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OPTICAL ROTATION AND ATOMIC DIMENSION FOR THE FOUR OPTICALLY ACTIVE 1-HALOGENO-2-METHYLBUTANES [1]

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ABSTRACT

The pure optically active 1-fluoro-, chloro-, bromo-, and iodo-derivatives of 2-methylbutane have been prepared and values of their optical rotation, specific gravity, refractive index, and boiling point at various pressures, determined. A classification of their active forms is made, and on this basis the numerical relation of the differences of molecular rotations of these compounds (Cl-F), (Br-Cl), and (I-Br) is 41:18.1:21.6, which is in substantial agreement with the numerical relation for the differences of the respective atomic radii of the neutral halogen atoms (41:16:21).

CONTENTS

I. INTRODUCTION

It has been established in the writer's previous investigations on this subject [2] that certain halogen derivatives may be divided into two classes. Those compounds which compose the first class have the halogen directly attached to an asymmetric carbon atom and differ only in having one halogen replaced by another. For these substances the differences of their *specific rotations* (Cl–F), (Br–Cl), and (I–Br) have the numerical relation 41:17:21, which agrees with the numerical relation 41:16:21, for the differences in atomic radii of the respective neutral halogen atoms. Those in the other class have the halogen atom attached indirectly (by a chain of atoms) to the asymmetric

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[1] This article is the tenth contribution to a series on optical rotation and atomic dimension. The ninth article was published in BS J. Research **7**, 573 (1931) RP358.

[2] Fifth article, J. Am. Chem. Soc. **47**, 1285 (1925); ninth article, BS J. Research **7**, 573 (1931) RP358.

carbon atom. For these latter substances the differences of their *molecular rotations* have a numerical relation which likewise agrees with that for the differences in atomic radii of the respective nonionized halogen atoms. All the investigated compounds were carbohydrate derivatives which contain several asymmetric carbon atoms, so it was found desirable to prepare the halogen derivatives of two active amyl alcohols, 2-methylbutanol-1 and methylpropylcarbinol, for testing the above regularities, as these compounds are simple in structure and contain only one asymmetric carbon atom. The present paper reports the results obtained with the halogen derivatives of 2-methylbutanol-1, where the halogens are indirectly attached to the asymmetric carbon.

II. EXPERIMENTAL PART

1. PREPARATION OF PURE COMPOUNDS

(a) *l*-ROTATORY-2-METHYLBUTANOL-1

Since the beginning of the investigation of van't Hoff and Le Bel's postulate, as well as of Guye's hypothesis, derivatives of this alcohol have served for testing these theories. In the early days the active alcohol was prepared from fusel oil. This old, historical method has not been replaced by a better one, as the modern synthetic way for preparing active 2-methylbutanol-1 by the resolution of the racemic compound, obtained by the Grignard method, gives poor results.[3]

For separating the active amyl alcohol from the isoamyl alcohol, 3-methylbutanol-1, with which it is mixed in the fusel oil, Le Bel devised a method which has been applied by most investigators, although the final products were not more than about 85 percent pure, as was proved later by Marckwald and McKenzie,[4] who first obtained the alcohol in pure condition. Le Bel[5] found that the isoamyl alcohol was more easily converted to the chloride than 2-methylbutanol-1, and applied this observation for purification in the following manner: The fusel oil was saturated with hydrochloric acid and boiled under reflux or heated in sealed tubes for partially converting the mixture of the alcohols to chlorides, and finally fractionated for obtaining the unattacked alcohol. By repeating this process a fairly pure active amyl alcohol could be obtained, although the yield diminished appreciably by each treatment. Marckwald and coworkers[6] prepared the pure active 2-methylbutanol-1, and made several derivatives of it. Marckwald and McKenzie prepared the alcohol from beet-molasses fusel oil, which contains more active amyl alcohol (48 to 50 percent) than that from other usual sources (13 to 22 percent). The concentration was brought to 80 percent by the Le Bel method, and the pure, active 2-methylbutanol-1 obtained by recrystallization of the 3-nitrophtalic ester to constant melting point, followed by saponification and distillation. From the active amyl alcohol present in the fusel oil before treatment with Le Bel's process, Marckwald separated 5 percent in this way as pure alcohol. Klages and Sautter,[7] who repeated Marckwald and

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[3] von Falkenhausen, Biochem. Z. **242,** 472 (1931).

[4] Ber. deut. chem. Ges. **34,** 485 (1901).

[5] Bul. assn. chim. [2] **21,** 542 (1874); [2] **25,** 545 (1876).

[6] Ber. deut. chem. Ges. **34,** 479, 487 (1901); 35, 1595, 1602 (1902); **37,** 1038 (1904); **42,** 1583 (1909).

[7] Ber. deut. chem. Ges. **37,** 649 (1904).

McKenzie's method and checked their data, obtained only 2 percent of the original active alcohol in the pure form. The Pasteur process[8] for making active 2-methylbutanol-1, which is based on the recrystallization of the barium amylsulfate, was also studied by Marckwald, but the yield is not better and Marckwald recommended the first-mentioned method.

For the present investigation it was found desirable to have a larger amount (at least 1 liter) of pure active 2-methylbutanol-1 available for studying different methods for obtaining the pure optically active chloro-, bromo-, and iodo-derivatives, and further for preparing, if possible, the active fluoro-derivative. A large amount of pure optically active 2-methylbutanol-1 was obtained in the following way: One-hundred liters of fusel oil was prepared by the Rossville Co., Laurenceburg, Ind., from cane sugar molasses which contained the largest possible amount of beet sugar molasses (beet sugar molasses alone cannot be fully fermented). This fusel oil was distilled from a steam-heated, tin-lined, copper fractionating still and gave 70 liters of amyl alcohol, a sample of which, in a 2-dm tube, gave the rotation, $\alpha = -4.0$ circular degrees (the pure optically active 2-methylbutanol-1 gives, in a 2-dm tube, $\alpha = -9.6$ circular degrees). This alcohol was put through the Le Bel process as described above, using borosilicate glass tubes in the beginning, and later, as some of the tubes cracked, a steel, glass-lined autoclave. Twenty-four liters of amyl alcohol having $\alpha = -5.4$ circular degrees (2 dm) was obtained. A second treatment gave 8 liters having $\alpha = -6.3$ circular degrees (2 dm). A third milder treatment gave 1.75 liters of amyl alcohol having $\alpha = -8.8$; 1 liter having $\alpha = -8.3$; and 2 liters having $\alpha = -7.3$, all in circular degrees, for a 2-dm tube. The satisfactory increase by the last treatment is due more to a careful fractionation than to chemical purification, thus indicating that the pure alcohol may be obtained by fractionation only. If this active amyl alcohol had to be prepared again, fractionation only would be applied. Industrial as well as laboratory fractional distillation has been materially improved in recent years, and this method of fractionation now gives far better results than were possible at the time of Le Bel, or even of Marckwald. High efficiency of separation is needed because the boiling point of isoamyl alcohol (131°) is not far from that of 2-methylbutanol-1 (128.9°).

The fractionating column (see fig. 1*a*), made of borosilicate glass, has an inside diameter of 15 mm, a length of 1.5 m, and, for thermal insulation, it is surrounded by a sealed-in high-vacuum jacket, integral with it, which is wound with asbestos cord. The column has three sharp dents at the bottom, supporting the filling of soft glass tubing (5 mm outside diameter, 1 mm wall thickness, and 6 to 8 mm long). The column is sealed at the lower end to a round flask of 500 ml capacity provided with a side tube for filling, in which is ground a tube drawn out at one end to a capillary and at the other sealed to a stopcock which is connected with a drying apparatus for supplying dry air to prevent bumping of the boiling liquid. The distilling flask, which is also insulated with asbestos cord, may be cleaned by heating with some distillate, which can be siphoned off through the side tube. The upper part of the fractionating column consists of a tube 15 mm in diameter with ground stopper from which a short thermometer is suspended. The lower part (160 mm) of this upper section is jacketed

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[8] Compt. rend. **41**, 296 (1873).

and may be cooled by blowing air through the jacket. However, this was not found necessary, as more conservation of heat was required, which was obtained by proper insulation. The lower half of this upper section, which is slightly constricted at the bottom, is filled with pieces of soft glass tubing. This constricted part is connected by an inner seal into the upper part of the fractionating column, thus allowing the

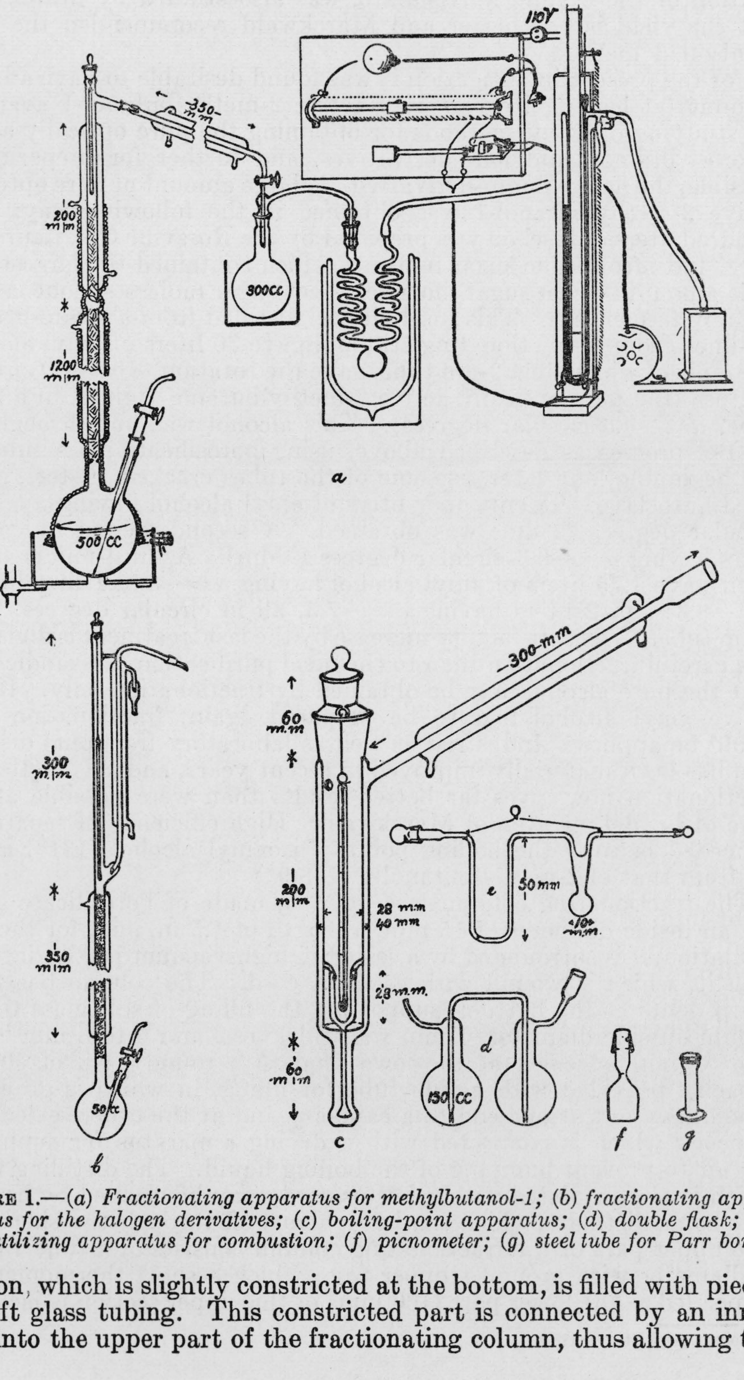

FIGURE 1.—(a) *Fractionating apparatus for methylbutanol-1;* (b) *fractionating apparatus for the halogen derivatives;* (c) *boiling-point apparatus;* (d) *double flask;* (e) *volatilizing apparatus for combustion;* (f) *picnometer;* (g) *steel tube for Parr bomb.*

observation of the rate of reflux. Above the jacket is a side tube provided with a ground joint for connection with the condenser, which in turn is connected by ground joints to the receiver and the spiral tube. The spiral tube cooled by ice water prevents the loss of distillate by evaporation in the vacuum. The manipulation of a stopcock permits changing of receivers without materially disturbing the vacuum in the column. All joints are accurately ground, no lubricant being used. The distillation pressure was maintained with a fluctuation of not more than 0.5 mm by a device described by H. L. Cox.[9] Some improvements were introduced as follows (see fig. 1): The glass tubes of the manostat were situated closer together so that a sliding rule between the tubes can be accurately read for obtaining the pressure; and further, the electric current passing through the manostat-manometer was obtained by reducing the 110-volt current to the proper value by an arrangement shown in figure 1 (*a*). A Hyvac oil vacuum pump was used.

The flask was heated by an electric heater constructed in the following way: A hemisphere of asbestos paper, made by using the next larger size round flask as a mold around which the wet mass of paper was built up and gradually loosened by a thin pliable spatula, was placed in a rectangular box of transite board, containing a circle of no. 20 nichrome wire, of triangular spiral cross section. This spiral was placed around the hemisphere of asbestos paper inside the box somewhat below the largest diameter by fastening to two binding posts near each other outside the box. The flask used for the molding was now clamped in place inside the asbestos hemisphere and the space between the transite walls and the asbestos paper filled with the proper mixture of water and plaster of paris and allowed to dry. The diameter of the inside hemisphere is about 11 cm, the width of the transite box 17 cm, and the height 9 cm. A hole 5 cm in diameter was then made in the center of the bottom of the box and also the plaster of paris beneath that hole carefully removed, leaving the asbestos lining intact. The heater was then wired on a ring clamp of suitable size by which it could be easily kept in place for heating the fractionating flask. The advantage of this heater is that bumping is minimized, as the heat energy is delivered nearer to the surface than to the bottom of the flask, which is kept comparatively cool. A substantially constant input of electrical energy, obtained from a storage battery, was used in order to secure a slow fractionation at constant rate (about 10 drops per minute). For collecting the so-called "hold-up" of the column at the end of a fractionation, which is especially desirable when small amounts are fractionated, as in the last fractions of the halogen derivatives, it is only necessary to apply suddenly a higher vacuum and remove the heater after the quick delivery of the distillate has stopped.

Two of the fractionating stills were constructed and could be operated simultaneously at the same pressure, using the one pressure-regulating system. The efficiency of these distillation columns, operating at a pressure of 150 mm of Hg, is indicated by the following figures, which give the optical rotation in a 2-dm tube, of middle fractions, corresponding to 50 percent of the charge, obtained from successive distillations: (1) −6.9° to −8.3°; (2) −8.3° to −8.8°; (3) −8.8° to −9.2°; (4) −9.2° to −9.3°; (5) −9.3° to −9.4°; (6) −9.4° to −9.5°;

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[9] Ind. Eng. Chem., Anal. Ed. 1, 7 (1929).

and (7) −9.5°. After many series of such fractions there was obtained 1.35 kg of 2-methyl-butanol-1 having an optical rotation of −9.5° in a 2-dm tube.

The purity of our preparation of 1,350 g, based on Marckwald and McKenzie's value (see table 1) is about 98 percent. As the impurity is an optically inactive substance, our preparation seemed a sufficiently pure starting product for preparing the pure active halogen derivatives. This conclusion was further substantiated by the close agreement of the values obtained by Marckwald (and also by Klages and Sautter) for their active iodine derivative with the value obtained for the iodine derivative in this investigation.

(b) *l*-ROTATORY-1-FLUORO-2-METHYLBUTANE

The method of Moissan [10] and of Moissan and Meslans [11] for preparing the fluoro derivatives of the aliphatic alcohols by the action of silver fluoride on the iodine derivatives of the alcohols is used at the present time, with minor modifications. By his method Moissan prepared methyl, ethyl, propyl, and isobutyl fluorides. Paternò and Spallino [12] found that sec-hexyl fluoride and normal octyl fluoride can be prepared by the action of silver fluosilicate on the respective iodine derivatives, and they observed that the fluoro derivative of the secondary alcohol is liable to split off hydrofluoric acid, forming hexylene. Swarts [13] prepared the fluorides of primary and secondary heptyl and octyl alcohol by the action of silver fluoride or mercurous fluoride on the iodo- or bromo-derivatives of the alcohols, and confirmed the observation of the Italian authors regarding the instability of the fluorides of the secondary alcohols. Further, Swarts tried to prepare a fluoride of fermentation amyl alcohol (mixture of 2-methylbutanol-1 and 3-methylbutanol-1) by the action of silver fluoride or mercurous fluoride on the iodo-derivative of fermentation amyl alcohol. The results were not satisfactory, as the impure fluorine compound partly decomposed on further fractionation, yielding small amounts of amylene. These results of Swarts were not encouraging, although the possibility existed that the fluoro derivative of 3-methylbutanol-1 was the unstable compound, whereas the fluoro derivative of 2-methylbutanol-1 could be stable. After several methods of fluorination had been tried out, it was found that the method of fluorination with silver fluoride, as given by Helferich and Gootz,[14] gave good results. They obtained β-fluorotetraacetylglucose by shaking at room temperature α-bromotetraacetylglucose with silver fluoride, using acetonitrile as a solvent in which silver fluoride is appreciably soluble. This modification of the fluorination with silver fluoride was successfully applied in the present investigation, as pure active 1-fluoro-2-methylbutane could be prepared. The method was used as follows: Commercial silver fluoride [15] was broken up in a mortar and thoroughly dried in a platinum dish in a vacuum desiccator over sodium hydroxide. Commercial acetonitrile was distilled a few times over phosphorus pentoxide and fractionated (boiling point, 83° C). As a platinum and a gold-palladium still-body of about 450 ml capacity each, and a gold-palladium receiver

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[10] Compt. rend. **107**, 261 (1888).
[11] Compt. rend. **107**, 1155 (1888).
[12] Gaz. chim. Ital. **37II**, 309 (1907).
[13] Bul. acad. roy. Belg. [5] **7**, 438 (1921).
[14] Ber. deut. chem. Ges. **62B**, 2505 (1929).
[15] E. de Haen, Seelze (Hanover), Germany.

of about 300 ml were available, the procedure had to be repeated once for obtaining a sufficient amount of 1-fluoro-2-methylbutane. The amounts given below were worked up in one still-body.

Sixty g (49.5 ml) of pure *d*-rotatory-1-bromo-2-methylbutane (see below) with 60 g of silver fluoride and 240 ml of acetonitrile were shaken for 1 month at room temperature in a still-body, which was tightly closed with a rubber stopper. Every 3 days 1 g of silver fluoride was added, and every 7 days the rotation of the liquid was determined by filtering a small amount and making a reading with a tube 0.25 dm in length, the rotation remaining about the same after 3 weeks of shaking. After the shaking the liquid was allowed to stand undisturbed for 24 hours (reaction of the dissolved silver fluoride) and only the clear liquid was carefully decanted on a folded filter, keeping containers and funnel covered as much as possible, as the fluorine derivative is easily volatilized. The filtrate is distilled from a flask heated on a water bath, using a wide capillary and thermometer. The condenser and the ground-on receiver are cooled with ice water. The distillate up to 80° was collected and kept in a well-stoppered bottle. The residue in the flask was added to the wet residues in the platinum and palladium-gold containers, some acetonitrile added, and after 1 hour of shaking again allowed to settle and then decanted, distilling the filtrate as before. The two distillates were fractionated in small borosilicate glass fractionating columns until a constant-rotating material was obtained.

The smallest fractionating apparatus is constructed as follows (see fig. 1*b*): A flask 50 ml in capacity is sealed to a jacketed column with an inside diameter of 10 mm and a length of 350 mm, the jacket being evacuated. The flask has a side neck with ground-in capillary tube provided with a small stopcock for regulating the dry air current. The column tube is extended above the jacketed part to a length of about 250 mm in which the thermometer is suspended from a ground stopper. Parallel to this thermometer tube is the dephlegmator consisting of a tube 8 mm in diameter which is surrounded by a jacket 170 mm long for cooling with water or air. The dephlegmator is sealed at its lower end inside a wider tube, which, in turn, is sealed to the thermometer tube, thus allowing observation of the rate of reflux. At its upper end (where it is supported with a sealed-in glass rod by the thermometer tube) the dephlegmator is connected by a ground joint to the condenser. The filling consists of spiral rings made according to Wilson, Parker, and Laughlin.[16] The larger fractionating apparatus is constructed as follows: A flask 200 ml in capacity is sealed to a jacketed column, which has an inside diameter of 15 mm and is 500 mm in length. The apparatus is further constructed as described for the smaller one, the same filling being used. The ground connections of both columns fit into the ground part of the same condenser, which is, in turn, connected by ground joints to two test tube-shaped receivers in series, cooled by ice water contained in Thermos bottles, providing in this way facilities for vacuum fractionation, which is especially necessary for the bromo- and iodo-derivatives.

The fractionation of the fluoro-derivative is performed at ordinary pressure, cooling the condenser and receivers with ice water and heating with a small gas flame, the flask resting on an asbestos plate and surrounded by an asbestos box. By slow fractionation the liquid can

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[16] J. Am. Chem. Soc. **55**, 2795 (1933).

be separated in five parts, namely, first a small amount of low-boiling liquid having little optical activity, then three parts having increasing optical activity, and finally a residue of high-boiling impurities. Separate fractionations are then performed for the three main parts, the apparatus being always thoroughly cleaned and dried between distillations. Six fractionations had to be performed until a substance substantially homogeneous in boiling point and optical rotation was obtained. Many more fractionations were required for purifying the less pure fractions. A yield of the pure compound of 30 percent of the theory can be obtained. No further change in the recorded rotation could be observed by further fractionation. It will be noted that no chemical treatment is applied for obtaining the pure compound, which can be distilled without any decomposition.

Special methods had to be found for determining the fluorine, carbon, and hydrogen content of 1-fluoro-2-methylbutane, as this compound is very volatile.

The method used for determining fluorine is a combination of the one devised by Hahn and Reid[17] (who applied the Parr bomb for fluorine determinations) and that of Ost as applied by Helferich and Gootz,[18] who determined the fluorine by the loss of weight of a watch glass by etching. A specially constructed weighing tube made of steel is necessary (see fig. 1*g*). The tube is 25 mm high, has an inside diameter of 7 mm, a wall thickness of 1 mm, and has a well-fitted stopper. The flat bottom has a diameter of 15 mm, so as to make more difficult its upsetting. The description of a determination is as follows: 0.3 g of starch is carefully mixed with 15 g of sodium peroxide and kept in a closed bottle. The sample, 0.0813 g of 1-fluoro-2-methylbutane, is weighed off in the steel weighing tube and placed in the Parr bomb. The weighed sodium peroxide mixture is then added and the bomb closed. Without shaking, the bomb is ignited by a blast flame and kept hot for a few minutes, and then thoroughly cooled by running water for at least 10 minutes. The contents of the bomb are dissolved in water, filtered, neutralized with 10-percent hydrochloric acid, and made alkaline with sodium carbonate solution, as described by Hahn and Reid. The solution is concentrated by hanging the borosilicate glass beaker in the steam bath by means of a closely fitting copper ring, filtered from the silicic acid, the filtrate concentrated in the same manner to 100 ml, and 10 ml of 20-percent calcium chloride added drop by drop to the hot solution. The mixture is heated almost to boiling, making the precipitate granular, and cooled. The precipitate is filtered on a filter 7 cm in diameter. It is not necessary to wash the precipitate, and some of the precipitate may be left in the beaker. The filter with contents is dried and most of the contents shaken into the beaker, and the filter with the adhering precipitate is ashed in a platinum crucible. The crucible is rinsed with about 1.5 ml of glacial acetic acid and the solution stirred into the beaker, and 10 ml of water is used for cleaning the crucible and gradually added, with stirring, to the contents of the beaker. The contents of the beaker are evaporated by hanging the beaker in the steam bath, some water is added, and the evaporation repeated to remove all acetic acid. Five ml of water is added, the beaker is cooled and filtered on a filter 5.5 cm in diameter, using the filtrate over and over

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[17] J. Am. Chem. Soc. **46**, 1652 (1924).

[18] Ber. deut. chem. Ges. **62B**, 2502 (1929).

again in order to bring all the precipitate of calcium fluoride on the filter. A few milliliters of water may be used in addition, but the precipitate is not washed. The filter is dried and ashed in a platinum crucible, which is fairly deep and has a sturdy, straight rim. Two watch glasses are weighed on an analytical balance and a few drops of 75-percent sulphuric acid are added to the contents of the crucible, which is directly covered with a tared watch glass. The crucible is heated in a sand bath for 2.5 hours at 150° C and then for a half hour at 200° C. The crucible is taken from the sand bath, cooled, the watch glass replaced by the second one, and the crucible again heated for a half hour at 200° C. The loss in weight of the cleaned watch glasses was found to be $0.0141+0.0003=0.0144$ g. A loss in weight of 0.00085 g corresponds to 0.001 g of fluorine. Fluorine found: 20.84 percent; theory: 21.09 percent.

In order to determine the carbon and hydrogen, the 1-fluoro-2-methylbutane was weighed into a specially constructed volatilizer (see fig. 1*e*) made of borosilicate glass. The rubber stopper of the combustion tube, having two holes of small diameter, is connected through one small tube directly to the dry oxygen and air supply; through the other hole the small tube of the volatilizer is introduced and the cork thoroughly fastened. The U-tube of the volatilizer is cooled in a beaker of ice water and cracked ice in order to prevent spreading of the volatile substance, and only at the end of the combustion is the ice water removed and heat applied to displace all the substance. With this arrangement the rate of delivery of vapor introduced into the combustion tube is easily controlled by regulating the oxygen stream through the volatilizer. Oxygen can also be introduced directly into the combustion tube through a by-pass. In the beginning combustions were made in a copper tube cooled at the end by copper spirals with running water for protecting the stoppers, the tube being filled with copper oxide and lead oxide (Moissan method)[19] or with the copper tube filled with copper oxide and lead chromate.[20] Both methods, however, were found unsatisfactory on account of the volatility of copper fluoride. Good results were obtained with a borosilicate glass tube filled with lead chromate and silver gauze, copper and copper compounds being excluded.[21]

The results of these analyses are: mass of substance, 0.1637 g; CO_2, 0.4009 g; H_2O, 0.1789 g. Calculated for $C_5H_{11}F$: C, 66.60; H, 12.31. Found: C, 66.79; H, 12.23.

(c) *d*-ROTATORY-1-CHLORO-2-METHYLBUTANE

The method of Le Bel for obtaining the chloro-derivative by heating a saturated solution of hydrochloric acid in active 2-methylbutanol-1 in sealed tubes at 100° C and further purifying by washing with water and sulphuric acid and sodium carbonate solution and finally fractionating, has been used by several investigators.[22] The products obtained by these investigators were not pure, probably on account of inadequate fractionation. This is essentially apparent for the product of Hardin and Sikorsky, who used only one distillation and one

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[19] Compt. rend. **107**, 993 (1888).

[20] Schliemann and Pillarsky, Ber. deut. chem. Ges. **62**, 3035 (1929).

[21] Wallach and Heusler, Liebigs Ann. Chem. **243**, 243 (1888).

[22] Le Bel, Bul. assn. chim. [2] **21**, 542 (1874); [2] **25**, 545 (1876). Guye, Bul. soc. chim. [3] **25**, 547 (1901). Hardin and Sikorsky, J. chim. phys. **6**, 207 (1908).

fractionation and obtained a purity of 82 percent (taking a purity of 100 percent for the preparation of McKenzie and Clough, which is identical with the preparation obtained in this investigation).

In the preparation by Le Bel's process, the following procedure was used in the present investigation: 150 g of 98-percent *l*-rotatory-2-methylbutanol-1 was saturated at 0° C with hydrochloric acid and heated in sealed tubes in a steam bath for 5 hours. The reaction product was washed with water, dried with sodium sulphate, and fractionated in the fractionating columns used for the preparation of the active fluoro-derivative. By repeated fractionation, about 20 percent of the theoretical amount of pure active 1-chloro-2-methylbutane was separated and about 50 percent of active amyl alcohol recovered.

In the preparation by McKenzie and Clough's method[23] the following procedure was used: 20 g (24.5 ml) of 98-percent *l*-rotatory-2-methylbutanol-1 was gradually dropped from a burette in the course of a half hour through a condenser into a round flask, which contained 50 g (30 ml) of pure thionyl chloride. The flask was cooled in a dish with cracked ice. After addition of the 2-methylbutanol the mixture was kept at room temperature for 1 hour and then distilled in a vacuum of about 500-mm pressure, using a water pump and cooling the condenser and receiver with ice water. Fractionation gave about 28 g of dextrorotatory amyl chlorosulphinate with the properties described by McKenzie and Clough. In repeating the preparation several times with the double amount, the yield was somewhat diminished. The active amyl chlorosulphinate was converted to active amyl chloride according to McKenzie and Clough by refluxing for 2 hours at 120° C from an oil bath and fractionating the residue with the 500-mm column at ordinary pressure, cooling with ice water. The fractions with largest optical rotation were further fractionated, yielding a final product which did not change in boiling point or optical rotation upon subsequent fractionation and which was found to be identical in properties with the active amyl chloride by Le Bel's process.

(d) *d*-ROTATORY-1-BROMO-2-METHYLBUTANE

By the action of hydrobromic acid on pure *l*-rotatory-2-methylbutanol-1, Marckwald obtained a product which, on purification with sulphuric acid and fractionation, gave an active bromo-derivative with a specific rotation of $[\alpha]^{20}_{D}=+3.68$. Hardin and Sikorsky,[24] who started from 2-methylbutanol-1 of 92 to 95 percent purity (taking Marckwald's preparation as 100 percent), obtained, by the same procedure, for the bromo-derivative, $[\alpha]^{20}_{D}=+3.8$. Later Marckwald[25] applied the action of phosphorus tribromide on 2-methylbutanol-1 of 95 percent purity, and using the same method of purification, obtained for the specific rotation of the bromo-derivative, $[\alpha]^{20}_{D}=+4.05$. Marckwald remarked that on account of the presence of 5-percent isoamyl alcohol (which is inactive) in the starting material, the specific rotation of the pure bromo-derivative must be $+4.05+(5\times 0.04)=+4.25$. In the light of recent results the validity of this correction of Marckwald is questionable, as the impure bromo-derivative is treated with sulphuric acid, which besides eliminating the unchanged alcohol, may act also on the isoamyl bromide, which is less stable than the 2-methylbutanol derivative (see results of

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[23] J. Chem. Soc. **103**, 698 (1913). [24] J. chim. phys. **6**, 207 (1908). [25] Ber. deut. chem. Ges. **42**, 1583 (1909).

[24] J. chim. phys. **6**, 207 (1908).
[25] Ber. deut. chem. **42**, 1583 (1909).

Swarts on isoamyl fluoride). Further, the fractionation may also separate the different bromo-derivatives. Experimental evidence given below shows that both methods of bromination yield a product of identical specific rotation, which value agrees with the highest one actually found by Marckwald (+4.05).

In the preparation by the hydrobromic acid method the following procedure was employed: A special so-called double flask[26] (see fig. 1*d*), which can be used for saturating a liquid with a gas, as well as for drying a gas, was used for preparing the bromo- and iodo-derivatives. 60 g (73 ml) of 98-percent *l*-rotatory-2-methylbutanol-1 was cooled in ice in a double flask, which was connected at one end with a drying tube filled with asbestos and dry sodium sulphate, and connected at the other end with the hydrobromic acid generator. After saturation of the alcohol with hydrobromic acid, the double flask was connected with a reflux condenser having a drying tube at the upper end, and heated for 2½ hours in a water bath at 95° C, with a slow stream of hydrobromic acid passing through the liquid. The reaction product was cooled and separated from the watery layer in a separatory funnel, shaken two times with ice water, filtered clear through a dry filter, cooled in a dry separatory funnel, and shaken twice with about 8 ml of sulphuric acid which had been cooled with ice and salt, then with ice water, then with cold 10-percent sodium carbonate solution, and finally with ice water until a neutral preparation was obtained. Most of the water was removed by pouring the preparation from a dry Erlenmeyer flask. It was finally dried over potassium carbonate, and fractionated at 150-mm pressure, the condenser being cooled with ice water. The yield of the constant-boiling and rotating substance is about 70 percent of the theoretical. The preparation was repeated several times with slight variations but gave identical final products with properties recorded below.

In the preparation by the phosphorus tribromide method the following procedure was used: 80 g (28 ml) of phosphorus tribromide was slowly dropped through a condenser into 40 g (49 ml) of 98-percent *l*-rotatory-2-methylbutanol-1 contained in a flask cooled by ice. The condenser was sealed to the flask. A few "boiling" stones of unglazed porcelain were added. The mixture was allowed to stand overnight, the condenser being connected with an inverted calcium chloride tube. The next morning the flask was heated for about 10 minutes on the steam bath, the liquid turning turbid when the reaction started. The reaction product was cooled in ice and salt and poured on ice in a beaker which was cooled in an ice and salt mixture. The reaction product was separated from the watery layer in a separatory funnel and further purified as described for the method with hydrobromic acid. The preparation was repeated a few times, yielding identical final products.

(e) *d*-ROTATORY-1-IODO-2-METHYLBUTANE

This compound has been prepared by Klages and Sautter[27] and also by Marckwald,[28] applying the method of Just,[29] namely, heating a saturated solution of hydriodic acid in pure active 2-methylbutanol-1 at 100° C, purifying with cold dilute potassium hydroxide solution and ice water, drying over potassium carbonate, and fractionating.

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[26] This device is not new, as it was used many years ago in a physical laboratory at Amsterdam. The advantage of this flask is that the liquid cannot be sucked into the gas generator by change of pressure.

[27] Ber. deut. chem. Ges. **37**, 649 (1904).

[28] Ber. deut. chem. Ges. **37**, 1038 (1904).

[29] Liebigs Ann. Chem. **220**, 149 (1883).

The specific rotation found by these authors is identical with that found in the present investigation. It was found, as described below, that the iodo-compound can be prepared by heating at 60 to 65° C, instead of 100°.

In the present investigation the following procedure was used: 40 g (49 ml) of 98-percent *l*-rotatory-2-methylbutanol-1 was cooled in ice in a double flask (see under 1-bromo-2-methylbutane), which was connected at one end with a drying tube filled with asbestos and dry sodium sulphate and connected at the other end to the hydriodic acid generator. After saturation of the active alcohol with pure dry hydriodic acid at 0°, the flask was heated in a water bath for 1 hour at 60 to 65° C, with a slow stream of hydriodic acid passing through the liquid. The reaction product was cooled and separated from the top watery layer in a separatory funnel, shaken once with 10 ml of ice water, then with 15 ml of cold 10-percent sodium hydroxide solution until acidity was removed, and finally with ice water until a neutral preparation was obtained. Most of the water was removed by pouring the preparation from a dry Erlenmeyer flask. It was finally dried over potassium carbonate, and fractionated at 50-mm pressure, the condenser and receiver being cooled with ice water. The yield of the "constantly boiling" and "constantly rotating" substance is about 65 percent.

2. PROPERTIES OF PURE COMPOUNDS

(a) OPTICAL ROTATION

The optical rotation was determined with a polariscope with circular scale and double-field Lippich polarizer. Jacketed glass polariscope tubes were used, which were checked for the recorded length. For each pure compound investigated, the rotation was determined for the two wave lengths, 5892.5 and 5461 A, on the circular-scale polariscope, using spectrally purified light from an electric sodium lamp and an electric mercury lamp, respectively. A third determination was made, using the same sample and tube with the Bates saccharimeter, and using white light and a bichromate filter, which gives an effective wave length of about 5850 A. These data are given in table 1, together with values reported by Marckwald and McKenzie,[30] McKenzie and Clough,[31] and Klages and Sautter.[32] The data of the many other investigators who prepared optically active 2-methylbutanol-1 and its derivatives are not included because their compounds were very impure.

(b) SPECIFIC GRAVITY

No concordant results were obtained with picnometers in which the liquid is in contact with ground joints. Picnometers of 5 and 10 ml capacity, with ground caps were constructed and served well for the purpose (see fig. 1). The liquid level was conveniently adjusted by the use of strips of hardened filter paper, and the loss of liquid by evaporation was prevented by the cap. The picnometer was filled and emptied by using a pipette with a capillary stem. The specific gravity was determined with the picnometer at 20° C, and a formula applied for obtaining the specific gravity at 20°/4° in vacuo. These data, together with those of some earlier investigators, are given in table 1.

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[30] Compt. rend. **41**, 296 (1873).
[31] Ber. deut. chem. Ges. **37**, 649 (1904).
[32] Compt. rend. **107**, 1155 (1888).

TABLE 1.—*Optical rotation, specific gravity, and refraction of 1-halogeno-2-methylbutanes*

Substance	Optical rotation							Specific gravity		Refractivity	
	Observed rotation α for:			Specific rotation $\frac{\alpha}{ld}$ for:			Specific rotation reported by other investigators	d^{20}_4 vac.	d By other investigators	Refractive index	Molecular refraction
	λ5892.5 A	λ5461 A	White light and bichromate filter	λ5892.5 A	λ5461 A	White light and bichromate filter (5850 A at 20° C)				n^{20}_D	$M\frac{n^2-1}{(n^2+1)d}$
l-Rotatory-2-methylbutanol-1.	−9.432 (2 dm)[a]	−11.200 (2 dm)	−9.47 (2 dm)	−5.756 (at 20.4° C)	−6.835 (at 20.4° C)	−5.78	$[\alpha]_{58}{}^{20}{}_{92}=-5.90$ (Marckwald and McKenzie.)	0.8193	$d^{20}_4=0.816$ (Marckwald and Mckenzie.)	1.4107	35.605
l-Rotatory-1-fluoro-2-methylbutane.	−7.009 (1 dm)	−8.283 (1 dm)	−7.01 (1 dm)	−8.865 (at 20.1° C)	−10.477 (at 20.1° C)	−8.87	---	.7906	---	1.3576	24.997
d-Rotatory-1-chloro-2-methylbutane.	+1.456 (1 dm)	+1.636 (1 dm)	+1.49 (1 dm)	+1.644 (at 20.1° C)	+1.847 (at 20.3° C)	+1.68	$[\alpha]^{15}_D=+1.7$ (McKenzie and Clough.)	.8857	$d^{15}_4=0.8868$ (McKenzie and Clough.)	1.4124	29.957
d-Rotatory-1-bromo-2-methylbutane.	+4.946 (1 dm)	+5.758 (1 dm)	+5.00 (1 dm)	+4.043 (at 20.6° C)	+4.707 (at 20.6° C)	+4.09	$[\alpha]^{20}_D=+4.05$ (Marckwald.)	1.2234	---	1.4451	33.512
d-Rotatory-1-iodo-2-methylbutane.	+8.672 (1 dm)	+10.107 (1 dm)	+8.71 (1 dm)	+5.685 (at 19.8° C)	+6.626 (at 19.8° C)	+5.71	$[\alpha]^{15}_D=+5.78$ (Klages and Sautter.) $[\alpha]^{20}_D=+5.64$ (Marckwald.)	1.5253	$d^{20}_4=1.524$ (Marckwald.)	1.4977	38.033

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[a] Length of tube.

(c) REFRACTIVE INDEX

The values of refractive index were determined with an Abbe refractometer at 20° C. These data, together with calculated values of the molecular refraction, are given in table 1.

(d) BOILING POINTS AT VARIOUS PRESSURES

A Cottrell-Washburn boiling-point apparatus[33] was used with some modifications (see fig. 1*c*): The withdrawal tube was omitted. The boiling tube is sealed to the condenser and is constricted at the bottom. This constricted part is 60 mm long and 15 mm in diameter and has a flat bottom. The upper part of the boiling tube is 200 mm long and is 40 mm in diameter. The glass sheath, which is ground into the boiling tube, has at its top, just above the ground connection, a ground stopper with an eye from which a short accurately standardized thermometer, graduated in 0.2° C intervals, is suspended by a platinum wire. The glass sheath, 28 mm in diameter, extends slightly above the constriction of the boiling tube, and has a hole 6 mm in diameter at the height at which the condenser is sealed on. The pumping tubes, 3 mm in diameter, are attached from their top to the inside of the sheath, the holes being about 28 mm above the end of the sheath and about 10 mm apart. The pumping tube is widened at its lower end to a funnel 8 mm wide extending to near the bottom of the boiling tube. Inverted melting-point tubes or small pieces of unglazed porcelain were used for preventing bumping. These modifications allowed the use of small amounts of liquid for the determination. For low pressures the reflux condenser was cooled with ice water, which could be kept running without a pump by slowly siphoning water through the condenser from the bottom of a large crock filled with big chunks of ice, which was kept filled at a constant level by tap water. The pressure of the boiling liquid was maintained within fluctuations of about 0.1 mm of Hg by increasing the volume at constant pressure to about 5 liters. Calibration corrections were applied to the thermometer readings. The values of the boiling points correspond to the given pressures in terms of millimeters of Hg at 0° C and standard gravity (g=980.665). The results are compiled in table 2, and shown graphically in figure 2.

TABLE 2.—*Boiling points*

Pressure	*l*-Rotatory-2-methylbutanol-1	*l*-Rotatory-1-fluoro-2-methylbutane	*d*-Rotatory-1-chloro-2-methylbutane	*d*-Rotatory-1-bromo-2-methylbutane	*d*-Rotatory-1-iodo-2-methylbutane
mm of Hg	°C	°C	°C	°C	°C
50	65.7	------	27.7	45.0	66.5
100	79.6	------	43.0	61.4	84.1
150	88.2	14.1	53.1	71.7	95.4
200	94.6	20.7	60.4	79.5	103.5
300	104.1	30.4	71.5	91.1	115.7
400	111.4	37.8	80.0	100.1	125.3
500	117.3	43.7	86.8	107.4	132.6
745[a]	------	55.4	------	------	------
747[a]	128.6	------	------	------	------
758[a]	128.7	55.85	100.2	121.5	------
763.6[a]	------	------	100.7	------	------
760[b]	128.9	55.9	100.45	121.6	(c)

[a] Atmospheric pressure, observed.
[b] Values calculated to normal boiling point.
[c] Decomposed.

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[33] J. Am. Chem. Soc. **41**, 730 (1919).

III. DISCUSSION OF RESULTS

The similar procedure used for preparing the chlorine, bromine, and iodine derivatives makes it very probable that these derivatives are of the same configurational form, whether or not a Walden inversion is involved in their preparation. It is immaterial for our present purpose whether this form fits into any particular scheme of classification as a *d*-form or as an *l*-form, and it will be noticed that we have described the compounds as *d-rotatory.* In the case of the fluorine compound, however, it is not certain whether the *negatively* rotating form must be classified with the other halogen derivatives which are positively rotating (possibility 1) or whether the positively rotating form must be taken (possibility 2).

TABLE 3.—*Comparison of the numerical relation* (Cl–F):(Br–Cl):(I–Br) *of the molecular rotations of 1–halogeno–2–methylbutanes for 5892.5* A *and for 5461* A *at 20°* C *with the numerical relation of the atomic-radii differences between the respective halogens*

Explanation of table.—The values given in column 5 have been obtained by multiplying the values of column 3 by a factor, which will reduce the first value to 41. This value has been chosen in order to conform to the values given in column 4 for the numerical relation between the differences of neutral atomic radii.

1	2	3	4	5
Compounds	Molecular rotation in circular degrees	Differences between molecular rotations	Relation of the differences between atomic radii in angstroms	Reduced relation of the differences between molecular rotations
	For λ *5892.5* A:			
F	−799.1			
Cl	+179.0	978.1	0.41	0.41
Br	+610.1	431.1	.16	.181
I	+1124.7	514.6	.21	.216
	For λ *5461* A:			
F	−943.8			
Cl	+196.8	1140.6	.41	.41
Br	+710.8	514.0	.16	.185
I	+1312.0	601.2	.21	.216

In table 3 the first possibility is tested for the atomic-dimension relationship and it will be seen that the numerical relationship of (Cl–F):(Br–Cl):(I–Br) of the molecular rotations is 41:18.1:21.6 for 5892.5 A, and 41:18.5:21.6 for 5461 A, which agrees well with the numerical relationship of the successive differences in the radii of the neutral halogen atoms, 41:16:21. These differences (Cl–F), (Br–Cl), and (I–Br) are obtained by averaging the ratio of the differences in the radii given by van Arkel and de Boer and the ratio of the differences derived from the values given by Goldschmidt.[34] Probably the numerical relationship of these differences of atomic radii is most accurately represented by 41:17.1:21.4, as suggested by the author,[35] which shows even a closer agreement with the observed numerical relationship. It is further noteworthy that in spite of the very different values of the rotations for the two wave lengths, the ratio of their differences is the same.

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[34] BS J. Research **7,** 573 (1931) RP 358.

[35] J. Am. Chem. Soc. **47,** 1285 (1925); BS J. Research **7,** 573 (1931) RP358.

For the second possibility no apparent regularity is obtained (if the positively rotating fluorine derivative is included). This will be observed from the rotations given which, with the positively rotating fluorine derivative, show first a decrease and then an increase in value for both the specific and the molecular rotation. Thus the above reasoning classifies the *positively* rotating chlorine, bromine, and iodine derivatives with the *negatively* rotating fluorine derivative. This appears strange. However, we arrive at the same conclusion by taking into consideration that it is very improbable that in any of the reactions used for preparing the halides a Walden inversion is involved, as the reactions take place at inactive carbon atom, and temperatures (at most 100°) are applied for which no racemization of the alcohol or the halides can be observed.[36] Further, it is obvious from these data that the differences in weight of the four groups attached to the asymmetric carbon atom (Guye's hypothesis) cannot be used for correlating the rotations in both possibilities, as theory would require for the differences in rotation (Cl–F):(Br–Cl):(I–Br) the proportionality 16.5:44.4:47.0. This differs greatly from the observed data.

The reduced differences in the boiling points at the same pressure of the (Br–Cl) and (I–Br) derivatives have a numerical relationship which agrees with that for the differences in atomic radii of the respective neutral atoms, whereas a deviation for the (Cl–F) difference exists. In table 4 the reduced ratio for one pressure is given, the ratio for other pressures being substantially the same. This behavior is not unexpected, as such restricted relationship has been pointed out and discussed by the author for the elements F, Cl, Br, and I in a former publication.[37]

TABLE 4.—*Comparison of boiling points at equal pressure of 1–halogeno–2–methylbutanes with the differences in the atomic radii of halogens*

The values given in column 3 have been obtained by multiplying the values of column 2 by a factor, which will reduce the second value to 16. This value has been chosen in order to conform to the values given in column 4 for the numerical relation between the differences in the radii of neutral atoms (Br-Cl):(I-Br), 16:21. There is a deviation of the (Cl–F) value. Closer agreement is obtained by comparing with the numerical relation of the atomic radii as observed by the author (J. Am. Chem. Soc. **47**, 1280 (1925)) 41:17.1:21.4, the reduced numerical relation of the boiling-point differences for 150 mm Hg then being 35.8:17.1:21.8.

1	2	3	4
Pressure	Numerical relation between boiling-point differences (Cl-F):(Br-Cl):(I-Br)	Reduced numerical relation between boiling-point differences (Cl-F):(Br-Cl):(I-Br)	Numerical relation between differences in radii of neutral atoms (Cl-F):(Br-Cl):(I-Br)
mm of Hg 150	39.0:18.6:23.7	33.5:16:20.4	41:16:21

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[36] Marchwald and Nolda (Ber. deut. chem. ges. *42*, 1591 (1909) investigating the possibility of a Walden inversion also came to the conclusion that the negatively rotating 2-methyl butanol-1 and the positively rotating bromine and iodine derivatives are of the same configuration. The writer does not agree however, with Marchwald's and Nolda's generalisation that a racemic influence is due to silver salts. This will be discussed in a later paper.

[37] NBS J. Research **17**, 337 (1936) RP915. The same regularity holds for the molecular refractivities and the cube roots of the molecular volumes according to Kopp.

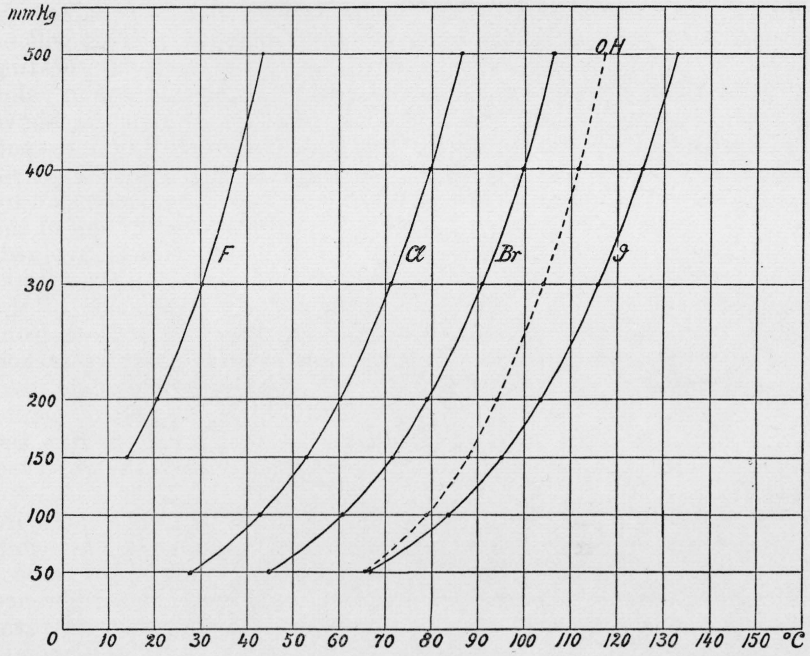

FIGURE 2.—*Boiling-point curves for l-rotatory-2-methylbutanol-1 and its halides.*

IV. CONCLUSIONS

The results of this investigation show that the differences in the molecular rotations (Cl–F), (Br–Cl), and (I–Br) of the four pure active halogeno–2–methylbutanes have the numerical relation 41:18:21.6 (for λ 5892.5 A, as well as for λ 5461 A), which agrees well with the numerical relation 41:16:21 for the differences in the radii of the respective neutral atoms. As the halogens of these simple compounds are attached *indirectly* (by a chain of atoms) to the asymmetric carbon, these results support the rule proposed by the author [38] for this class of compounds for the more complicated carbohydrate derivatives.

The other crucial test for that part of the regularity which applies to halogen derivatives in which the halogen is *directly* attached to the asymmetric carbon, and contains only one asymmetric carbon atom, and which involves the specific rotation, will be given in a forthcoming publication.

WASHINGTON, January 18, 1937.

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[38] J. Am. Chem. Soc. **47**, 1285 (1925).