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

The Action of Aluminum Bromide on Paraffin Hydrocarbons. I. *n*-Hexane and *n*-Heptane

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Since the early work of Gustavson[1c] many studies have been made of the action of aluminum halides on paraffin hydrocarbons. The results of these studies may be summarized as follows: (1) the reaction requires a promoter such as a hydrogen halide; (2) reactions of decomposition (cracking), alkylation, and isomerization occur; (3) in the case of certain paraffins the isomerization is a reversible catalytic process[2]; (4) in the ordinary course of the liquid phase reaction two layers form in the reaction mixture; the upper layer consists of paraffin hydrocarbons, the lower layer of addition compounds between the aluminum halide and complex unsaturated hydrocarbons.[3]

Nenitzescu and Dragan[4] studied the reaction of aluminum chloride with *n*-hexane and *n*-heptane promoted with water. *n*-Hexane yielded a hydrocarbon layer boiling 25–76°, which appeared to contain some 2-methyl and some 3-methyl pentanes, and a higher boiling fraction consisting of cyclohexane. Since subsequent work, including the present study, has shown that cycloparaffins are not formed in these reactions it is likely that the *n*-hexane contained cyclohexane or 2-methylcyclopentane.[5] From *n*-heptane there formed propane, isobutane and a liquid layer consisting of pentanes, hexanes, branched chain heptanes and higher hydrocarbons. No other individual hydrocarbons were identified but physical constants indicated methylhexanes and dimethylpentanes.

Ipatieff and Grosse[6] studied the reaction of *n*-hexane and *n*-heptane with aluminum chloride at reflux temperatures with hydrogen chloride as a promoter. *n*-Hexane formed isobutane and a mixture of paraffin hydrocarbons boiling above and below *n*-hexane, of which one component appeared to be 2-methylpentane. Similar results were obtained with *n*-heptane.

Moldavskii[7] isomerized *n*-hexane with 3–8% of aluminum chloride in sealed tubes at 45–95°. Isomeric hexanes formed but the analysis of the mixtures was not given. When *n*-heptane and 1% of aluminum chloride was heated in a sealed tube at 220° under 50 atmospheres of hydrogen, 8% of isomerization was obtained but individual hydrocarbons were not identified.

Schuit, Hoog and Verheus[2] allowed a mixture of *n*-hexane and aluminum chloride to react in an atmosphere of hydrogen at 80° for sixteen hours. The hexane fraction comprised 93% of the products. Analysis by distillation through a column of 22 plates efficiency indicated 35% of *n*-hexane, 52% methylpentanes and 13% dimethylbutanes. The efficiency of the distillation was insufficient to separate the two mixtures.

Calingaert and Beatty[8] studied the action of aluminum chloride on *n*-heptane at reflux temperature in an apparatus which permitted the lower boiling products to escape as fast as formed. They obtained a butane–pentane fraction boiling below 45°, a hexane–heptane fraction at 45–98°, and a higher hydrocarbon fraction boiling above 98°. By repeated distillation of the middle cut a number of branched chain hexanes and heptanes were separated and were identified by physical constants. It is doubtful, however, whether the fractionation was sufficient to yield pure heptanes.

The present investigation was undertaken to study the action of aluminum bromide on *n*-hexane and *n*-heptane using highly purified materials and carefully controlled conditions. Particular care was taken to exclude water and air from the reactions. Efficient fractional distillation equipment was employed to separate the reaction products. Aluminum bromide, rather than aluminum chloride, was selected because its hydrocarbon solubility permits the initial reaction to be homogeneous.

Experimental

Preparation of Materials.—The *n*-hexane was prepared from hexanol. The alcohol was dehydrated to hexenes by passing the vapor over activated alumina at 340–360°. The product was dried, distilled, and a fraction boiling at 62–70° was hydrogenated in the vapor phase at temperatures below 160° using Raney nickel supported on glass wool as the catalyst. Yields of about 75% of hexane based upon hexanol were obtained. The hexane was purified by treatment with chlorosulfonic acid[9] followed by washing, drying, and distillation. The hexane used had the

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(1) (a) Present address: The Texas Company, Beacon, N. Y. (b) Present address: E. I. du Pont de Nemours and Co., Wilmington, Del.

(1c) Gustavson, *J. Russ. Phys.-Chem. Soc.*, **13**, 149 (1880); *Ber.*, **14**, 2619 (1881).

(2) Montgomery, McAteer and Franke, THIS JOURNAL, **59**, 1768 (1937); Schuit, Hoog and Verheus, *Rec. trav. chim.*, **59**, 793 (1940).

(3) A detailed discussion of the published work in this field is given in Thomas, "Anhydrous Aluminum Chloride in Organic Chemistry," Reinhold Publishing Co., New York, N. Y., 1941; Egloff, Hulla and Komarewsky, "Isomerization of Pure Hydrocarbons," Reinhold Publishing Corp., New York, N. Y., 1942; Burk, "Twelfth Report of the Committee on Contact Catalysis," John Wiley and Sons, Inc., New York, N. Y., 1940.

(4) Nenitzescu and Dragan, *Ber.*, **66B**, 1892 (1933).

(5) In the presence of aluminum chloride this would partly isomerize to cyclohexane; Nenitzescu and Cantuniari, *ibid.*, **66B**, 1097 (1933).

(6) Ipatieff and Grosse, *Ind. Eng. Chem.*, **28**, 461 (1936).

(7) Moldavskii, Kobuil'skaya and Livshitz, *J. Gen. Chem.*, U. S. S. R., **5**, 1791 (1935); Egloff, Wilson, Hulla and Van Arsdell, *Chem. Reviews*, **20**, 345 (1937).

(8) Calingaert and Beatty, THIS JOURNAL, **58**, 51 (1936).

(9) Shepard and Henne, *Ind. Eng. Chem.*, **22**, 356 (1930).

following physical constants: b. p. at 760 mm., 68.7°; n^{20}_D 1.3750; d^{20}_4 0.6594.

The *n*-heptane was obtained from the California Chemical Company. It was purified by treatment with chlorosulfonic acid[9] followed by washing with sodium bicarbonate solution, water, and drying with calcium chloride. It was finally treated with "Filtrol," a brand of acid-treated Bentonite clay. It was then fractionally distilled, and a fraction boiling over a range of 0.02° was taken. The physical constants of the heptane used were: b. p. at 760 mm. 98.4°; n^{20}_D 1.3878; d^{20}_4 0.6838.

The aluminum bromide was prepared by passing purified bromine over heated aluminum turnings. The aluminum, obtained from The Aluminum Company of America, was stated to be 99.45% pure, the impurities being iron, silicon, and a trace of copper. The aluminum bromide was purified by distillation from aluminum turnings and twice redistilled under reduced pressure to remove adsorbed hydrogen bromide. The hydrogen bromide promoter was prepared by hydrolyzing phosphorus bromide. It was purified by passing it over red phosphorus to remove bromine and over Drierite and phosphorus pentoxide to remove water.

Reaction Procedure.—The reaction was carried out in a one-liter round-bottom flask fitted with sealed glass or ground glass connections to auxiliary flasks, nitrogen and hydrogen bromide cylinders and a vacuum pump. The procedure in carrying out a reaction was as follows. The entire apparatus was evacuated, flamed, and rinsed dry with oxygen-free nitrogen. The aluminum bromide was distilled into the reaction flask under diminished pressure. The hydrocarbon after drying with phosphorus pentoxide was distilled also into the reaction flask. The aluminum bromide dissolved completely in the hydrocarbon with no sign of reaction. The reaction flask was immersed in an oil-bath heated by a steam coil and several immersion type electric heaters. At low temperatures a thermal regulator was employed to control the temperature; at high temperatures manual control was used. Hydrogen bromide was bubbled slowly through the solution of aluminum bromide in the hydrocarbon. As the reaction proceeded, gas was liberated and a lower liquid layer formed. This lower layer was transferred at frequent intervals into an alkaline hydrolyzing solution by means of a capillary siphon tube. The gaseous products were bled off intermittently as pressure built up in the reaction flask. They were passed through an ice trap, a wash bottle containing a solution of sodium hydroxide and collected in a gas holder over mercury. At the close of the reaction, the upper liquid layer was removed from the reaction flask by vacuum distillation.

Analysis of Products.—The low boiling material was distilled through a Podbielniak column. Two fractionating columns were employed for separating the mixture of hydrocarbons containing five or more carbon atoms. Both columns were jacketed and externally heated. The first (Column A) was packed with a piece of finned aluminum tubing 60 inches long, $^7/_8$ inch in diameter, with 9 fins per inch. It had a holdup of 25 g. of hydrocarbon. The second column (Column B) consisted of a 7-mm. O. D. Pyrex open tube 48 inches long. It had a holdup of 3 g. Both columns were calibrated with mixtures of *n*-heptane and methylcyclohexane to determine their efficiency. Using the formula of Calingaert and Beatty,[10] an efficiency of 90 theoretical plates was obtained for Column A and 80 theoretical plates for Column B. The boiling points of the fractions taken were usually determined in the fractionating column; in some cases, however, micro boiling points were determined. The density and the refractive index of the fractions were determined at 20 ± 0.05°. An Abbe refractometer was used for the refractive index and small specific gravity bulbs for the density determinations. The values for the boiling point, index of refraction, and densities of paraffin hydrocarbons selected from the literature for reference purposes are given in Table IV.

Results and Discussion

Four experiments were carried out with hexane, Nos. I, II, V and VI. In experiment I, a mixture of aluminum bromide in *n*-hexane in a molar ratio of approximately 1:17 was allowed to stand at room temperature for sixteen hours. No promoter was used. At the end of this time only a very small amount of lower liquid layer had formed. The upper layer on distillation gave four fractions boiling below *n*-hexane. These fractions represented only 0.35% of the starting material. The remainder was recovered as *n*-hexane with a loss of only 1%. This failure to react in the absence of a promoter is in agreement with results previously reported in the literature.[6] Experiment II was carried out at temperatures between −30 and 15° for a period of nine and three-quarters hours, using approximately the same ratio of aluminum bromide and hexane as in Experiment I. Hydrogen bromide was used as a promoter. The conversion under these conditions was less than 2%. Distillation of the products indicated isomerization without cracking, but the small amount of conversion prevented the positive identification of any of the products. In view of the small amount of conversion here, Experiments V and VI were carried out at somewhat higher temperatures. Experiment V was carried out at room temperature for four hours, Experiment VI at −20 to 0° for 143 hours. The results of these experiments are summarized in Tables I and II.

TABLE I

MATERIAL BALANCE

		Expt. V	Expt. VI
Before reaction	C_6H_{14}, g.	310.0	271.8
	$AlBr_3$, g.	50.5	74.4
	Total	360.5	346.2
After reaction	In Dry Ice trap, g.	24.7	....
	Upper layer, g.	262.9[a]	264.5[a]
	Lower layer, g.	66.4	62.1
	Samples removed, g.	...	5.8
	Loss, g.	6.0	13.8
	Total	360.5	346.2

[a] After washing and drying.

The upper layers were washed, dried, and distilled. The distillation curves of the products

TABLE II

COMPOSITION OF UPPER LAYER

	Expt. V[a]	Expt. VI
Isobutane	13.0%	4.3%
Isopentane	9.1	5.2
2,2-Dimethylbutane	1.8	9.6
2,3-Dimethylbutane	1.8	3.8
2-Methylpentane	5.5	10.4
3-Methylpentane	0.7	0.6
n-Hexane	57.2	64.5
Heptanes	7.8	
Higher hydrocarbons	3.6	1.1

[a] Includes the liquid in the Dry Ice trap.

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

Table III

Summary of Aluminum Bromide Treatment of *n*-Heptane

Experiment	VII	VIII	IX	X	XI	XII	XIII	XIV	XV	XVI
Time, hours	27.5	3	14.5	19	3.7	2.5	2.5	4	7.3	7.5
Temperature, °C.	25-40	98-100	98-100	25-42	32	25	22	23	25	24
Mole % heptane	92.2	94.7	94.8	93.82	95.21	88.53	88.89	90.09	83.67	85.94
Mole % $AlBr_3$	7.8	5.3	5.2	5.16	4.15	8.48	8.43	5.23	12.5	8.59
Mole % HBr	0	Trace	0	1.02	0.64	2.99	2.68	4.68	3.85	5.47
% Conversion to lower layer	0	0.07	0.01	1.8	0.09	4.2	4.3	4.3	6.0	4.6
% Conversion, total	0	0.89	0.14	20	13.7	40.3	44.4	52.9	91.7	65

boiling higher than isobutane are shown in Figs. 1 and 2. The composition of the upper layers, based upon the distillation, is shown in Table II.

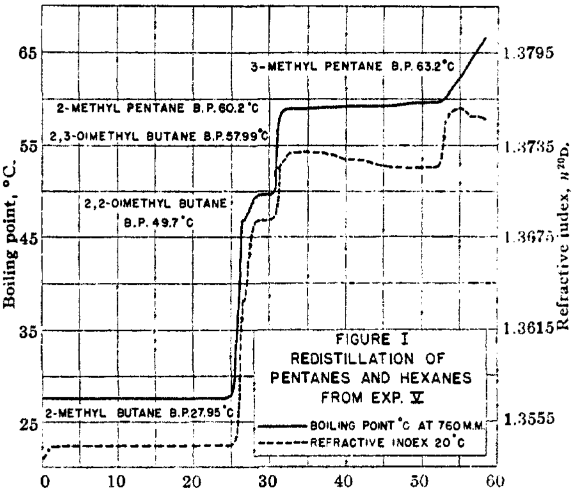

Fig. 1.—Redistillation of pentanes and hexanes from experiment V: ————, boiling point, °C. at 760 mm.; – – – – –, refractive index, 20°.

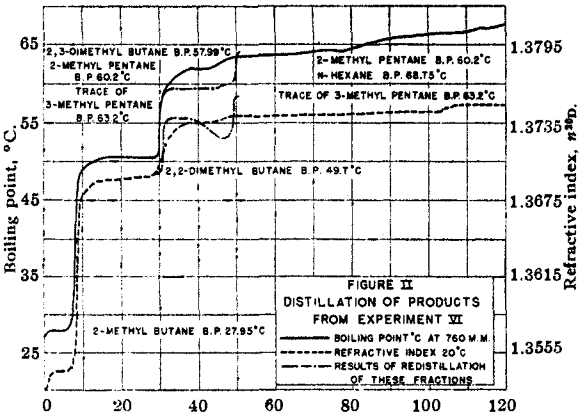

Fig. 2.—Distillation of products from experiment VI: ————, boiling point, °C. at 760 mm.; – – – – – –, refractive index, 20°; — – — – —, results of redistillation of these fractions.

The results of ten experiments with *n*-heptane are summarized in Table III.

Analysis of the off gases and the material boiling below room temperature showed the presence of traces of methane, ethane, and propane. Traces of hydrogen were found in the non-condensable gas from some of the last experiments. Isobutane was present in large quantity. Neither *n*-butane nor neopentane was detected in the distillation of the product.

The hydrocarbon fractions boiling above room temperature from experiments XII to XVI were distilled separately through Column A. The material was then combined into four fractions as follows: (1) 27 to 50°, (2) 50 to 79°, (3) 79 to 98°, (4) all residues. Fractions 1 and 2 were distilled through Column A and fractions 3 and 4 were distilled through Column B. The weight of the individual fractions collected from Column A was approximately 0.6 g. and from Column B, 0.3 g. The distillation of fraction 4 was continued until the residue contained no hydrocarbons boiling below *n*-heptane. These data are summarized in the distillation curves of Fig. 3. Figure 3 shows that the isomers present in the

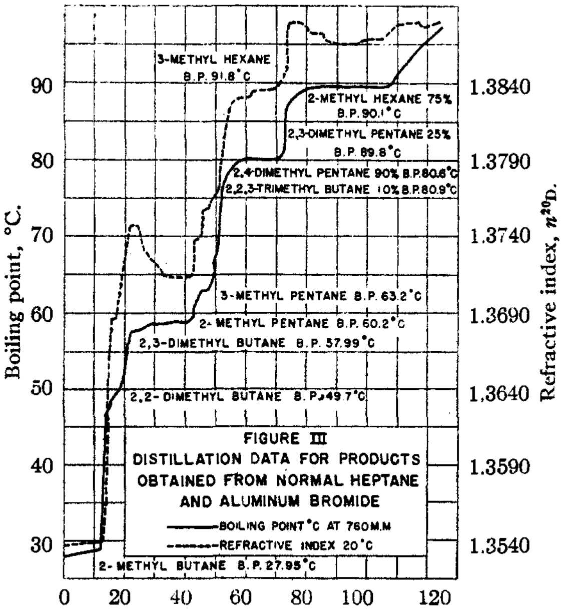

Fig. 3.—Distillation data for products obtained from normal heptane and aluminum bromide: ————, boiling point, °C. at 760 mm.; – – – – –, refractive index, 20°.

TABLE IV

PHYSICAL CONSTANTS OF SELECTED FRACTIONS FROM FINAL DISTILLATION

	Literature			Selected fractions		
Hydrocarbon	Boiling point, °C.	n^{20}_D	d^{20}_4	Boiling point, °C.	n^{20}_D	d^{20}_4
Pentanes						
2-Methylbutane	27.95	1.35396	0.6198	28.0–28.8	1.3540	0.6200
n-Pentane	36.0	1.35769	.6263		Absent	
Hexanes				47.4–49.2	1.3687	.6491
2,2-Dimethylbutane	49.7	1.3686	.6490	49.2–49.4	1.3687	.6482
				49.4–50.0	1.3690	.6484
2,3-Dimethylbutane	58.0	1.3749	.6615	57.6–58.1	1.3748	.6599
2-Methylpentane	60.2	1.37156	.6532	58.7	1.3712	.6525
3-Methylpentane	63.2	1.3764	.6642	63.0	1.3758	.6621
n-Hexane	68.75	1.3750	.6595	Absent		
Heptanes						
2,2-Dimethylpentane	79.3	1.3823	.6737	Absent		
2,4-Dimethylpentane	80.6	1.3823	.6745	79.8	1.3830	0.6761
2,2,3-Trimethylbutane	80.88	1.3894	.6900	79.9	1.3834	.6752
3,3-Dimethylpentane	86.1	1.3911	.6934	Absent		
				89.9	1.3867	.6829
				90.0	1.3865	.6831
2,3-Dimethylpentane	89.8	1.3921	.6951	90.0	1.3867	.6820
2-Methylhexane	90.1	1.3850	.6787	90.0	1.3868	.6823
				90.0	1.3868	.6829
3-Methylhexane	91.8	1.3887	.6870	91.5–92.8	1.3875	.6852
3-Ethylpentane	93.47	1.3937	.6984	Absent		
n-Heptane	98.4	1.38777	.68378	97.26	1.3878	.6837

largest quantity are 2-methyl compounds. 2-Methylhexane is present in the largest amount and 2,4-dimethylpentane, 2-methylpentane, 2-methylbutane, 2,3-dimethylpentane, 2,3-dimethylbutane, 3-methylpentane, 2,2-dimethylbutane, and 3-methylhexane are present in descending order of abundance. The composition of the mixtures boiling at 80° and 89.5° was calculated from the density and refractive index data assuming a straight line function of these constants and composition. It is believed that 3-ethylpentane, boiling at 93.3°, is absent. The refractive index, 1.3937, of this isomer is considerably higher than that of the isomers boiling near it and none of the fractions in this region of the curve had a refractive index above 1.3880.

The refractive index of all fractions from the final distillation was determined and the density of the selected combined fractions was determined also. Table IV gives a summary of these results along with the boiling point, refractive index and density of the pure hydrocarbons taken from the literature.

The original literature cited in tables published by Egloff,[11] Doss,[12] and Ward and Kurtz[13] was reviewed and the data tabulated and compared. The values selected here are those which appear to be the most reliable.

Chemical tests and physical properties showed that olefin, aromatic, and cycloparaffin hydrocarbons were absent in the portion of the upper layer boiling below *n*-heptane. Traces only of unsaturated material were found in the fractions boiling above heptane. No aromatic or cycloparaffin hydrocarbons were found in the high boiling fractions of the upper layer. The oil obtained by hydrolysis from the lower layer complex proved to be highly unsaturated as shown by its action with bromine and with alkaline potassium permanganate. No attempt was made to separate the constituents by distillation.

In the absence of a promoter, aluminum bromide had no appreciable effect upon *n*-hexane or *n*-heptane at temperatures up to the boiling point of the hydrocarbons. Using hydrogen bromide as a promoter reaction occurred readily at temperatures as low as −20°. This is in agreement with results obtained previously with aluminum chloride[6,14] and with the suggestion made by others that the catalyst is $HAlX_4$.[15]

At room temperature and higher, cracking was the principal reaction. *n*-Hexane gave isobutane, isopentane and four isomeric hexanes. The principal products were paraffins with methyl groups in the 2-position. In addition, heptanes and higher paraffins were obtained but individuals were not identified. Normal paraffins, cycloparaffins and aromatic hydrocarbons were absent. Neopentane was not obtained.

The conversion of the heptane to lower boiling

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[11] Egloff, Universal Oil Products, Bulletin No. 219.

[12] Doss, "Physical Constants of the Principal Hydrocarbons," The Texas Company, New York, N. Y., 1939.

[13] Ward and Kurtz, *Ind. Eng. Chem., Anal. Ed.*, **30**, 559 (1938).

[14] Schneider, Abs. Sci. Tech. Publ. Mass. Inst. Tech., Jan., 1928.

[15] Since this paper was submitted for publication work has appeared [Heldman, THIS JOURNAL, **66**, 1786 (1944); Powell and Reid, New York Meeting, Am. Chem. Soc., September, **1944**] in support of this theory.

products was approximately three to four times as great as the conversion to products boiling higher, showing that under the conditions used here, the principal reactions were cracking and isomerization.

Of the two butanes, only isobutane was found in the products of the reaction. This agrees with the results reported by Ipatieff and Grosse,[6] and Nenitzescu and Dragan.[4]

The formation of *n*-hexane and 3,3-dimethylpentane from the action of aluminum chloride on *n*-heptane has been reported.[8] Neither of these hydrocarbons was obtained in our work. Cycloparaffins have been reported among the products from the action of aluminum chloride on *n*-heptane.[4] In agreement with the results reported by Calingaert and Beatty,[3] we found no cycloparaffins in the reaction products.

The hydrocarbons present in the largest amount in the reaction products had a methyl group in the 2-position of the carbon chain. The prominence of this type of product must be accounted for in any mechanism which is proposed for this reaction.

Summary

The action of aluminum bromide on *n*-hexane at temperatures from −30° to room temperature and *n*-heptane at temperatures from 22 to 98° has been studied.

In the absence of a promoter no appreciable reaction occurs. In the presence of hydrogen bromide as a promoter, cracking, isomerization and alkylation occur with the formation chiefly of branched chain paraffins with methyl groups in the 2-position.

The results indicate that cracking is preceded by isomerization. Under mild conditions isomerization is the chief reaction.

No normal paraffin, cycloparaffin or aromatic hydrocarbons were found.

CLEVELAND, OHIO RECEIVED MAY 29, 1944

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

The Action of Aluminum Bromide on Paraffin Hydrocarbons. II. Branched Chain Hexanes

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Introductory

Previous work done in this Laboratory has shown that the principal products from the action of aluminum bromide on *n*-hexane at low temperatures are isomeric hexanes.[1] The present investigation is an extension of this study to the four branched chain hexanes.

Experimental

Preparation of Materials.—The preparation and purification of the aluminum bromide was carried out as described by Winter and Cramer.[2] The hydrogen bromide was prepared by the action of bromine on tetrahydronaphthalene.[3] The isomeric hexanes were obtained as follows:

The 2-methylpentane and 3-methylpentane were prepared from the alcohols 4-methylpentanol-2 and 2-ethylbutanol-1, respectively. The alcohol was dehydrated to olefin by passing the vapor over activated alumina at 360–400°. The olefin was fractionated in Column C, described in the experimental section, and then hydrogenated to the hexane at 140–160° over Raney nickel catalyst. The product was treated with sulfuric acid, washed with water, and dried with "Drierite."

2,3-Dimethylbutane was prepared from pinacol. Pinacol was dehydrated to diene over activated alumina at 450–470°. The diene was hydrogenated over Raney nickel and the product purified as described above.

2,2-Dimethylbutane was obtained through the courtesy of the Phillips Petroleum Company. It was found to contain no unsaturated hydrocarbons and was distilled in Column C without further treatment. Oberfell[4] and Frey report that it contains about 2% cyclopentane. This could not be removed by distillation since the difference in boiling point between the two hydrocarbons is only 0.4°. This small amount of cyclopentane would not, however, interfere with the identification of the reaction products since 2,2-dimethylbutane is the only paraffin hydrocarbon which boils within 9° of it. A middle fraction of this material was taken.

The physical constants of the four hexanes used in this work were as follows

	Boiling point, °C. (760 mm.)	n^{20}_D	d^{20}_4
2-Methylpentane	60.2	1.3716	0.6528
3-Methylpentane	63.0–63.3	1.3765	.6639
2,3-Dimethylbutane	58.0–58.1	1.3749	.6613
2,2-Dimethylbutane	49.6–49.7	1.3697	.6508

Experimental Procedure.—The apparatus and the technique used for carrying out the reactions were essentially those described by Grummitt.[1] Dry hydrogen bromide was used as a promoter in all the reactions.

Analysis of Products.—Products of the reaction were separated by distillation. For this purpose, two fractionating columns were used. Column A was a concentric tube vertical surface type with three annular spaces.[5] The efficiency of this column using the formula of Calingaert and Beatty was 104 theoretical plates at total reflux.[6] Low boiling material, isobutane, and isopentane were collected in a Dry Ice trap at the head of this column and redistilled through a Podbielniak type column. Column C was 40 inches long and about 15 mm. in internal diameter. It was packed with 3-mm. stainless steel

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[1] Grummitt, Sensel, Smith, Burk and Lankelma, THIS JOURNAL, 67, 910 (1945).

[2] Winter and Cramer, *Ind. Eng. Chem.*, **32**, 856 (1940).

[3] Duncan, "Inorganic Syntheses," McGraw-Hill Book Co., New York, N. Y., 1939, Vol. I, page 151.

[4] Oberfell and Frey, *Refiner Nat. Gasoline Mfg.*, **18**, 486 (1939).

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

[6] Calingaert and Beatty, *Ind. Eng. Chem.*, **26**, 504 (1934).