed in considerable amounts.

In the present work 1,1,2-trimethylcyclopropane was prepared from 2-methyl-2,4-dibromopentane by the Freund reaction at low temperature. The yield of crude hydrocarbon was 86%. Infrared absorption spectra indicated a purity of about 72%, distillation gave 64%. This yield is much higher than those previously reported, the most recent, a yield of 58% of hydrocarbon containing a negligible amount of the cyclopropane, being reported by Shortridge and Boord.[3] The improved yield obtained in the present work may be attributed largely to the use of a lower temperature for the ring closure reaction. At the lower temperature the dibromide is much more stable. The loss of hydrogen bromide is consequently greatly reduced. Infrared absorption spectra indicated that the principal impurities in the product were 2-methyl-1-pentene and 2-methylpentane in about equal amounts. The boiling point, refractive index, and density of 1,1,-2-trimethylcyclopropane reported by earlier workers and obtained in the present study are shown in Table I.

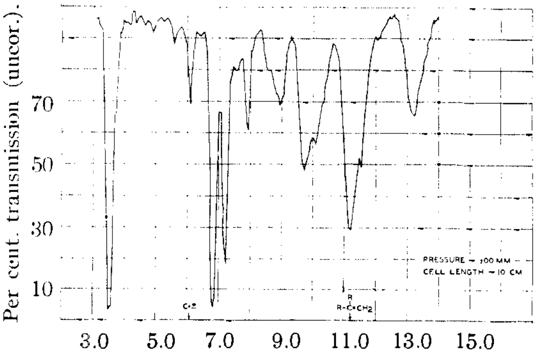

Fig. 1.—Infrared absorption spectrum of crude 1,1,2-trimethylcyclopropane product.

Table I

	B. p., °C.	n^{20}_D	d^{20}_4
Zelinsky and Zelikow[4]	56–57 (750 mm.)	1.3848	0.6822[a]
Kishner[7]	52.8 (756 mm.)	1.3866	.6949
Oestling[5]	59–60	1.3896[b]	.6888[c]
Whitmore and Carney[6]	56.5–57.0 (760 mm.)	1.3880	.6967
	55.5–56.5 (760 mm.)	1.3876	.6941
Present work	51.7–52.7 (735 mm.)	1.3850	.6853

[a] At 19.5°. [b] At 14.5°. [c] At 15.3°.

These values indicate that Zelinsky and Zelikow's product, because of the permanganate washing used in its purification, probably contained a considerable amount of 2-methylpentane while the products of the others contained olefins, presumably largely 2-methylpentene.

Infrared absorption spectra were employed in the present work to study the composition of the crude product and selected fractions obtained in its purification by distillation. The absorption curve of the crude 1,1,2-trimethylcyclopropane is shown in Fig. 1. Two of these bands, at 9.75μ and 11.55μ have been reported as typical of cyclopropane,[10] while the 6.10μ band is always attributed to the C=C bond. Distillation of this product from a vertical surface column under operating conditions which gave an efficiency of 100 theoretical plates gave a plateau fraction, an end fraction and a residue, distillation curve Fig. 2. The infrared absorption curve of the plateau fraction is shown in Fig. 3. It shows a sharp increase in absorption at the 9.75 and the 11.55μ bands and corresponding decreases in the 6.10 and 11.20 μ bands indicating an increased concentration of cyclopropane hydrocarbon and a diminished concentration of olefin in this fraction. Since the cyclopropane product apparently boiled lower than the olefin impurities the plateau fraction was redistilled, using the same column, and a front end fraction was taken. The infrared absorption curve of this fraction is shown in Fig. 5. It shows a further increase in absorption at 9.75 μ, 11.55 μ and several other prominent bands while the olefin bands at 6.10 μ and 11.20 μ have virtually disappeared. Assuming the principal impurities 2-methyl-1-pentene and 2-methylpentane to be present in equal amount (see below), the purity of this fraction calculated from Beer's law is about 95%. The

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(8) Ipatieff, *J. Russ. Phys.-Chem. Soc.*, **30**, 292 (1890).

(9) Hass, McBee, Hinds and Gluesenkamp, *Ind. Eng. Chem.*, **28**, 1178 (1936).

(10a) King, This Journal, **58**, 1580 (1936). (b) Kohlrausch and Koppl, *Z. physik. Chem.*, **26B**, 213 (1934).

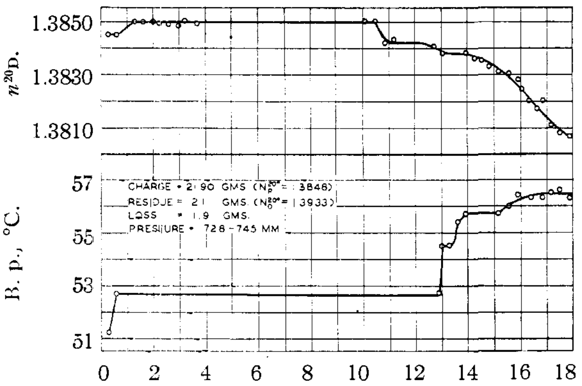


Fig. 2.—Boiling point and refractive index data from fractional distillation of crude 1,1,2-trimethylcyclopropane.

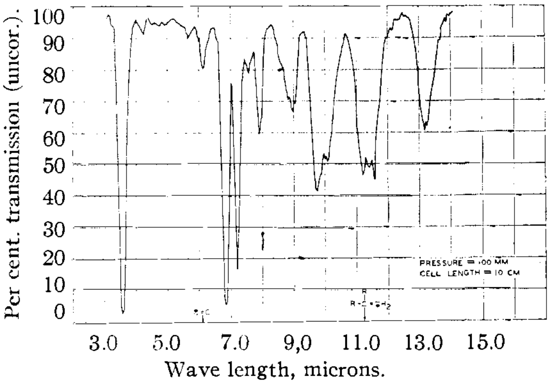


Fig. 3.—Infrared absorption spectrum of plateau fraction from the fractional distillation of crude 1,1,2-trimethylcyclopropane.

following results show the by-product impurities to be 2-methyl-1-pentene and 2-methylpentane in about equal amounts. The distillation curve, Fig. 2, shows that after the plateau region was passed the refractive index of the distillate dropped sharply to a value of 1.3807. Since this value is lower than that of any of the probable hexenes (2-methylpentenes) and is in fact lower than that of any hexene except 3,3-dimethyl-1-butene which boils at 41°, the presence of a hexane is indicated. The composition of this fraction appears to be a mixture of 1,1,2-trimethylcyclopropane, 2-methyl-1-pentene and 2-methylpentane. 4-Methyl-1-pentene might be an impurity because of its relatively low refractive index. However, its presence may be ruled out on the basis of spectral data for it has strong infrared absorption bands at 10.02 μ and 10.94[11] μ both of which were absent in all of the fractions studied. The infrared map of the residue from the distillation, Fig. 4, indicates more clearly the identity of the by-products. This curve is almost identical with that of pure 2-methyl-1-pentene,

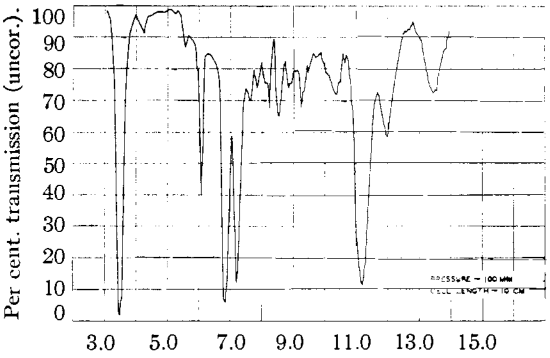
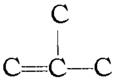


Fig. 4.—Infrared absorption spectrum residue from the fractional distillation of 1,1,2-trimethylcyclopropane.

Fig. 7. Calculation of the amount of 2-methyl-1-pentene in the residue using Beer's law with either the 6.10 μ band of C=C or the 11.20 μ band of  $\overset{\overset{\textstyle C}{|}}{C}{=}C{-}C$ shows 45% of the olefin to be present. These data indicate that the only olefin present is 2-methyl-1-pentene and that the remainder is non-olefinic in character. Since no trace of the 9.75 μ band of cyclopropane is present it may be concluded that the remainder is paraffinic in nature. The principal paraffinic constituent here is thought to be 2-methylpentane. All of the stronger bands of 2-methylpentane[12] were present in the infrared absorption curve of the residue, Fig. 4. The most convincing evidence for the presence of 2-methylpentane is the 8.80–8.50 μ doublet. These are strong bands in the spectra of 2-methylpentane but are absent from the spectra of 2-methyl-1-pentene.

The effect of aqueous potassium permanganate for the removal of olefins was also studied. A sample of crude 1,1,2-trimethylcyclopropane was washed with successive portions of fresh 1% potassium permanganate solution and the per cent. transmission of the principal olefin bands and the cyclopropane bands was determined after each treatment. The results are shown in Table II. These results show that the permanganate removed both the olefin and the cyclopropane hydrocarbons from the mixture and concentrated to some extent the paraffins.

The second cyclopropane homolog, 1,2-dimethyl-3-ethylcyclopropane, was prepared from 3-methyl-2,4-dibromohexane. A yield of 90% was obtained in the ring closure reaction. This is substantially higher than the 68% yield reported by Lespieau and Wakeman[13] for a similar reaction of a secondary-secondary dibromide. The crude product was separated by distillation into two fractions, b. p. 87 and 94°; the lower boiling fraction constituted about $^1/_3$, the higher boiling fraction the remainder. The infrared absorption

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[11] Thompson and Torkington, *Trans. Faraday Soc.*, **41**, 249 (1945).

[12] Lambert and LeCompte, *Ann. Phys.*, **10**, series 2, 518 (1938).

[13] Lespieau and Wakeman, *Bull soc. chim.*, **51**, 384 (1932).

TABLE II

EFFECT OF POTASSIUM PERMANGANATE SOLUTION UPON OLEFIN AND CYCLIC CONTENT OF CRUDE 1,1,2-TRIMETHYLCYCLOPROPANE AS SHOWN BY INFRARED ABSORPTION SPECTRA DATA

Sample	% Transmission					% Olefin based on 6.10 line	% Cyclic based on 9.70 line	% Paraffin by diff.
	6.10	11.20	11.55	9.70	13.20			
Crude 1,1,2-trimethylcyclopropane	69.0	29.2	49.0	48.0	65.6	13	72	15
1st $KMnO_4$ wash	69.7	34.4	48.0			13		
2nd $KMnO_4$ wash	76.1	42.0	47.7			8		
3rd $KMnO_4$ wash	79.5	49.3	48.3	46.1	64.6	7	74	19
Trimethylcyclopropane purified by one distillation	80.5	46.5	44.5	41.5	60.7	5	90	5
Trimethylcyclopropane purified by two distillations	84.5	52.0	42.0	39.8	61.0	3	95	2

spectra of the crude product and of the two fractions were obtained. The crude product had a weak 6.10 μ band indicating little olefin. The two strongest bands in the two fractions were at 7.60 and 9.75 μ both of which were also strong bands in 1,1,2-trimethylcyclopropane. The two fractions appear to be stereosiomers or mixtures of stereoisomers.

The secondary-tertiary and secondary-secondary 1,3-dibromides were prepared in 90% yields by the action of phosphorus tribromide on the diols at low temperature. The low temperature prevents the loss of hydrogen bromide from the reaction mixture. The method may be applied with equally good results to the preparation of secondary and tertiary alkyl bromides such as isopropyl, *t*-butyl and *t*-amyl bromides. Previously reported yields of secondary alkyl bromides are about 70–80% and of tertiary alkyl bromides about 40%.[14]

Experimental

Apparatus.—The routine infrared spectrometer[15] developed by Shell Development Laboratories and manufactured by National Technical Laboratories of South Pasadena, Calif., was used in this work.

2-Methyl-2,4-dibromopentane.—The apparatus consisted of a one-liter three-necked reaction flask fitted with a mechanical stirrer and a rubber tube sealed stirrer shaft, a low temperature thermometer, a calcium chloride tube and a dropping funnel. To the flask was added 177 g. (1.5 moles) of 2-methyl-2,4-pentanediol (b. p. 99–101° (12 mm.)) courtesy of Commercial Solvents Corp. The diol was cooled to −24° and 298 g. (1.1 moles) of phosphorus tribromide was added dropwise with efficient stirring. The temperature was kept below −15°. About four hours were required for the addition of the phosphorus tribromide. The reaction mixture changed gradually from a viscous emulsion to a homogeneous amber liquid. The stirring was stopped and the flask was left in a dry ice-bath and the contents allowed to warm to room temperature over a period of about two days. After standing at room temperature from one to three days two liquid layers separated. The lower layer (d. 1.70) consisted of phosphorus acid. The upper layer weighing 360–380 g. represented an almost quantitative yield of 2-methyl-2,4-dibromopentane. It was washed rapidly with several 200-cc. portions of ice water and dried over anhydrous sodium sulfate. It was purified by distillation under diminished pressure. The product was collected at 61–62° (4 mm.) and weighed 330 g. (90% of the theoretical yield); d^{23}_4 1.551, n^{20}D 1.4980. It had a very small vapor pressure of hydrogen bromide upon standing at room temperature.

1,1,2-Trimethylcyclopropane.—The reaction was carried out in a one-liter, three-necked flask fitted with a reflux condenser, thermometer, dropping funnel and mercury sealed stirrer. To the flask was added 100 cc. of water, 300 cc. of *n*-propyl alcohol and 196 g. (3 g. atoms) of oxygen-free zinc dust[16] prepared from commercial grade zinc dust. The flask was placed in an ice-bath and 244 g. (1 mole) of freshly distilled 2-methyl-2,4-dibromopentane was added dropwise with efficient stirring over a period of about ninety minutes. The ice-bath was then removed and the mixture was stirred at room temperature for about thirty-two hours. After about ten hours an immiscible layer of hydrocarbon had formed. At the end of the reaction the hydrocarbon product was separated by distillation. The product was collected over a temperature range of 49–51° and weighed 78.1 g., a yield of 86%. The distillate contained a small amount, 2 or 3 cc., of propyl alcohol and water. It was washed twice with 100-cc. portions of ice water to remove the alcohol, cooled to freeze the aqueous layer, and the hydrocarbon poured off. The refractive index of the crude product was n^{20}D 1.3847. The crude 1,1,2-trimethylcyclopropane was purified by distillation in a vertical surface column[17] operating under conditions which gave an efficiency of 100 theoretical plates calculated by the method of Calingaert and Beatty.[18] The distillation curve is shown in Fig. 2. The material balance was:

Charge	21.90 g.
Distillate	17.88 g.
Residue	2.10 g.
Loss	1.92 g.

A portion of the crude product (charge), the plateau fraction of the distillate and the residue were examined in the infrared spectrometer, Figs. 1, 3 and 4, respectively. The plateau fraction from this distillation was redistilled in the same column for further purification. The material balance was

Charge	4.7 g.
Fraction 1	0.31 g.
Fraction 2[a]	1.35 g.
Residue	2.80 g.
Loss	0.23 g.

[a] n^{20}D 1.3850; d^{20}_4 0.6853.

The boiling point of fraction 2 was determined by the micro method of Siwoloboff[19]; b. p. 52.1° (736 mm.). The spectral map of this fraction is shown in Fig. 5.

The effect of aqueous potassium permanganate for the removal of olefins was studied by washing a 10-cc. sample of the crude 1,1,2-trimethylcyclopropane at room temperature with three successive 90-cc. portions of 1% potas-

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(14) "Organic Syntheses," Coll. Vol. I (2nd ed.) and Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1941 and 1943.

(15) Brattain and Beeck, *J. Applied Phys.*, **13**, 699 (1942); Brattain, *Oil Gas J.*, **41**, 34 (1943).

(16) Roscoe and Schorlemmer, "A Treatise on Chemistry," Vol. II, The Macmillan Co., New York, N. Y., 1923, p. 760.

(17) Selker, Burk and Lankelma, *Ind. Eng. Chem., Anal. Ed.*, **12**, 352 (1940).

(18) Calingaert and Beatty, *Ind. Eng. Chem.*, **26**, 504 (1934).

(19) Siwoloboff, *Ber.*, **19**, 795 (1886).

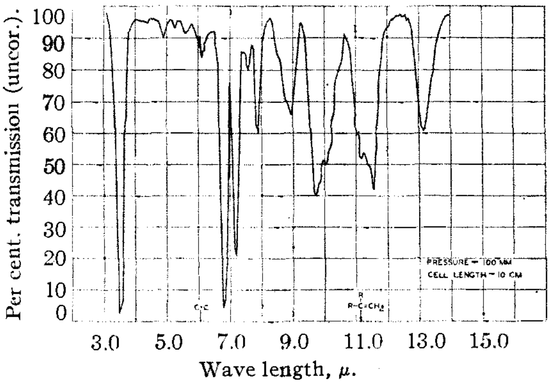

Fig. 5.—Infrared absorption spectrum of distillate from plateau fraction of 1,1,2-trimethylcyclopropane.

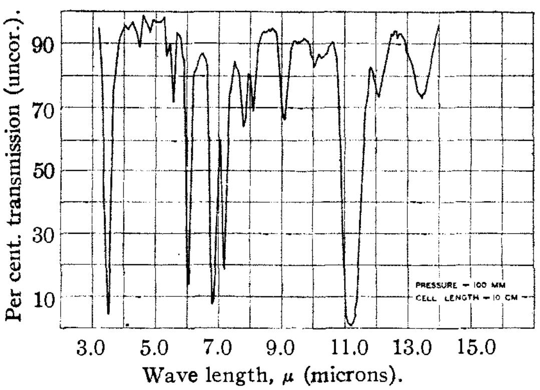

Fig. 7.—Infrared absorption spectrum of purified 2-methyl-1-pentene.

sium permanganate solution and determining the per cent. transmission of the principal olefin and cyclopropane bands. In the first two treatments the permanganate was completely decolorized after thirty minutes and two hours, respectively. In the third treatment the permanganate was not completely decolorized after six hours. The results of infrared absorption studies are shown in Table II.

2-Methyl-1-pentene.—This hydrocarbon was prepared from 2-methyl-3-choro-1-propene and ethylmagnesium bromide by the method of Whitmore[20] and co-workers. It was purified by distillation in a column packed with steel helices followed by redistillation in a column with an efficiency of 25 theoretical plates. The fraction taken for spectral mapping had the physical constants: b. p. 61.2–61.4° (737 mm.); $n^{20}D$ 1.3921; d^{20}_4 0.6817.

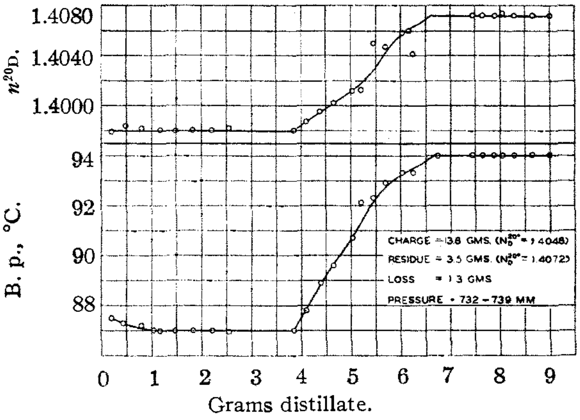

Fig. 6.—Boiling point and refractive data from the fractional distillation of crude 1,2-dimethyl-3-ethylcyclopropane.

3-Methyl-2,4-hexanediol.—This diol was prepared by the reduction of the ketol, 3-methylhexanol-4-one-2. The ketol was prepared by condensing propionaldehyde with methyl ethyl ketone by the method described by Powell.[21] A yield of 64%, b. p. 85° (17 mm.); $n^{20}D$ 1.4400, was obtained. This ketol was hydrogenated in a two-liter Aminco high pressure hydrogenation bomb. A nickel catalyst as recommended by Schmerling[22] and *i*-propyl alcohol as a diluent[23] were employed. The catalyst, nickel oxide precipitated on kieselguhr, courtesy of The Harshaw Chemical Co., was prepared for use by reduction with hydrogen at 450°. A mixture of 83 g. of catalyst 520 g. (4 moles) of 3-methylhexanol-4-one-2 and 173 g. of 99% *i*-propyl alcohol was placed in the bomb and heated to 105° and the bomb pressured to 1500 p. s. i. with hydrogen. Over a period of five hours at 105° and in a pressure range of 1100–1500 p. s. i. a total pressure drop of 750 p. s. i. occurred. The catalyst was filtered off, the *i*-propyl alcohol removed by distillation from a steam-bath and the residue distilled under diminished pressure. A

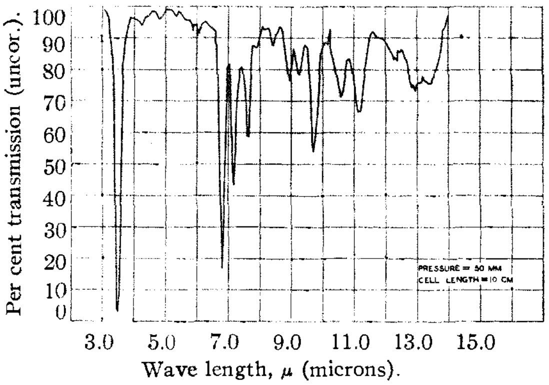

Fig. 8.—Infrared absorption spectrum of low boiling plateau fraction from the fractional distillation of crude 1,2-dimethyl-3-ethylcyclopropane.

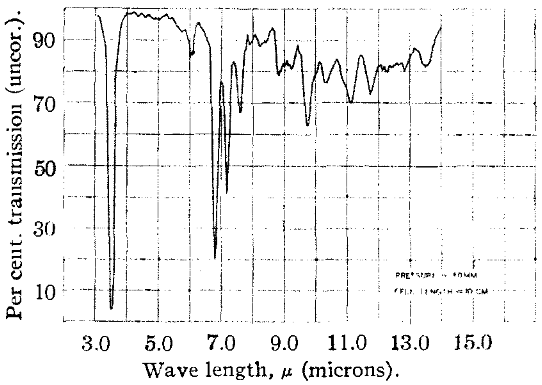

Fig. 9.—Infrared absorption spectrum of high boiling plateau fraction from the fractional distillation of crude 1,2-dimethyl-3-ethylcyclopropane.

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[20] Whitmore, This Journal, **62**, 795 (1940).

[21] Powell, *ibid.*, **46**, 2514 (1924); **53**, 1153 (1933).

[22] Schmerling, *ibid.*, **62**, 2446 (1940).

[23] Sprague and Adkins, *ibid.*, **56**, 2672 (1934).

54% yield of 3-methyl-2,4-hexanediol, b. p. 109° (9 mm.); $n^{20}{}_D$ 1.4450; $d^{20}{}_4$ 0.9588 was obtained. Its identity was shown by analysis for carbon and hydrogen. Calcd. for $C_7H_{16}O_2$: C, 63.54; H, 12.18. Found: C, 63.48; H, 12.17.

3-Methyl-2,4-dibromohexane.—The method of preparation here was the same as that described for 2-methyl-2,4-dibromopentane. A 90% yield of crude product of high purity was obtained. It was purified by distillation under diminished pressure. The purified dibromide had the following physical constants, b. p. 71.5–72.5 (1 mm.); $n^{20}{}_D$ 1.4967; $d^{20}{}_4$ 1.4504. Analysis for bromine gave results in agreement with the formula assigned. Calcd. for $C_7H_{14}Br_2$: Br, 61.97. Found: Br, 62.07.

1,2-Dimethyl-3-ethylcyclopropane.—This hydrocarbon was prepared from the dibromide by the method described for 1,1,2-trimethylcyclopropane. A 90% yield of product, $n^{20}{}_D$ 1.4048, was obtained. Analysis for carbon and hydrogen gave results in agreement with the formula C_7H_{14}. Calcd. for C_7H_{14}: C, 85.62; H, 14.38. Found: C, 85.51; H, 14.32. A spectral map was made of this product. A portion of this product was distilled in the vertical surface column. The distillation is shown in Fig. 6. The infrared absorption spectra of the two plateau fractions were determined, Figs. 8 and 9.

Acknowledgment.—We are indebted to the Chemical Research Laboratory of the Standard Oil Co. of Ohio for the use of the infrared spectrometer and to Dr. Martval J. Hartig of the Standard Oil Co. of Ohio for assistance in the interpretation of infrared data.

Summary

1,1,2-Trimethylcyclopropane was prepared in high yield from 2-methyl-2,4-dibromopentane by the Freund reaction at low temperatures.

In the ring closure reaction to form 1,1,2-trimethylcyclopropane from 2-methyl-2,4-dibromopentane the principal by-products were found to be 2-methyl-1-pentene and 2-methylpentane. These by-product hydrocarbons have the same carbon skeleton as the dibromide from which they were formed.

1,1,2-Trimethylcyclopropane was obtained in a purity of about 95% by fractional distillation in a high efficiency distilling column.

Infrared absorption spectra show that aqueous potassium permanganate was not very selective for removing 2-methyl-1-pentene from 1,1,2-trimethylcyclopropane.

1,2-Dimethyl-3-ethylcyclopropane was prepared in high yield from 3-methyl-2,4-dibromohexane. It was separated into two fractions by distillation.

An improved method is described for the preparation of secondary and tertiary organic bromides from alcohols or diols.

CLEVELAND, OHIO RECEIVED SEPTEMBER 20, 1945

[CONTRIBUTION FROM THE RESEARCH AND DEVELOPMENT LABORATORIES, UNIVERSAL OIL PRODUCTS COMPANY]

Isomerization of Alkanes. IV.[1] Deuterium Exchange in the Isomerization of *n*-Butane[2]

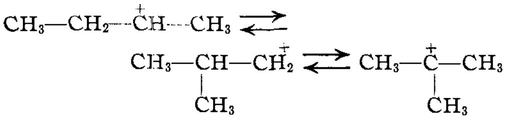
BY HERMAN PINES AND R. C. WACKHER

It was shown[2a] that under controlled conditions, aluminum bromide–hydrogen bromide catalyst does not cause isomerization of *n*-butane unless traces of olefins or their equivalent are present. On the basis of these results, a chain mechanism was suggested.[3] It was postulated that isomerization of *n*-butane proceeds in the presence of a catalyst and traces of olefins or their equivalent by a sequence of reactions as represented by the following equations.

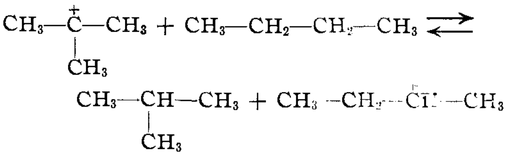
$$R{-}CH{=}CH_2 + HX^{a} \rightleftharpoons [R{-}\overset{+}{C}H{-}CH_3]X^- \quad (1)$$

[a] HX is HBr or $HAlBr_4$.

$$CH_3{-}CH_2{-}CH_2{-}CH_3 + R{-}\overset{+}{C}H{-}CH_3 \rightleftharpoons CH_3{-}CH_2{-}\overset{+}{C}H{-}CH_3 + R{-}CH_2{-}CH_3 \quad (2)$$



$$CH_3{-}CH_2{-}\overset{+}{C}H{-}CH_3 \rightleftharpoons \underset{\displaystyle CH_3}{CH_3{-}\underset{|}{C}H{-}\overset{+}{C}H_2} \rightleftharpoons \underset{\displaystyle CH_3}{CH_3{-}\underset{|}{\overset{+}{C}}{-}CH_3} \quad (3)$$



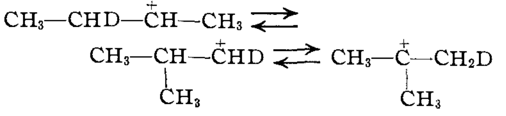
$$CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{\overset{+}{C}}}{-}CH_3 + CH_3{-}CH_2{-}CH_2{-}CH_3 \rightleftharpoons CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{C}H}{-}CH_3 + CH_3{-}CH_2{-}\overset{+}{C}H{-}CH_3 \quad (4)$$

If the isomerization steps as given above are correct, then, by substituting deuterium bromide for hydrogen bromide, one would expect an exchange reaction to occur between the deuterium of the catalyst and hydrogen of the butanes. This can be represented by the equations

$$CH_3{-}CH_2{-}\overset{+}{C}H{-}CH_3 \rightleftharpoons CH_3{-}CH{=}CH{-}CH_3 + H^+ \quad (3a)$$

$$H^+ + X^- \rightleftharpoons HX \quad (3b)$$

$$\begin{array}{l} CH_3{-}CH{=}CH{-}CH_3 + DX \rightleftharpoons CH_3{-}CD{=}CH{-}CH_3 + HX \\ \qquad \updownarrow \\ CH_3{-}CHD{-}CHX{-}CH_3 \rightleftharpoons [CH_3{-}CHD{-}\overset{+}{C}H{-}CH_3]X^- \end{array} \quad (3c)$$



$$CH_3{-}CHD{-}\overset{+}{C}H{-}CH_3 \rightleftharpoons CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{C}H}{-}\overset{+}{C}HD \rightleftharpoons CH_3{-}\underset{\displaystyle CH_3}{\underset{|}{\overset{+}{C}}}{-}CH_2D \quad (3d)$$

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[1] For paper III of this series, see R. C. Wackher and H. Pines, THIS JOURNAL, **68**, 1642 (1946).

[2] Presented before the Organic Division at the American Chemical Society Meeting, Atlantic City, April, 1946.

[2a] H. Pines and R. C. Wackher, THIS JOURNAL, **68**, 595 (1946).

[3] H. S. Bloch, H. Pines and L. Schmerling, *ibid.*, **68**, 153 (1946).