THE RELATIONSHIP BETWEEN THE ISOMERIC 2-BUTENES AND THE 2, 3-BUTANEDIOLS

Thesis by

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In Partial Fulfillment of the Requirement
for the Degree of Doctor of Philosophy

California Institute of Technology
Pasadena, California

1935

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INTRODUCTION

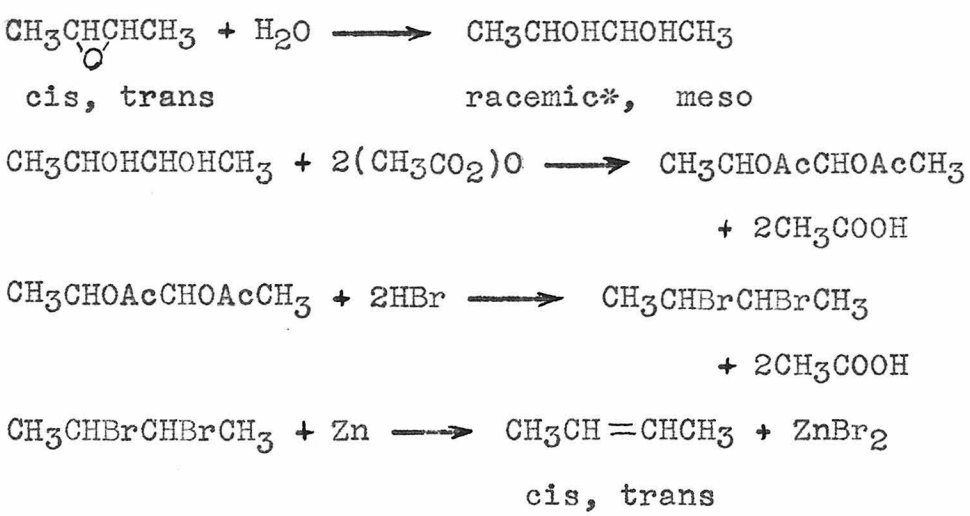
In studying problems of stereochemistry the cis and trans 2-butenes and the compounds derived from them should be very interesting and illuminating. In these hydrocarbons and in their oxides geometric isomers are possible; in the derivatives such as the 2,3-butanediols, optical isomers of the type associated with two asymmetric carbon atoms (possibility of internal compensation) should be found. Data on these compounds should be especially useful because of the simplicity of the compounds and because of the smoothness of the reactions. With only four carbon atoms, it is possible to study the properties of the asymmetric centers without the complications of large molecular weight or of strongly polar groups. None of the reactions showed any indications of leading to the slightest amount of "racemization".

The object of this research was to separate the isomeric 2-butenes. This involved the following steps:

$$CH_3CH{=}CHCH_3 + HOCl \longrightarrow CH_3CHOHCHClCH_3 \qquad (1)$$

$$CH_3CHOHCHCLCH_3 + KOH \longrightarrow CH_3\underset{O}{CHCH}CH_3 \qquad (2)$$

Fractionation of Butene oxides.



$$CH_3\underset{O}{CHCHCH_3} + H_2O \longrightarrow CH_3CHOHCHOHCH_3 \quad (3)$$

cis, trans racemic*, meso

$$CH_3CHOHCHOHCH_3 + 2(CH_3CO_2)O \longrightarrow CH_3CHOAcCHOAcCH_3 + 2CH_3COOH \quad (4)$$

$$CH_3CHOAcCHOAcCH_3 + 2HBr \longrightarrow CH_3CHBrCHBrCH_3 + 2CH_3COOH \quad (5)$$

$$CH_3CHBrCHBrCH_3 + Zn \longrightarrow CH_3CH{=}CHCH_3 + ZnBr_2 \quad (6)$$

cis, trans

The reactions from (3) to (6) inclusive were carried out separately with each of the two oxides.

The synthesis of the isomeric 2-butenes has been previously described[1,2]. If the configuration of each of these compounds could be ascertained and be related to their physical properties and to the configurations and physical properties of the materials from which each was derived, the relationships should be very valuable. Unfortunately, the configuration of many of the compound in the chain could not be determined. However, from the structure of some of the compounds together with known rules for relating structures of compounds in other similar series, it is possible to give a consistent picture of the whole chain.

*The word racemic is used for convenience in this thesis to represent the externally compensated substances and it does not imply that a definite compound has been formed.

DISCUSSION AND METHOD

2-Butene Chlorohydrin

2-Butene was prepared by dehydrating normal butyl alcohol with sulfuric acid under the conditions given by Young and Lucas[3]. The washed, dry butene was stored in weighed ampoules until needed. This hydrocarbon, when analysed by the above authors, was shown to contain no 1-butene.

The reaction,

$$CH_3CH{=}CHCH_3 + HOCl \longrightarrow CH_3CHOHCHClCH_3 \qquad (1)$$

has been carried out by Krassuski[4] and by Fourneau and Puyal[5]. The latter authors reported that the reaction (carried out by passing butene gas into a hypochlorite, boric acid solution) was slow. Early work showed that only small yields were obtained by passing butene gas into hypochlorus acid solution[6]. The method described here depends on slowly liberating the hypochlorus acid in a vigorously stirred emulsion of liquid butene and aqueous solution. These conditions were realized by placing calcium hypochlorite, water, and butene in a cooled flask and slowly adding acid. Acetic acid proved to be much more satisfactory than a strong acid and slightly better than carbonic acid. The limiting factor seemed to be stirring (with poor stirring the yield was low and a large amount of 2,3-dichlorobutane and a high boiling material was obtained). Apparently the chlorine

formed by the oxidation of chloride ion by hypochlorus acid dissolved in the organic phase and added to the unsaturated hydrocarbon. From the fact that by passing chlorine into a vigorously stirred emulsion of butene, water, and sodium acetate only 6 per cent chlorohydrin and 75 per cent dichloride was produced, it can be concluded that the addition of chlorine is much faster than its extraction by the aqueous phase, subsequent hydrolysis, and reaction. By liberating the hypochlorus acid slowly in an excess of butene the oxidizing action on the product is reduced to a minimum. The use of acetic acid resulted in a buffered solution in which the free hypochlorus acid concentration was low. Under the most favorable conditions (the stirring, the acid added, the concentrations, the rate of addition, and the temperature were varied[7]) yields of 60 per cent were obtained.

A portion of the chlorohydrin after five successive vacuum fractional distillations was separated into two main fractions, the properties of which are shown in table I[7].

TABLE I PROPERTIES OF FRACTIONS OF 3-CHLORO-2-BUTANOL.

	1.	2.	Literature[4,8]
B. p. 30 mm.	53.0-53.3°	57.0-57.4°	
B. p. 742 mm.	132.0-132.5°	135.0-135.5°	136-137.5°*
Sp. Gr. $\frac{20^\circ}{20^\circ}$	1.0677	1.0685	1.105
Refractive index n_D^{20}	1.4421	1.4388	1.44376
Weight	65.8 g.	86.0 g.	

*at 760 mm.

2-Butene Oxides

Butene oxide was prepared by Fourneau and Puyal[5] by dropping butene chlorohydrin on to hot solid sodium hydroxide.

$$CH_3CHOHCHClCH_3 + OH^- \longrightarrow CH_3\underset{O}{CH}CHCH_3 + H_2O + Cl^- \qquad (2)$$

Krassuski[4] found that it could be prepared either by the action of aqueous potassium hydroxide or lead oxide and water on butene chlorohydrin at room temperature. None of these conditions seemed to be very satisfactory for preparing large quantities of material. The first used a solid reactant; the others were slow because of the low temperature.

A very rapid, smooth reaction took place when chlorohydrin was slowly added to a well stirred, hot, concentrated solution of potassium hydroxide. The product was distilled from the flask as it was formed.

By using a moderate excess of hydroxide yields of from 80 to 85 per cent were obtained; with a larger excess yields of about 90 per cent.

The oxides can be fractionated with greater ease than any of the other isomeric substances in the chain. A boiling point difference of about six degrees was found. One portion of the material was fractionated six successive times by means of a Hemple column threeand a half feet tall with a Claisen neck[7]. A better separation was obtained after three distillations through a Hemple column five feet tall provided with a total reflux condenser. The distillation curves for these three fractionations are given in figure 1. By studying this figure it is possible to visualize the effectiveness of the distillations. The shape of the curve for the last distillation indicates the relative purity of the two main fractions. That is, the compound with the smaller rate of change of temperature with amount of distillate is the purer. The properties of the two main fractions of each fractionation are given in Table II.

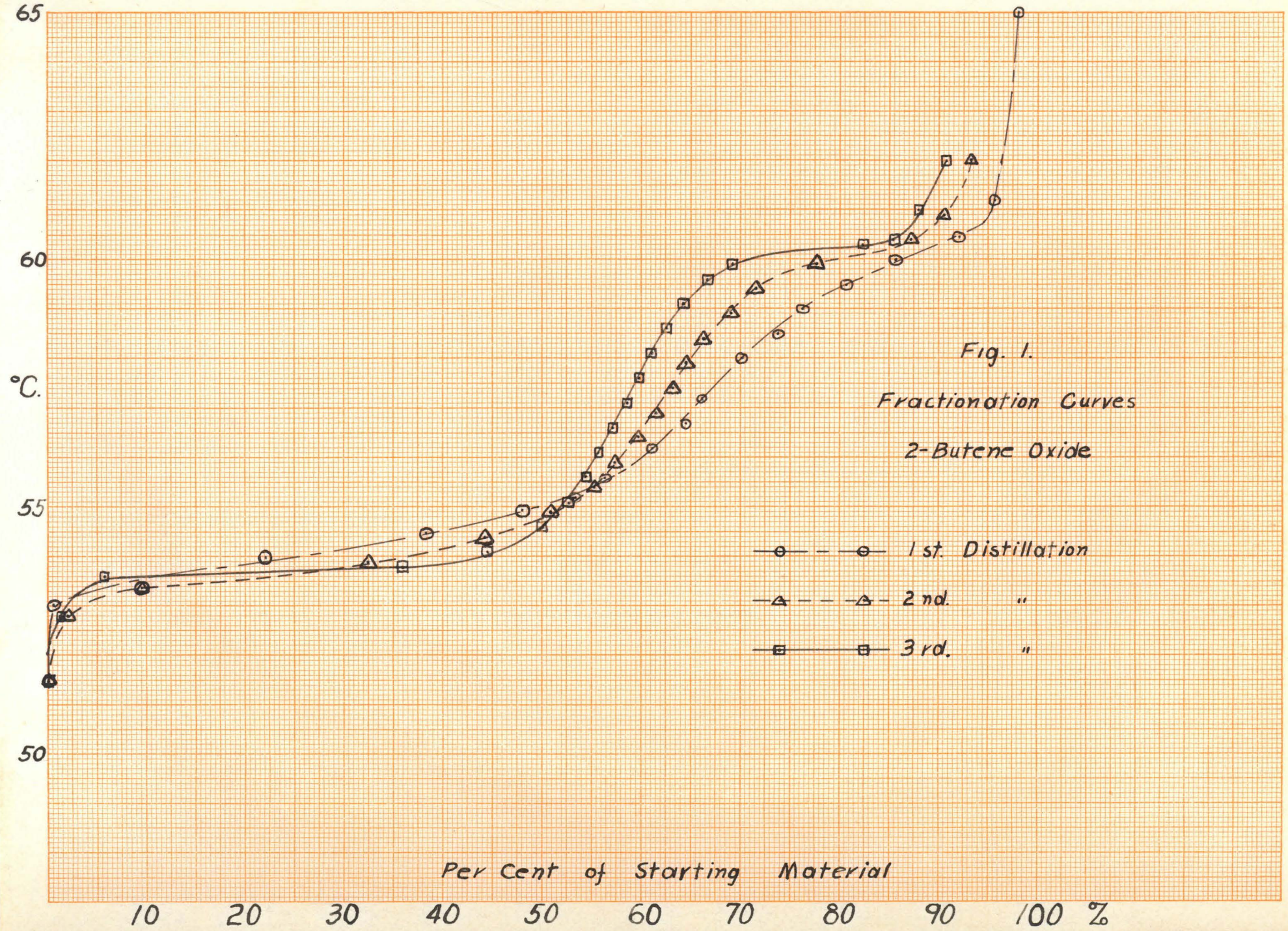


Fig. 1.

Fractionation Curves

2-Butene Oxide

TABLE II. PROPERTIES OF THE FRACTIONS OF 2-BUTENE OXIDE.

Column	Short		Tall	
	cis(?)	trans (?)	cis (?)	trans (?)
B. p. 747 mm.	53.5-54.0°	59.5-60.0°	53.6-54.1°	59.9-60.4°
Sp.Gr. $\frac{20}{20}$	0.8063	0.8267	0.8053	0.8272
Refractive Index n_D^{20}	1.3739	1.3819	1.3736	1.3826
M. p.			-85°(?)	-80° ?
Weight	264 g.	87 g.	661 g.	280 g.

The structure of these oxides can be taken with some confidence from the relative melting points of the two fractions. It has been empirically determined that of a given pair of geometric isomers the trans form has a higher melting point than the cis. In this case with only five degrees difference in melting point, the validity of the conclusion might be questioned. However, from the distillation curve and from the purities of the crude glycols (as determined by comparison of the melting points with those of the purified products), it can be concluded that the higher melting oxide is more impure. This means that the difference in the melting point of the pure isomeric oxides will probably be greater than this difference observed on these fractions. This uncertainty will soon be removed by Dr. Brockway's electron diffraction determination of the structure.

2,3-Butanediols

The hydration of the separate butene oxides was carried out by simply adding them to a rather large excess of dilute perchloric acid solution. The kinetics of the hydration of ethylene, and others, oxides has been studied under various conditions by Bronsted, Kilpatrick and Kilpatrick[9]. They found that under certain conditions four reactions took place.

$$CH_2\text{-}CH_2 + H_2O \longrightarrow CH_2OHCH_2OH \quad (3a)$$

$$CH_2\text{-}CH_2 + H_3O^+ \longrightarrow CH_2OHCH_2OH + H^+ \quad (3b)$$

$$CH_2\text{-}CH_2 + Cl^- + H_2O \longrightarrow CH_2ClCH_2OH + OH^- \quad (3c)$$

$$CH_2\text{-}CH_2 + Cl^- + H_3O^+ \longrightarrow CH_2ClCH_2OH + H_2O \quad (3d)$$

Of the many acids studied by them, perchloric was the only one that did not add to the olefin oxide to some extent by reactions similar to equations (3c) or (3d).

When the hydration of butene oxide was attempted in a solution containing only one mol excess water, a yield of about 75 per cent was obtained. Distillation yielded a material boiling considerably higher than the glycol. This material has not been investigated; but since alcohols are known to add to oxides to form hydroxy ethers, it probably arises from a reaction of the type,

$$CH_3CHOHCHOHCH_3 + CH_3CHCHCH_3 \longrightarrow CH_3CHOHCH\text{-}OCHCHCHOHCH_3 \quad (3e)$$
$$\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad CH_3 \quad CH_3$$

By using about fifteen mols of excess water, this reaction could be largely eliminated, and yields of 90 to 95 per cent were attained.

The glycol from the lower boiling oxide (cis ?) became solid at room temperature. The melting point of the crude distillate was about 32.3°. From the freezing point-composition curve (determined later for water and for the isomeric glycol), this melting point indicates a purity of at least 96 mol per cent. Considering the facts that the oxide was purified from its isomer only by fractional distillation, and that one weight per cent of water is about equivalent to four mol per cent, it is possible to state that either no Walden inversion or that 100 per cent Walden inversion took place during the reaction. Or, this purity could be regarded as indicating that the corresponding oxide was at least 96 per cent pure.

The glycol from the higher boiling oxide (trans ?) could be solidified only by cooling below zero. The melting point of the crude glycol after one distillation was about 3°. This melting point indicates a purity of about 90 mol per cent. The opinion suggested by the fractionation curve of the oxides that the lower boiling material was purer than the higher, is thus confirmed.

The recrystallized glycols have been characterized by the melting points of some of their

esters. These were obtained by using a large excess of the corresponding acid chloride and dimethyl aniline or pyridine. They are diesters because the yields calculated on the basis of monoesters are more than 100 per cent. They have the same configuration as the corresponding glycols because a Walden inversion could not have taken place on the asymmetric carbon atoms because these atoms were not involved in the reactions.

$$CH_3CHOHCHOHCH_3 + 2RCOCl + 2(R^1)_3N \longrightarrow CH_3CH(OCOR)CH(OCOR)CH_3 + 2(R^1)_3NHCl \qquad (4a)$$

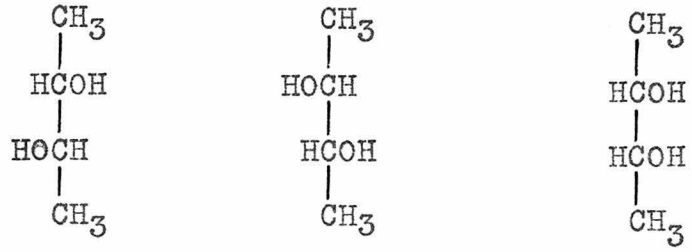
TABLE III. PROPERTIES OF THE ISOMERIC 2,3-BUTANEDIOLS

Structure	racemic (?)	meso (?)
Prepared from	cis (?) oxide	trans (?) oxide
B. p. 742 mm.	181.7°	176.7°
16 mm.	89°	86°
M. p.	34.4°	7.6°
M.p. of esters		
diacetate	2.5-3.0°	41.0-41.5°
dibenzoate	75.5-76.2°	liquid (?)
di-p-brombenzoate	139.0-139.8°	205-209°

Harden and Walpole[10] investigated the production of butene glycol by bacterial fermentations. They found the boiling point of the product to be 181-183°, the melting point to be 28°. The diphenylurethane could

be separated into two fractions, one of 90 per cent melting at 197-198°, and one of 10 per cent melting at 157°. Böeseken and Cohen[11] found the melting point of the glycol produced by a fermentation process to be 25°. The properties of the dibenzoates are in agreement with those obtained by Ciamician and Silber[12]. They prepared their compounds by fractional crystallization of a mixture of the two. It might be imagined that the reason one of them was reported as a liquid was because it was really a eutectic mixture of the two. In comparison with the other esters it seems very strange that this compound should be liquid. All attempts, starting from the known pure glycol, have thus far failed to produce a crystalline product.

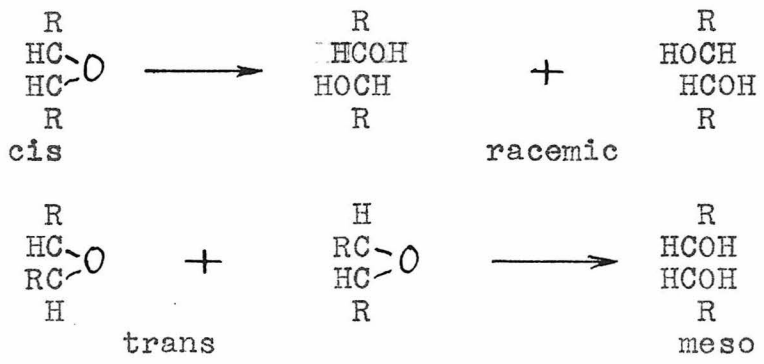
By noting that there are two asymmetric carbon atoms and a plan of symmetry in the structural formula of butene glycol, it is evident that there are three stereoisomers.



d- l- internally compensated

racemic meso

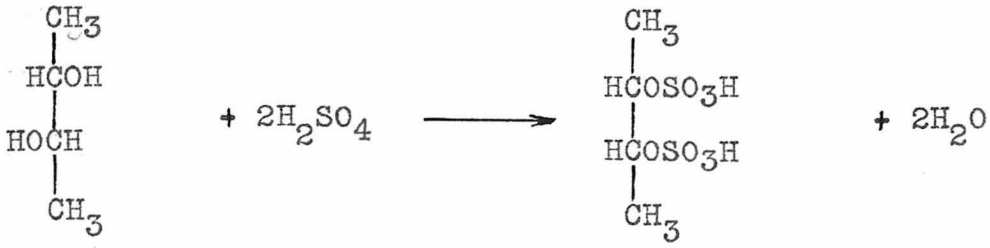
It would be very interesting to decide which configuration represents which compound, and to relate the structure of the glycol to the structure of the corresponding oxide. In the cases where the latter problem has been attacked successfully, it has been found that a Walden inversion takes place in the hydration reaction.



Kuhn and Ebel[13] found that cis-ethylene oxide-dicarboxylic acid yielded exclusively d, l-tartaric acid. However, the trans oxide yielded only 60 per cent meso tartaric acid and 40 per cent d, l-tartaric acid. Cis cyclopentene oxide gave only trans cyclopentanediol; cis cyclohexene oxide only the trans diol[14].

In the compounds that were investigated here it is not convenient to effect the resolution of the racemic glycol. This has been attempted by Böeseken and Cohen[11] by means of salts of the sulfuric acid esters. However, their results can be questioned on the ground that a Walden inversion was involved in the formation of the sulfuric acid esters. For

example the solid glycol (mp. 25) might be the racemic and behave as follows:



It would be of course impossible to resolve this compound by means of an optically active base because the molecule has a plain of symmetry. It is not stretching the point too far to speculate that such an inversion might take place. From the fact that in making esters of optically active alcohols with acids other than the carboxylic acids racemization frequently takes place, the following mechanisms for esterification has been proposed[15].

$$ROH + HOCOR^1 \longrightarrow ROCOR^1 + H_2O$$

$$ROH + HOSO_2R^1 \longrightarrow ROSO_2R^1 + H_2O$$

The slight increase in the conductivity of a boric acid solution when the low melting glycol was added is not good evidence for the structure of the compound because of free rotation around the bond connecting the two asymmetric carbon atoms. Böeseken's conclusions are further weakened by the fact that he did not have pure compounds, that the rotations of his esters were small, and that the increase in conductivity was of the same order of magnitude as

the experimental error.

Kling[16] found that by subjecting a mixture of 2,3-butanediols to bacterial oxidation an optically active glycol was left unattacked. This method was attempted here with the exception that it was not possible to use the exact organism that he used because of the changes and improvements of nomenclature. Dr. Thimann suggested an organism that has many of the properties of the one used by Kling. Some difficulty was encountered in obtaining growth on a mixture of the glycols. Finally it was possible to obtain growth on one of the isomers but an optically active residue did not result. Under further investigation this method may lead to positive results which will indicate which product is the d,l-glycol.

2,3-Dibromobutanes

Several of the usual methods for converting alcohols to bromides proved to be entirely unsatisfactory when applied to the higher melting glycol. The method[17] for secondary alcohols using a solution saturated with hydrobromic acid and zinc bromide resulted in a pinacol rearrangement and the formation of methylethylketone. This product was demonstrated by the formation and identification of the 3,5-dinitrophenylhydrazone. Methods using phosphorus

tribromide and phosphorus pentabromide resulted in very low yields and a very impure product (determination of specific gravity).

The method that was found to be satisfactory depends on the formation of the diacetate and the treatment of this with fuming hydrobromic acid solution. The diacetates were prepared by allowing acetic anhydride to remain in contact with the glycols for several days at room temperature. The products from this treatment were identical with those obtained by means of acetyl chloride. Therefore, either no Walden inversion took place or complete inversion took place about each asymmetric carbon atom. The properties of the 2,3-dibromobutanes when compared to the properties of the compounds prepared by Lucas, Young, and Dillon[2,18] indicate that no racemization took place in the reactions. Overall yields of 60 to 80 per cent were obtained for the two steps. The properties of the dibromides are given in Table IV.

TABLE IV. PROPERTIES OF THE DIBROMIDES OF THE NORMAL BUTENES

Name	Source	B.p at 50.0 mm °C	Sp.Gr. d_4^{20}	Refractive index n_D^{25}	Second-order rate with KI
d,l-2,3-dibromobutane	d,l-glycol mp.34.4°	76.4-76.6	1.7922	1.5120	0.0285
	cis-2-butene*	75.6-75.8	1.7916	1.5125	0.0297
meso-2,3-dibromobutane	meso-glycol mp 7.6°	73.2-73.4	1.7783(?)	1.5098	0.0541
	trans-2-butene*	72.7-72.9	1.7829	1.5092	0.0544
1,2-dibromobutane	1-butene*	80.5-80.7	1.7951	1.5125	0.0765

*These compounds were made and the properties determined by Young, Dillon and Lucas.

The rate constants for the reaction of the dibromides with potassium iodide in 99 per cent methanol at 75° were determined by Prof. Wm. G. Young and his students of University of California at Los Angeles. The meso dibromide may have suffered some decomposition during the latter part of the distillation. Only slightly more than was needed for the determination of the density was prepared; and it became super-heated in distilling the last material over. It is important to note that in each case where a divergence

is observed between the physical properties found here and those previously determined, the direction of the deviation is such that it could not be caused by the presence of an isomeric substance.

2-Butenes

The preparation of the butenes was accomplished by treating the dibromide with zinc and alcohol at about 80°. Young and Lucas[3] found that by converting a given dibromide to the corresponding butene, and then the butene to the dibromide by the addition of bromine, that the original material was obtained. This means that if the addition is trans it is completely trans, and that the elimination is also completely trans. It is a general rule that the addition of bromine to a double bond under ordinary conditions is more or less completely trans, that is, across the bond and not on the same side[19,20,21]. Therefore, in this case the configurations of the dibromide may be related with certainty to the structure of the butenes.

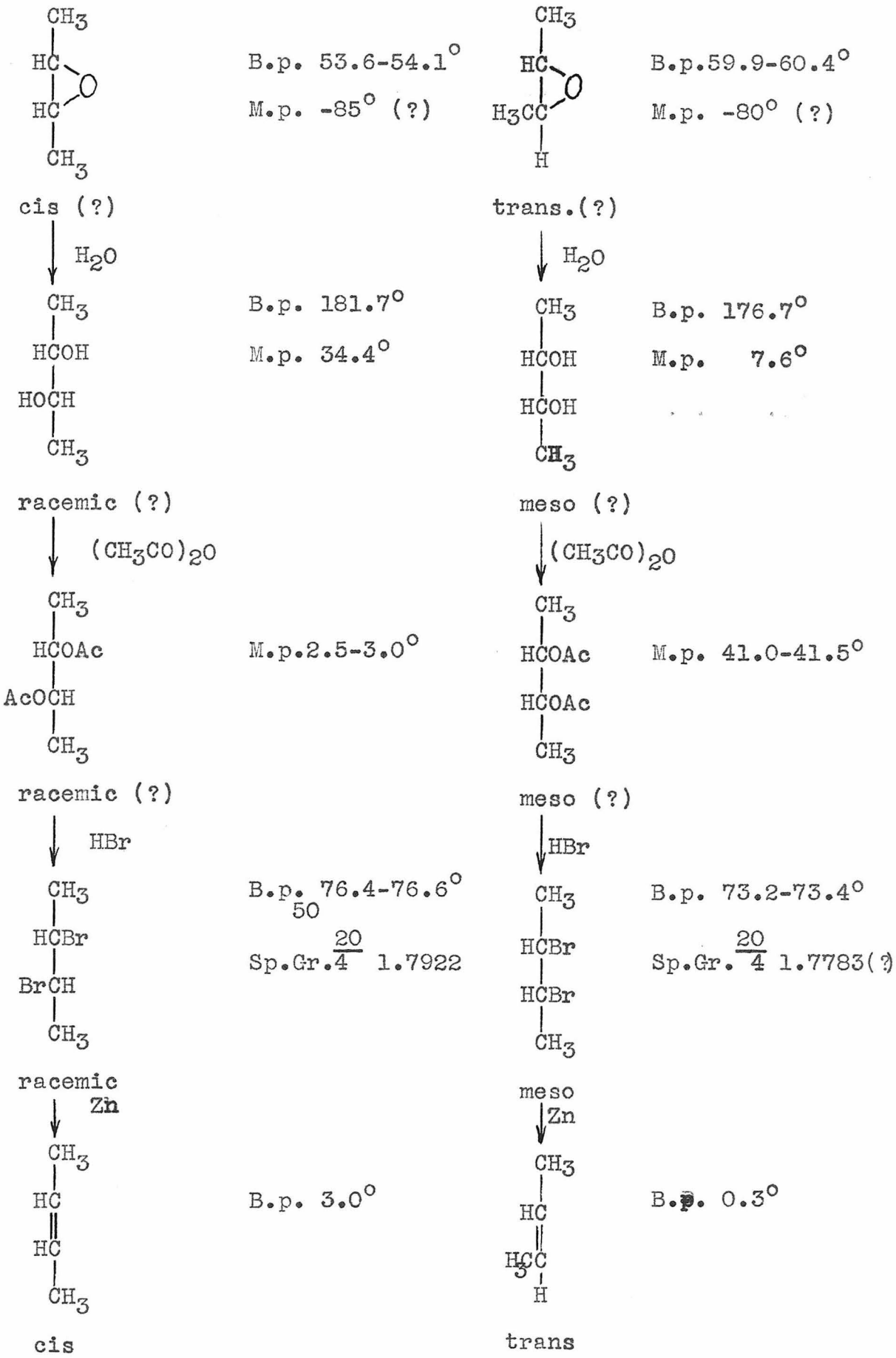
The structure of the two isomeric 2-butenes has been investigated by the electron diffraction method[22]. The material from cis-2-butene oxide and the d,l-glycol has the cis configuration. Therefore, the higher boiling 2,3-dibromobutane is the racemic.

CONCLUSIONS

A consistent relationship of all of the compounds is given in Table V. In going from the diacetate to the dibromide it is possible, although not at all probable, that a Walden inversion took place about one of the asymmetric carbon atoms and not about both. It does not seem at all possible that this would happen without some "racemization". In view of the recent work of Tronow and Ssibgatullin[23] and of Meer and Polanyi[24], it is more probable that in this particular reaction a Walden inversion does not take place about either carbon atom. However, if one Walden inversion did take place, the conclusion would be that the structures of the diacetates, the glycols, and the oxides should be reversed. This latter reversal means that either the melting points of the compounds were in error, or that the cis oxide has the higher melting point. This would be a contradiction of a general rule.

Certain phases of this work are to be continued, for example, the resolution of the glycols and the conversion of each of the butenes to the chlorohydrins and oxides for the purpose of investigating the possibilities of Walden inversions and "racemizations".

TABLE V RELATIONSHIPS



EXPERIMENTAL

2-Butene

A 2-liter three-neck flask was provided with a reflux condenser and a vertical safety tube about four feet in length, the lower end not far from the bottom of the flask and the upper end bent over so as to drain into a second flask (for collecting any material in case of a stoppage). In the flask was placed a mixture of 400 ml. of water, 600 ml. of concentrated sulfuric acid, about 10 g. of diatomaceous earth, and 444 g. (6.0 moles) of 1-butanol of commerce. The mixture was refluxed gently and the evolved butene, after passing up through the condenser, was passed in succession through a spiral wash bottle containing 3 n sodium hydroxide, two spiral wash bottles each containing 50-55% sulfuric acid, and a drying tower containing soda lime and calcium chloride. The gas was then passed downwards through a narrow tube into a previously weighed ampoule which was kept at a temperature of -15 to -20° by an ice-hydrochloric acid freezing bath. The stem of the ampoule was attached to a T-tube, the narrow tube passed through this T-tube and an airtight fit was made by means of rubber tubing. A calcium chloride drying tube was attached to the side arm exit. The yield was 220-220 grams (60-65% of the theoretical amount).

2-Butene Chlorohydrin

In a 3-liter three-neck flask provided with a mercury sealed stirrer, a delivery tube, and a reflux condenser cooled by solid carbon dioxide and alcohol were placed about 800 ml. of water, 500 of ice, and 570 g. of calcium hypochlorite (H.T.H. 65% available chlorine). The flask was cooled by a freezing bath of ice and salt at -10 to -15° and then 290 g. of 2-butene were poured in through the delivery tube from a weighed ampoule. The tube was then replaced by a dropping funnel and 700 ml. of 50% acetic acid was slowly added during vigorous agitation and continued cooling at -10 to -15°. If excessive refluxing was to be avoided, the addition of the acid required two or three hours.

The apparatus was disconnected, enough concentrated nitric acid was added to break up the emulsion, the chlorohydrin was separated and the aqueous phase extracted with three 100 ml. portions of isopropyl ether. A small amount of water was added to the combined chlorohydrin and extracts and this was neutralized by the addition of solid sodium carbonate in small portions. After this water phase was removed, the material was partially dried by shaking with anhydrous calcium chloride. The remainder of the water was removed by distillation as an azeotropic mixture with isopropyl ether. This distillation was through a 60 cm. Hemple

column provided with a Claisen neck, a reflux condenser, and with an apparatus for removing fractions of distillate without destroying the vacuum in the column. As the ether was removed the pressure was gradually lowered. The 2,3-dichlorobutane was distilled at 50-60° under 80 mm. pressure; the product at 50-60° under 30 mm. The yields were, dichloride about 115 g. (18-20%); chlorohydrin about 330 g. (55-60%). In addition there was a higher boiling residue of undertermined composition.

2-Butene Oxide

In a 3-liter three-neck flask equipped with a mercury sealed stirrer, a bent tube leading to a condenser, a dropping funnel, and a thermometer extending nearly to the bottom of the flask were added 1200 g. of solid potassium hydroxide and 600 ml. of water. At a temperature of 90 to 95°, 800 g. of chlorohydrin was slowly added with vigorous stirring. About two hours was required for the addition. After all had been added, the solution was boiled for a few minutes to carry all of the product out. The condenser and receiver were cooled with ice water during all this time. The distillate was saturated with potassium carbonate, the aqueous phase was removed, and finally the product was dried with anhydrous potassium

carbonate. Calcium chloride must not be used for this purpose because it forms an addition product with the higher boiling oxide. The material was distilled through a 60 cm. Hemple column provided with a Claisen neck and a reflux condenser. The fraction boiling at 52 to 62° was collected. Yields under different condition are given in Table VI.

TABLE VI. PREPARATION OF 2-BUTENE OXIDES

	KOH g.	Water ml.	Chloro-hydrin g.	Temp. °C.	Time hrs.	Yield g.	Yield %
1.*	20-30	15	10	90		3	45
2.	500	250	108	85	1	51	71
3.	500	250	75	70	1/4	34	68
4.	1000	500	327	90	1	202	93
5.	1000	500	409	90	2	246	91
6.	1000	500	425	90	2	250	88
7.	1000	500	400	90	2	193	73
8.	1000	500	400	90	2	215	81
9.	110	220	100	85	1/2	49	74
10.	200	300	200	90	1/2	99	75
11.	400	400	400	110	2	190	72
12.	410	400	400	105	3	200	75
13.	1000	800	880	95	3	450	77
14.	1200	600	695	95	2	380	83

*The yields for the first six experiments were calculated from the weight of undistilled product.

1700 g. of the oxide was subjected to three successive fractional distillations through a 5 ft. Hemple column equipped with a total reflux condenser and a stop-cock for removing the distillate at a controlled rate. The still was provided with a thermometer

and a separating funnel for introducing fractions at the appropriate times. It was not possible to make an estimate of the reflux ratio; the reflux was very nearly a continuous stream, the distillate about 1 drop per 1.8 sec. Fractions were removed at approximately one-half degree intervals. Bromobenzene was used as a still base for the last fractions. In order to minimize losses the distillation was carried out practically in a closed system except for a narrow exit through the cooled receiver. (Overall recovery 90 %).

The specific gravities of the fractions were determined with a ten gram piknometer; the refractive indices with an Abbé refractometer. In the determination of the melting points, a small test tube of the material containing a pentane thermometer was lowered into a Dewar flask containing a small amount of liquid air. By lowering or raising the test tube the material slowly froze or melted. The melting point was taken to be the point at which the thermometer bulb was half surrounded by crystals.

2-Butene Glycol

Six drops of 9 n perchloric acid, 300 ml. of water, and 90 g. of butene oxide were placed in a flask which was cooled under the tap from time to time to such an extent that the stopper was not forced out. In five or ten minutes enough of the oxide reacted

to change the nature of the solvent sufficiently that the remaining oxide dissolved. After one hour the solution was neutralized with 3 N sodium hydroxide and distilled. The distillation (through 12 cm. of glass rings) was done in such a manner that the temperature of the material in the flask did not go over 100°. As the water was removed the pressure was lowered and finally the product was distilled (through a dry condenser) at 15 to 20 mm. The water was saved and used for the next hydration of the same oxide, thus preventing possible loss. The yield was from 90 to 95%.

The glycols were purified by recrystallization from isopropyl ether. The higher melting one was only moderately soluble in this solvent and a very good recovery could be obtained by cooling from slightly above room temperature to about zero. The low melting one is miscible with the solvent above its melting point and it was necessary to cool to temperatures approaching that of solid carbon dioxide. The solvent was removed from the first by draining; from the second through a sintered glass filter stick by the pressure of carefully dried air. The last traces of solvent were removed from both by the continued passage of dried air. Four crystallizations of the higher melting material gave a very pure product. For the other five or six recrystallizations with a resultant large loss were necessary.

The melting points of the glycols and of different mixtures of the two were determined by weighing the materials into a stoppered test tube with a thermometer. (Since these materials are very hygroscopic, it was necessary to prevent them from coming into contact with air.) The melting point composition curve is shown in figure 2. It was not practical to make this determination for those mixtures melting much below zero because of the very slow crystallization rate. The tendency was to form a glass.

Diacetates

40 g. of 2,3-butanediol was dissolved in 135 g. of acetic anhydride. After four or five days at room temperature or slightly above, a small amount of water was added and the mixture was warmed for a short time. Then about 50 ml. of water was added and the solution was nearly saturated with calcium chloride. The product was separated and washed twice with about 25 ml. of strong calcium chloride solution. Finally the material was neutralized by adding water and small amounts of sodium bicarbonate. The product from the higher melting glycol was removed with a separatory funnel; that from the low melting glycol became solid and was filtered out.

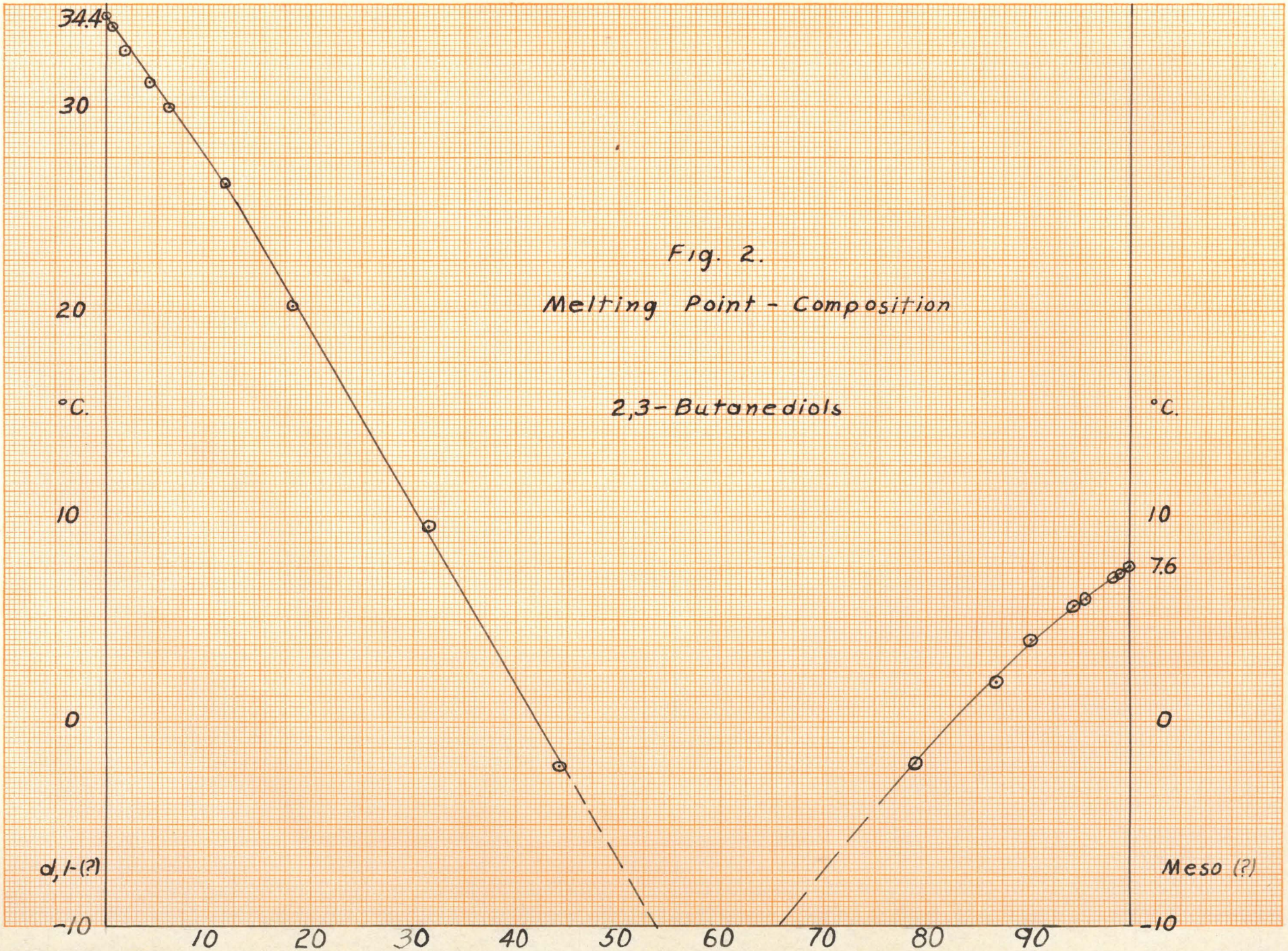
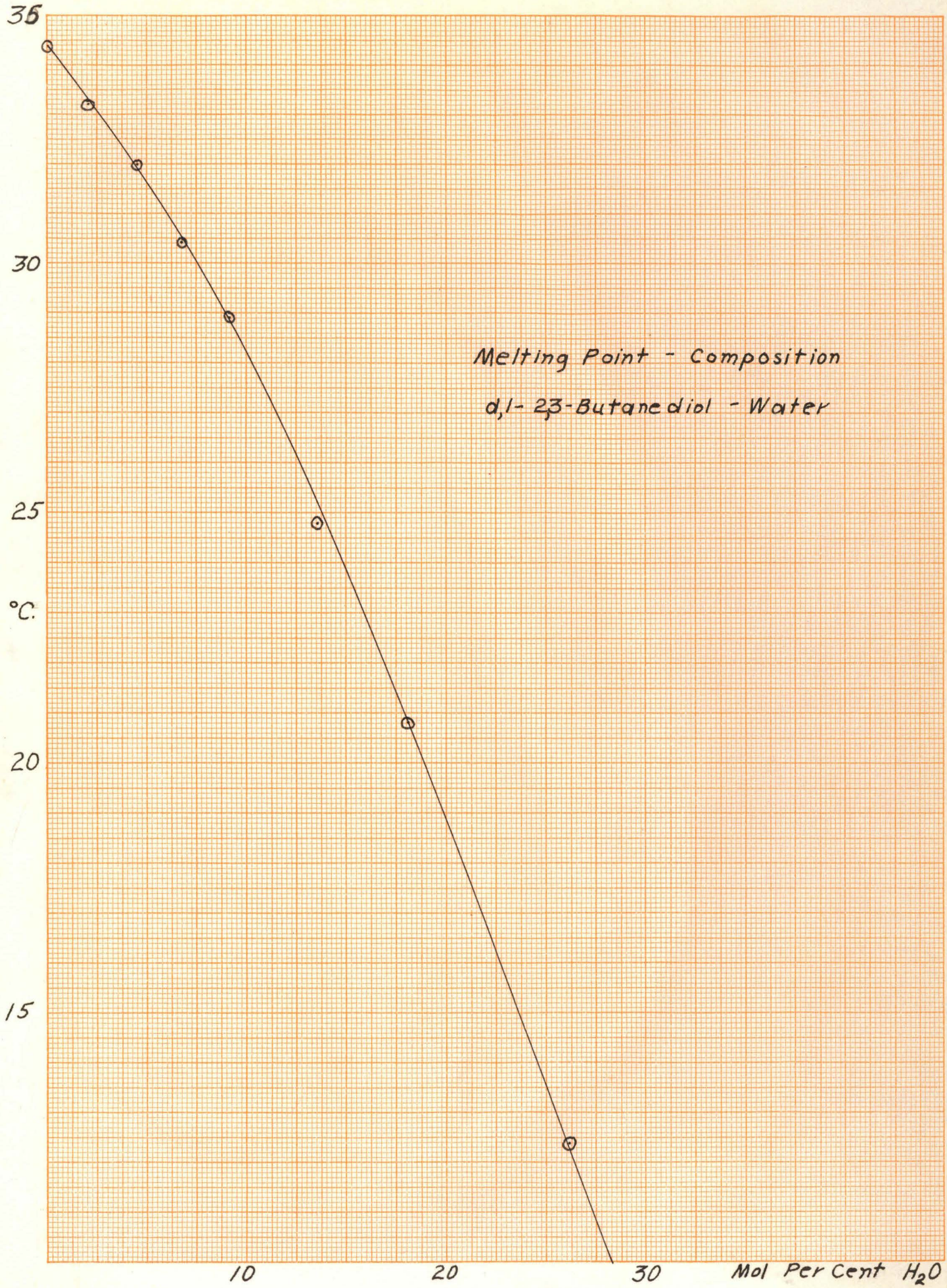


Fig. 2.

Melting Point - Composition

2,3-Butanediols


Melting Point - Composition
d,l- 2,3-Butanediol - Water
35
30
25
°C.
20
15
10
20
30
Mol Per Cent H_2O

Incidentally, advantage can be taken of the high melting point of the diacetate obtained from the low melting glycol by recrystallizing this material instead of the glycol. This glycol is rather difficult to purify; its diacetate can be easily recrystallized from petroleum ether.

2,3-Dibromobutanes

Hydrogen bromide generated by dropping bromine on to boiling tetralin and purified by passing through a drying tower filled with naphthalene was dissolved in cold constant boiling hydrobromic acid. The diacetate from 26 g. of glycol dissolved readily in 200 ml. of this saturated hydrobromic acid solution. In a short time the solution became cloudy and after three or four days the oil was separated and washed with water, sodium carbonate solution, and again with water. The overall yield for the two steps was from 60 to 80%. It is quite probable that this step could be effected with much less hydrobromic acid. This possiblity was not investigated because the reaction was carried out only twice for each of the glycols.

The products were dried with calcium chloride and distilled through a 40 cm Weston column at 50.0 mm pressue. The specific gravity of the d, l-dibromide

was determined in a ten gram piknometer; that of the meso in a five. The refractive indices were determined in an Abbé refractomer.

2-Butene

10 g. of granular zinc and 3 ml. of alcohol was placed in a 100 ml. round bottom flask which was immersed in a beaker of water at 80°. 10 g. of dibromide was dissolved in 3 ml. of alcohol and slowly added to the flask through a small separatory funnel. The evolved butene was washed by bubbling through two small traps containing 23% perchloric acid. After passing through a drying tube containing soda lime and calcium chloride, it was condensed in a tube immersed in solid carbon dioxide and alcohol. The yield was 2 grams or 80%.

SUMMARY

1. A method is given for the preparation of large quantities of 2-butene chlorohydrin.

2. A convenient method is given for the preparation of large quantities of 2-butene oxide.

3. The fractional distillation of the isomeric 2-butene oxides is described, and the properties of the two main fractions are given.

4. The hydration of the 2-butene oxides is described.

5. A method of purification and the properties of the 2,3-butanediols are given.

6. The conversions of the 2,3-butanediols to the 2,3-dibromobutanes are described.

7. The structures of the isomeric 2-butenes are given, and the relationships to the other compounds are given provisionally.

ACKNOWLEDGMENT

The author wishes to express his gratitude to Professor H. J. Lucas for suggesting this problem and for his continued help and advice in its execution. Thanks are due Professor Wm. G. Young for the determination of the reaction rates of the dibromobutanes and to Doctors Brockway and Cross for the electron diffraction measurements of the butenes. The author is also grateful to Doctor K. V. Thimann for his advice in bacteriology. Mrs. A. M. Morrill and Mr. S. E. Parker are to be commended for their cooperation.

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