7. Insulin repeatedly equilibrated in this way with conductivity water never contained more than two atoms of zinc per molecule.

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[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, NO. 782]

The Isomeric 2,3-Epoxypentanes and 2-Pentenes. The Extent to which Mixtures of Diastereomers Are Formed in Reactions of Some Pentane Compounds

BY H. J. LUCAS, M. J. SCHLATTER AND R. C. JONES

The isomeric *cis* and *trans*-2-pentenes have been the subject of numerous investigations.[1–6] Their preparation from the isomeric 2,3-epoxypentanes analogous to the preparation of *cis* and *trans*-2-butene from *trans* and *cis*-2,3-epoxybutane,[7] and from *cis* and *trans*-2,3-epoxybutane[8] has been accomplished. In addition, a study has been made of the extent to which a single reaction only takes place during a given chemical change, that is to say, if the change takes place with complete retention of configuration or with complete inversion of configuration, whichever the case may be. This could not be done for any single chemical change, however, but only for a group of two or more changes.

The changes investigated are shown in Fig. 1. Here only one of the two antipodes of *dl*-mixtures is shown. The configurations have been assigned on the basis that they are analogous to the configurations of the corresponding butane derivatives, for no evidence is available from these reactions or from the physical properties of the pentane derivatives themselves. This assignment of configuration to the pentenes, however, agrees in general with those made previously.[1,3,4,5b,6c,9] Walden inversions are indicated by the conventional arrow and circled shaft. The dotted arrows indicate that the reaction was not tried, but is predicted.

Figure 1 shows how each isomeric 2,3-epoxypentane can be converted into *cis* and *trans*-2-pentene by two different paths. One path involves the following steps: oxide -○→ glycol ⟶ diacetate -○→ dibromide -○→ 2-pentene. The other path is: oxide -○→ bromohydrin ⟶ dibromide -○→ 2-pentene. In the first case three inversions are involved and in the second, two inversions. It is possible to pass from any one compound shown to any other compound (for this purpose each bromohydrin mixture is regarded as a compound) if it can be assumed that hypobromous acid adds to 2-pentene with one inversion, as it does to 2-butene.[8] The step involved here, *viz.*, 2-pentene -○→ bromohydrin, was not investigated. Although it would be possible to prepare the *cis* oxide from the *trans* oxide, and *vice versa*, and also the *cis*-2-pentene from the *trans*-2-pentene, and *vice versa*, no product would be entirely free of its isomer, as discussed later.

The starting materials for the cycle were the *cis*- and *trans*-2,3-epoxypentanes, which were obtained as 100% and 98% pure products, respectively, by fractional distillation at 200 mm. of a mixture of the two isomers.[10] This mixture was obtained from a mixture of the isomeric 2-pentenes[11] through the chlorohydrins by the procedure employed with the corresponding C_4 compounds.[7] The much greater separation of the boiling points of the oxides (4.9 at 200 mm. and 5.2° at 748 mm., Table II) as compared to 0.6° in the case of the 2-pentenes, shows the advantage of fractionating the oxides.

The lower boiling oxide, approximately 75% of the total, was assigned the *trans* configuration and the higher boiling oxide the *cis* configuration, analogous with the butene oxides.[7,12]

The stereochemical relationship between *trans*-2-pentene, *trans*-2,3-epoxypentane, and the intermediate chlorohydrin presumably is correctly

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(1) (a) Bourguel, *Bull. soc. chim.* [4] **41**, 1475 (1927); (b) Bourguel, Grédy and Piaux, *Compt. rend.*, **195**, 129 (1932); (c) Grédy, *Bull. soc. chim.*, [5] **2**, 1029 (1935).

(2) Clark and Hollonquist, *Trans. Roy. Soc. Can.*, [3] **24**, Sect. 3, 1115 (1930).

(3) Kharasch, Walling and Mayo, THIS JOURNAL, **61**, 1559 (1939).

(4) Lauer and Stodola, *ibid.*, **56**, 1215 (1934).

(5) (a) Lucas and Moyse, *ibid.*, **47**, 1459 (1925); (b) Lucas and Prater, *ibid.*, **59**, 1682 (1937).

(6) (a) Sherrill, Otto and Pickett, *ibid.*, **51**, 3023 (1929); (b) Sherrill, Baldwin and Haas, *ibid.*, **51**, 3034 (1929); (c) Sherrill and Matlock, *ibid.*, **59**, 2134 (1937); (d) Sherrill and Launspach, *ibid.*, **60**, 2562 (1938).

(7) Wilson and Lucas, *ibid.*, **58**, 2396 (1936).

(8) Winstein and Lucas, *ibid.*, **61**, 1576 (1939).

(9) Carr and Stücklen, *ibid.*, **59**, 2138 (1937).

(10) The authors are indebted to Mr. Herbert Sargent for his assistance in carrying out this separation.

(11) From secondary amyl alcohol, by the method of Norris and Reuter, THIS JOURNAL, **49**, 2624 (1927).

(12) Brockway and Cross, *ibid.*, **59**, 1147 (1937).

represented by the scheme, Fig. 1, analogous with the C_4 compounds, for it has been shown that *trans*-2-butene yields *trans*-2,3-epoxybutane,[7] and that one inversion accompanies the formation of *cis*-2,3-epoxybutane from the corresponding bromohydrin.[8]

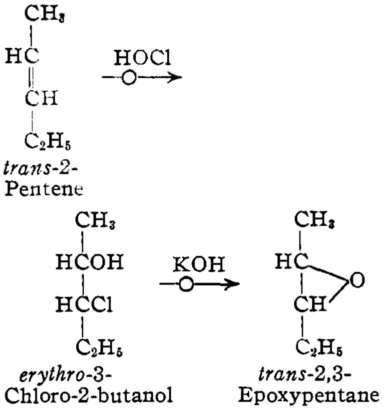
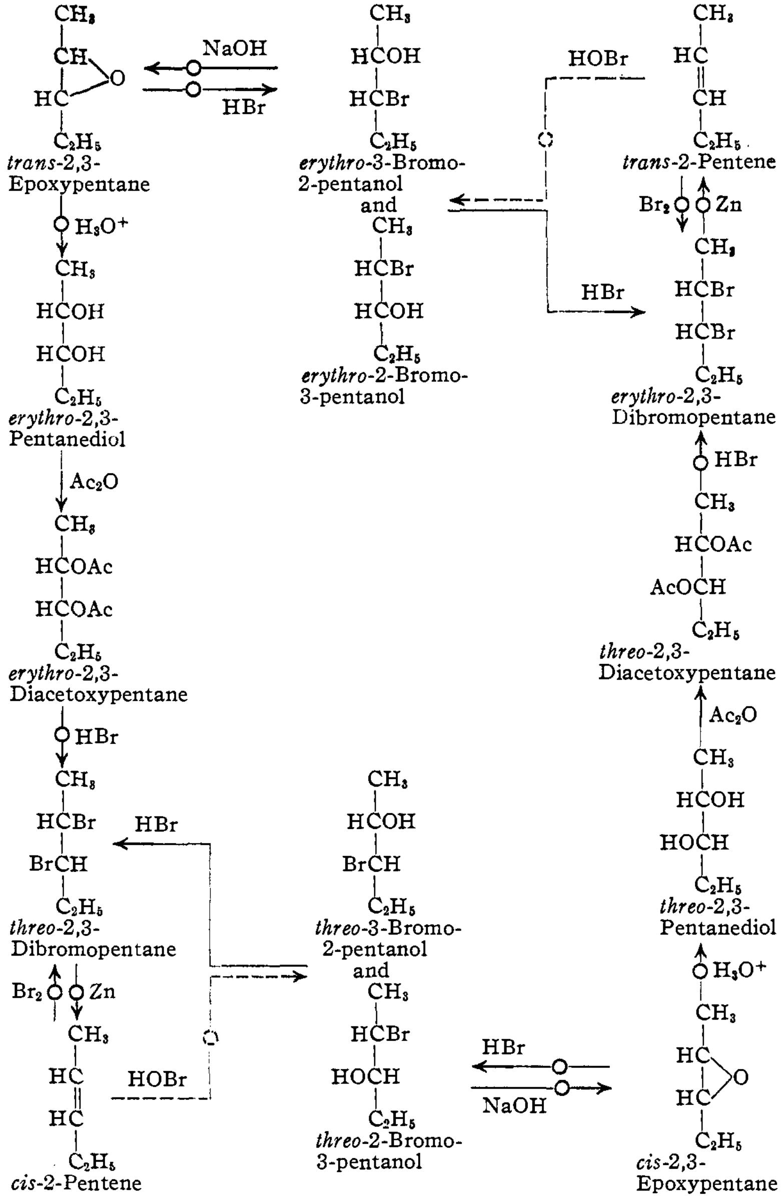


Fig. 1.



Presumably a similar relationship holds for *cis*-2-pentene and *cis*-2,3-epoxypentane.

The composition of the original crude 2-pentene mixture therefore is approximately 75% *trans* and 25% *cis*, on the basis of the oxide composition. This agrees with conclusions drawn previously.[5b,6c,d]

The conversion of the epoxypentanes to dibromopentanes by both methods (Fig. 1) presented no particular difficulty, for all the reactions proceed at room temperature, although slowly in the case of hydrobromic acid with bromohydrins and diacetates, and all the products can be purified by distillation at 50 mm. without alteration. In order to obtain the two dibromides in a high state of purity each was purified by a systematic process of crystallization at −80° from aqueous methanol. Kharasch, Walling and Mayo[3] have used this solvent for purifying the higher melting (*threo*) isomer.

The purity of different specimens of the diastereomeric 2,3-dibromopentanes can be ascertained by comparing their properties with the properties of the specimens purified by crystallization. As in the case of the 2,3-dibromobutanes,[8,13] the property most useful for this purpose is the dielectric constant, ϵ, which differs markedly for the two *dl* forms. On the other hand, the refractive index and specific gravity values differ by only small amounts (Table I).

The dielectric constant of mixtures of the dibromides deviates slightly from linearity, as shown in Fig. 2. The corrections to be applied, as shown in Fig. 3, reach a maximum at a composition of 50%. This correction, although small, must be taken into account. The error of the method is less than 0.1%.

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[13] Wood and Winstein, THIS JOURNAL, **62**, 548 (1940).

Table I

Properties of *dl*-2,3-Dibromopentanes

Isomer	Source	Path	Crystallization	F. p., °C.	B. p. °C.	B. p. Mm.	n^{20}_D	d^{25}_4	ϵ	Purity, %
erythro	2-Pentene		Yes	−56.0	91	50	1.5087	1.6724	5.4288	100.00
erythro	*trans* Oxide	Bromohydrin	No		91	50			5.4288	100.00
erythro	*cis* Oxide	Diacetate	No		91	50			5.5151	91.41
erythro	*erythro* Dibromide	*trans*-2-Pentene	No		91	50			5.4476	98.13
threo	*cis* Oxide	Bromohydrin	Yes	−32.4	94	50	1.5089	1.6745	6.5072	100.00
threo	*cis* Oxide	Bromohydrin	No		94	50			6.4857	98.14
threo	*trans* Oxide	Diacetate	No		94	50			6.4316	93.61
threo	*threo* Dibromide	*cis*-2-Pentene	No		94	50			6.4723	97.09

Purity of the 2,3-Epoxypentanes.—Since the *erythro* dibromopentane obtained from the *trans* oxide through the bromohydrin was 100% pure, as measured by the dielectric constant, it is reasonable to conclude that the *trans* oxide was 100% pure also. Thus in the following changes

$$\text{Oxide} \xrightarrow{\circ} \text{Bromohydrin} \longrightarrow \text{Dibromide}$$

the first reaction takes place with 100% inversion, the second with 100% retention of configuration. Assuming that a similar relation holds in the conversion of the *cis* oxide to the *threo* dibromide, the purity of the *cis* oxide was 98.14%, *i. e.*, the same as the purity of the dibromide.

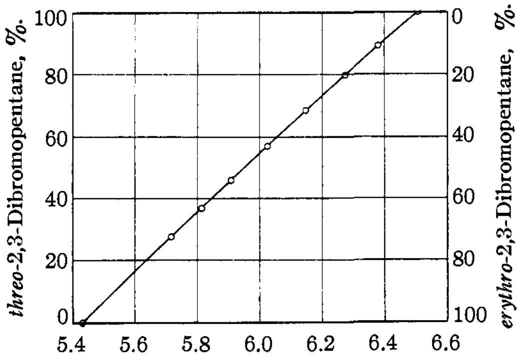

Fig. 2.—Plot of $\epsilon^{25°}$ for mixtures of *erythro*- and *threo*-2,3-dibromopentane.

Extent of Diastereomer Formation.[14]—When the 2,3-epoxypentanes are converted into bromohydrins with hydrobromic acid, and the latter to 2,3-dibromopentanes with hydrobromic acid, only one product results, as pointed out above. However, when the dibromide is made from the oxide through the steps

$$\text{Oxide} \xrightarrow{\circ} \text{Glycol} \longrightarrow \text{Diacetate} \xrightarrow{\circ} \text{Dibromide}$$

the extent of diastereomer formation is approximately 7.5%, as shown by the purity of 93.61% of the *threo* dibromide from the 100% pure *trans* oxide, and the purity of 91.41% of the *erythro* dibromide from the 98.14% pure *cis* oxide. In these two cases the extent of the side reaction is 6.4 and 7.0%, respectively.

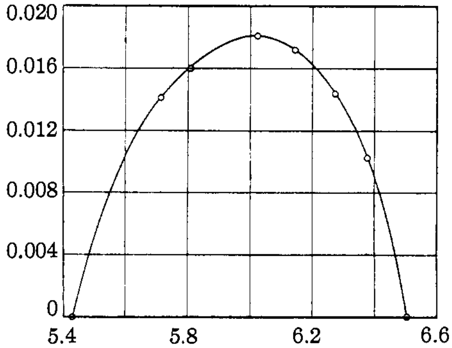

Fig. 3.—Deviation of $\epsilon^{25°}$ from linearity plotted against $\epsilon^{25°}$ of 2,3-dibromopentane mixtures.

The side reaction in the cycle above probably takes place during the opening of the oxide ring, for the glycols themselves did not melt sharply and the solid 3,5-dinitrobenzoates prepared from the glycols for identification purposes were somewhat impure. Five or six crystallizations were necessary before the melting points were constant. It seems probable therefore that the glycols and diacetates were not better than 93% pure.

The extent of the side reaction in the cycle of changes involved in preparing the pentene from the pure dibromide and then reconverting the hydrocarbon to dibromide is 2 or 3%:

$$\text{2,3-Dibromopentane} \xrightarrow{\circ} \text{2-Pentene} \xrightarrow{\circ} \text{2,3-Dibromopentane}$$

From Table I it can be seen that the purity of the final dibromide from the initially pure *erythro* and *threo* dibromide is 98.13 and 97.09% respectively. Although it is not possible from the data available to decide at which step the side reaction comes in, it seems reasonable to believe that it accompanies

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(14) The expression diastereomer formation is used to indicate that the replacement at one of the two asymmetric carbon atoms is less than 100% retention or inversion of configuration, whichever the case may be, *i. e.*, a second reaction accompanies the main reaction. Essentially this is equivalent to racemization, but since these compounds are optically inactive, no change in rotatory power is observable.

the addition of bromine to the hydrocarbon. In any case, the hydrocarbons are better than 97% pure.

The extent of the side reaction in the following cycle is zero, within experimental error:

2,3-Epoxypentane —○→ Bromohydrin —○→ 2,3-Epoxypentane

The refractive index of each of the final epoxypentanes was identical with the initial value. Although from the refractive index values alone (1.3867 and 1.3941; see also Table II) a contamination up to 2% might not be detected, the constancy of the refractive index in the different fractions obtained by fractional distillation of each oxide indicates that the products were essentially 100% pure.

***cis-* and *trans*-2-Pentenes.**—These were obtained from the corresponding 2,3-dibromopentanes by the action of metallic zinc. They were distilled in an all glass apparatus in an atmosphere of nitrogen. The physical constants of the hydrocarbons are shown in Table VI.

There is a difference of 0.6° in the boiling points of the two hydrocarbons. Compared to the values observed by others, the boiling points recorded here are slightly lower. The refractive index of the *trans* isomer agrees well with the values of others,[3,4,5] but that of the *cis* isomer is higher than any other value.[3,5b,6c,6d] Hydrogenation of 2-pentyne[1c,3,6d] does not appear to give as pure *cis*-2-pentene as does debromination of the *threo* dibromide.[8]

Experimental

2-Pentene.—Secondary amyl alcohol was fractionally distilled and the fraction distilling at 115–120° was dehydrated according to the method of J. F. Norris and Reuter.[11] 520 g. (5.9 mole) of the alcohol was added slowly to a cold mixture of 600 ml. water, 600 ml. concentrated sulfuric acid and 3 g. diatomaceous earth in a liter. 3-necked flask equipped with safety tube and short Hempel column attached to a long condenser, the latter attached to a 1-liter flask surrounded by ice. The mixture was heated at 90–110° for about three hours, or until no more pentene distilled; crude yield 398 g. (5.7 moles). This was shaken with dilute sodium hydroxide, dried with calcium chloride and combined with several other batches. This was subjected to careful fractional distillation so as to obtain a fraction over the range, 35.5–35.8° at 742 mm.; yield, 55%.

2-Pentene Chlorohydrin.—The mixture of isomeric 2-pentenes (4.5 kg.) was converted into the mixed chlorohydrins in the usual manner.[7] Working in batches of 250 g. (3.57 moles) of 2-pentene, 392 g. of H. T. H. (65% available chlorine),[15] 600–700 g. of a mixture of water and ice, and 240 g. (4.0 moles) of glacial acetic acid, a 47.5% yield of mixed chlorohydrin, b. p. 64–71° at 30 mm., was realized. The total amount was about 3900 g.

2,3-Epoxypentane.—A total of 3850 g. (31.4 moles) of the mixed chlorohydrins was converted into the oxide[7] in batches as follows: In a 3-liter 3-necked flask provided with a mercury seal stirrer, a bent tube leading to a condenser for downward distillation, a dropping funnel, and a thermometer extending nearly to the bottom of the flask, 1350 g. (24 moles) of technical potassium hydroxide flakes was dissolved with stirring in 675 ml. of water. With the temperature in the flask at about 125°, 625 g. (5.10 moles) of 2-pentene chlorohydrin was added slowly with agitation over a period of three hours. Wet 2,3-epoxypentane distilled and was partially dried with potassium carbonate. The rest of the water was removed by cooling the oxide to −80° in a carbon dioxide–alcohol freezing mixture and drawing off the dry oxide from the ice crystals through a filter stick while the mixture was still in the cooling-bath. The yield of mixed 2,3-epoxypentane was 2612 g. (30.4 moles) or 96%.

The Isomeric 2,3-Epoxypentanes.—The mixture was fractionally distilled through a four-foot, total reflux column filled with glass helices and equipped with a manostat which maintained the pressure within ±0.5 mm. Fractionation was carried out at 200 mm. because of the possibility that some rearrangement might take place if the mixture were subjected to extended heating at higher temperature. Four fractionations resulted in almost complete separation of the two isomers.

The lower boiling oxide was obtained over a range of less than 0.1°, the higher boiling over a range of about 0.2°. There was a loss of about 50% during the fractionations which were conducted intermittently over a period of more than a year. The approximate weight of pure *trans* isomer obtained was 900 g. and of the *cis* isomer, 200 g. These oxides are pleasant smelling liquids, slightly soluble in water, readily soluble in the usual organic solvents.

TABLE II

2,3-Epoxypentane	B. p., °C., at mm. 748	200	n^{20}_D	n^{25}_D	d^{25}_4
cis	85.4	48.6	1.3941	1.3915	0.8195
trans	80.2	43.7	1.3867	1.3840	0.8031

From the form of the distillation curve, it was determined that the original oxide mixture was approximately 75% *trans*. This indicates that the pentene mixture obtained from secondary amyl alcohol is about 75% *trans*-2-pentene.

The Isomeric 2,3-Pentanediols.—240 g. (2.78 moles) of *trans*-2,3-epoxypentane, 1500 ml. of water and 0.2 ml. of concentrated sulfuric acid were stirred vigorously at room temperature for eight hours in a 2-liter flask equipped with a reflux condenser and mechanical stirrer. The initially heterogeneous system became homogeneous after three hours. The acid was neutralized with sodium hydroxide and the water distilled off on a water pump, keeping the bath temperature below 70°. On distilling the residue at 10 mm. from a Claisen flask, *erythro*-2,3-pentanediol distilled as a viscous liquid; yield, 236 g. (81%). A like yield was obtained with the *threo* isomer, from the *cis* oxide.

Both compounds are viscous liquids, readily soluble in

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(15) Calcium hypochlorite, Mathieson Alkali Works, Inc.

water, alcohol and isopropyl ether. Attempts to crystallize them were unsuccessful. Each reacted readily when heated with 3,5-dinitrobenzoyl chloride to yield a solid di-3,5-dinitrobenzoate, which required five or six crystallizations from pyridine before the melting point was constant.

Table III

dl-2,3-Pentanediol	B. p., °C., 10 mm.	n^{20}_D	d^{25}_4	M. p. (cor.) of di-3,5-dinitrobenzoate, °C.
erythro	89	1.4431	0.9782	207
threo	83	1.4320	0.9654	160.5

The Isomeric 2,3-Diacetoxypentanes.—Fifty-two grams (0.50 mole) of *erythro*-2,3-pentanediol and 117 g. (1.15 mole) of freshly distilled acetic anhydride were mixed in a 500-ml. flask equipped with reflux condenser and drying tube, and two drops of concentrated sulfuric acid added.[7] The mixture began to reflux spontaneously and was kept under control by cooling with an ice-bath when necessary. The mixture was allowed to stand overnight, the acetic acid and excess acetic anhydride distilled off using a water pump and the residue fractionally distilled through a short Vigreux column at 10 mm., yielding 83 g. of *erythro*-2,3-diacetoxypentane (88%). A like yield was obtained with the *threo* isomer.

Both compounds are liquids less viscous than the diols, but more viscous than the dibromides made from them. They are insoluble in water, readily soluble in the usual organic solvents. The dielectric constant ϵ, has been reported previously.[13]

Table IV

dl-2,3-Diacetoxypentane	B. p., °C. at 10 mm.	n^{20}_D	d^{25}_4	ϵ^{25}
erythro	85	1.4167	1.0022	6.734
threo	89	1.4195	1.0073	5.228

The 2,3-Dibromopentanes from the 2,3-Diacetoxypentanes.—In 350 ml. of hydrobromic acid saturated with hydrogen bromide[16] at 0° was dissolved 125.5 g. (0.67 mole) of *erythro*-2,3-diacetoxypentane. The liquid was sealed in an ampoule made from a 500-ml. round bottom flask, allowed to warm to room temperature and shaken occasionally for two days. After two or three hours the liquid turned cloudy, due to the separation of dibromopentane, and later a distinct second phase was visible. In some preparations of dibromide, from diacetates, bromohydrins or oxides, the dibromide phase was lighter, in others heavier, than the aqueous phase, depending upon the degree of saturation with hydrogen bromide. The ampoule was opened, resaturated with hydrogen bromide at 0°, sealed and shaken occasionally for four days, at which time both phases were clear and the reaction was over. The organic phase was always the lighter. The ampoule was chilled, opened and the phases separated without dilution in a separatory funnel. The organic phase after washing with water and dilute sodium carbonate and drying with calcium chloride, was fractionated at reduced pressure through a 60-cm. total reflux column packed with glass helices to yield 138 g. (0.60 mole) of *threo*-2,3-dibromopentane, 90% of theory. A like yield was obtained with the *erythro* isomer. The physical constants are given in Table I and the purity is discussed in the first part of this paper.

The 2-Pentene Bromohydrins.—In a 500-ml. 3-necked flask fitted with a mechanical stirrer, dropping funnel and thermometer dipping into the reaction mixture was placed 200 ml. of 48% hydrobromic acid. Into the flask surrounded by an ice-bath, 86 g. (1 mole) of *trans*-2,3-epoxypentane was run in over a period of three hours, the temperature of the reaction mixture never rising above 5°. The mixture was stirred one hour longer and separated. The aqueous phase was diluted with 200 ml. of water and extracted with two 50-ml. portions of ether. A little anhydrous potassium carbonate was added to the extracts. After standing overnight, the ether phase was concentrated on a water-bath. The bromohydrin was distilled through a short Vigreux column at 10 mm., yielding 151 g. of *erythro* bromohydrin, 90% of theory. A like yield was obtained with the *threo* isomer. These compounds are liquids only slightly soluble in water, soluble in organic solvents. On standing for some time specimens of the bromohydrins became colored, some samples more quickly than others. The *erythro* isomer became blue-violet, the *threo*, wine red. When redistilled at 10 mm., the distillate was colorless, and the small undistilled residue was dark colored, almost black. On high dilution the characteristic color developed.

The physical constants, Table V, may have little significance for each preparation probably is a mixture of two compounds (Fig. 1). However, each acts as a pure substance to give a single oxide when heated with aqueous potassium hydroxide.

Table V

dl-2-Pentene bromohydrin	B. p., 10 mm., °C.	n^{20}_D	d^{25}_4
erythro	59	1.4717	1.3654
threo	53	1.4758	1.3636

The 2,3-Dibromopentanes from the 2-Pentene Bromohydrins.—One hundred eighty ml. of 48% hydrobromic acid in a 300-ml. ampoule was sautrated with hydrogen bromide[16] at 0°, and 50 g. (0.30 mole) of *erythro*-2-pentene bromohydrin added. The ampoule was sealed and allowed to come to room temperature. Cloudiness developed in about one hour. The mixture was shaken occasionally for seven days. By this time both phases were clear. The product was worked up as described above, yielding 65 g. (0.28 mole) of *erythro*-2,3-dibromopentane, 94%. A like yield was obtained with the *threo* isomer. The physical constants are given in Table I, and the purity is discussed in the first part of this paper.

The 2,3-Dibromopentanes from the 2,3-Epoxypentanes.—The dibromides may be prepared directly from the epoxides without isolating the bromohydrins. To 500 g. of 48% hydrobromic acid in a 1-liter 3-necked flask equipped with dropping funnel, thermometer and mechanical stirrer and surrounded by an ice-bath, was added 172 g. (2 moles) of *trans*-2,3-epoxypentane over a period of three hours, the temperature never rising above +5°. The mixture was transferred to an ampoule made from a 1-liter round-bottom flask, enough 48% hydrobromic acid added to make the volume about 750 ml. and the mixture saturated with hydrogen bromide.[16] The ampoule was sealed, then allowed to warm to room temperature. Cloudiness

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(16) From bromine and tetralin.

appeared in one to three hours. The mixture was shaken occasionally over a period of three days. The ampoule was opened, again saturated with hydrogen bromide, sealed, allowed to warm to room temperature and shaken occasionally. At the end of three more days both phases were clear. The organic phase was worked up as before, and fractionally distilled through a 40-cm. Vigreux total-reflux column at 10 mm., to yield 428 g. of *erythro*-2,3-dibromopentane, 93%. A like yield was obtained with the *threo* isomer. The physical constants are given in Table I, and the purity is discussed in the first part of this paper.

Crystallization of Dibromides.—The dibromides were diluted with one-half to two times their volume of methanol[3] in 250 ml. centrifuge bottles, and then cooled to −78° in carbon dioxide–isopropyl ether freezing mixtures. The liquids were seeded with crystals obtained by cooling small samples of the mixtures in liquid air until they were frozen solid and then placing them in the carbon dioxide–isopropyl ether mixtures. The chilled methanol solutions were stirred frequently to hasten crystallization and to prevent the formation of cakes. *threo*-2,3-Dibromopentane crystallized easily in a coarse, loose form, but the *erythro* isomer crystallized with more difficulty in leaflets which were harder to centrifuge. The more impure the dibromide, the longer the time required for complete crystallization. This varied from eight to ten hours for the 75% *erythro*-2,3-dibromopentane diluted with one-half volume of methanol to ten or fifteen minutes for the pure *threo*-2,3-dibromopentane diluted with one volume of methanol. The *erythro* isomer, because of its greater solubility (necessitating the use of more concentrated and therefore more viscous solutions) and lower melting point, was much more difficult to purify in good yield by crystallization than was the *threo* isomer. With both isomers, it was sometimes found advantageous to use methanol containing a small amount of water in place of pure methanol as a solvent.

When crystallization was thought to be complete, the crystals were loosened from the sides of the centrifuge bottle with a stirring rod and the mixture centrifuged rapidly for 2 to 5 min. in a centrifuge chilled with "dry ice." The supernatant liquid was poured off, the crystals washed with a small portion of methanol at −78°, the mixture centrifuged and the washings combined with the mother liquor. In this way a network of crystallizations was carried out, using the mother liquor from one crystallization for a less pure batch of dibromide. From time to time the dibromide crystals (after melting) were diluted with an equal volume of water, separated, washed with water, dried with calcium chloride and distilled at 50 mm. The dielectric constants were then determined and in this way the progress of the purification was followed. A network of about 35 or 40 crystallizations in all was made in the purification of each isomer.

The centrifuge used in this work was heat insulated and chilled by keeping the floor of the shield covered with a considerable amount of powdered "dry ice." In addition, the heavy bronze centrifuge cups were cooled in carbon dioxide–isopropyl ether before placing the chilled centrifuge bottles in them.

In order to obtain a large amount of the pure *erythro* dibromide, crude 2-pentene, from *s*-amyl alcohol and sulfuric acid,[11] was converted into the dibromide and this was subjected to fractional crystallization. The crystallization of the *erythro* isomer was difficult at first. The method probably would work better if the dibromide mixture were subjected beforehand to fractional distillation so as to remove some of the *threo* isomer.

The Dielectric Constants.—These were determined according to the procedure described by Wood and Winstein, using the same apparatus.[13] It was found that the dielectric constant of mixtures is not strictly additive (Fig. 2) but that correction must be made. The maximum deviation from a straight line is about 1.5% for a 50-50 mixture (Fig. 3). There is less than 0.1% error in the analysis of mixtures of the two *dl*-2,3-dibromopentanes by means of the dielectric constant, when the proper correction is made. This method of analysis is superior to any others because of accuracy and rapidity, and also because the material can be recovered.

***cis* and *trans*-2-Pentene.**—In a 500-ml. flask equipped with a dropping funnel and a 15-cm. Vigreux column with a cold finger condenser cooled by ice water, was placed 75 g. (1.15 mole) of 10 mesh zinc shot and 250 ml. of absolute alcohol. The mixture was held at 70° by means of a water-bath while 230 g. (1.0 mole) of *erythro*-2,3-dibromopentane was added over a period of one and one-half hours. The pentene distilled out as formed along with some alcohol, and was collected in a receiver at −80°. The condensate was washed with three 100-ml. portions of ice water and allowed to stand overnight with magnesium perchlorate. The pentene was fractionated in an atmosphere of nitrogen without removing the solid, through a 60-cm. total reflux column packed with glass helices. The *trans*-2-pentene which distilled completely with no range, weighed 52 g., 74% of theory. For preparing *cis*-2-pentene, 140 g. (0.61 mole) of the *threo* dibromide was taken. A like yield resulted. The thermometer used was calibrated against a thermometer having a Bureau of Standards calibration. The constants are shown in Table VI.

TABLE VI

2-Pentene	B. p. °C.	B. p. Mm.	$n^{20}D$	d^{20}_4	d^{25}_4
cis	36.08	744	1.3828	0.6554	0.6504
trans	35.48	744	1.3798	0.6475	0.6426

The 2,3-Dibromopentanes from the *cis*- and *trans*-2-Pentenes.—Into a 50-ml. 3-necked flask surrounded by an ice-bath and equipped with a mechanical stirrer and two dropping funnels, was run in simultaneously 13.0 g. (0.186 mole) of *trans*-2-pentene and sufficient bromine to maintain at all times a slight excess of bromine.[17] The addition required about one and one-half hours. A small amount of hydrogen bromide was given off. The dibromide was shaken with sodium bisulfite solution, water and dilute sodium carbonate, separated, dried with calcium chloride and distilled. The product, *erythro*-2,3-dibromopentane, weighed 37.0 g., 87%. A like yield was obtained with the *threo* isomer. The properties of these dibromides are given in Table I. The purity is discussed in the first part of this paper.

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(17) In order to minimize the coupled reaction of addition and substitution, which is aided by excess of pentene and by rapidity of addition, the bromine should be in slight excess and the reaction should be carried out slowly in diffused light.

The 2,3-Epoxypentenes from the 2-Pentene Bromohydrins.—The procedure is similar to that described for preparing the epoxide from the chlorohydrin. When 33.4 g. (0.2 mole) of *erythro*-2-pentene bromohydrin was added slowly with agitation to a solution of 56 g. (1 mole) of potassium hydroxide pellets in 25 ml. of water at 100–110° in a 100-ml. 3-necked flask equipped with mercury sealed stirrer, thermometer, dropping funnel and condenser arranged for distillation, wet epoxypentane distilled over. This was dried with magnesium sulfate and distilled through a 30 cm. Vigreux column with finger condenser at a reflux ratio of ten, yielding 12 g. (70% yield) of *trans*-2,3-epoxypentane, 80% of which distilled between 80.0 and 80.2° at 746 mm. Nothing came over above 80.2°. The refractive index of the last 2 ml. of distillate was $n^{25}D$ 1.3840, identical with the value for pure *trans*-2,3-epoxypentane (Table II). Thus the reaction product was pure *trans*-2,3-epoxypentane, for any *cis* isomer, had it been present, would have become concentrated in the last 2 ml. of distillate.

Similarly 18 g. (0.108 mole) of *threo*-2-pentene bromohydrin with 35 g. (0.6 mole) of potassium hydroxide in 20 ml. of water gave 7 g. (0.08 mole) of *cis*-2,3-epoxypentane, distilling 85.2–85.4° at 750 mm. As soon as the water was removed, the rest of the distillate (90% of the total) was collected in two approximately equal fractions. The refractive index of these two was $n^{25}D$ 1.3915, identical with the value for pure *cis*-2,3-epoxypentane.

Summary

The oxide of 2-pentene has been separated into the *cis* and *trans*-2,3-epoxypentanes by fractional distillation.

cis-2-Pentene and *trans*-2-pentene have been synthesized from the isomeric 2,3-epoxypentanes.

With hydrobromic acid, *trans*-2,3-epoxypentane is converted into 100% pure *erythro*-2,3-dibromopentane and *cis*-2,3-epoxypentane into *threo*-2,3-dibromopentane.

Through the steps, 2,3-pentanediol, 2,3-diacetoxypentane and 2,3-dibromopentane the *cis* oxide yields the *dl-erythro* dibromide, and the *trans* oxide the *dl-threo* dibromide mainly. The formation of the other isomer takes place to the extent of about 7%.

When a pure *dl*-2,3-dibromopentane is converted into the corresponding 2-pentene, and this is allowed to react with bromine, the resulting dibromide contains 2 or 3% of the other isomer.

When a pure *cis* or *trans*-2,3-epoxypentane is converted into the bromohydrin and the oxide regenerated from this, the resulting oxide is pure.

Measurement of the dielectric constant is an accurate method of analysis of mixtures of the diastereomeric *dl*-2,3-dibromopentanes.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF WASHINGTON]

A Thermodynamic Study of the System Zinc Sulfate–Sulfuric Acid–Water at 25°

BY H. V. TARTAR, W. W. NEWSCHWANDER AND A. T. NESS

During recent years considerable work has been done on the thermodynamics of aqueous solutions containing two electrolytes. In nearly all of these investigations the activity of only one of the three components has been determined and the solutions have been dilute.

In only one case have the thermodynamic properties of all three components been studied. This was done by MacDougall and Blumer[1] in the investigation of the three component system of sulfuric acid, acetic acid and water, a solution containing a strong and a weak electrolyte. This system may be also classified as one composed of one non-volatile and two volatile components.

Since very little work has been accomplished on systems of three components in the more concentrated solutions, it was deemed a worthy task to make a study of some of the thermodynamic properties of each of the components in the system: sulfuric acid–zinc sulfate–water at 25°. These two strong electrolytes are both non-volatile, have a common ion, and are of different valence types.

The data are also of practical interest, particularly here in the Northwest, because the solutions used in industry for the electro-winning of zinc[2] lie within the concentration range used. By means of the free energies which have been calculated it is possible for the first time to determine the electrolysis energy efficiencies of the electrolytic zinc plants throughout the world.

Discussion of Method

The thermodynamic activities of the water, the zinc sulfate, and the sulfuric acid in solutions of varying molalities were determined independently at 25°.

The vapor pressure of the water was determined

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[1] MacDougall and Blumer, THIS JOURNAL, 55, 2236 (1933).

[2] Mantell, "Industrial Electrochemistry," McGraw-Hill Book Co., New York, N. Y., 1931.