words, for the permanganate oxidation of aldehydes, substituents have a greater effect upon the withdrawal of two electrons, by the oxidant, than upon the removal of the proton which also accompanies the reaction. From this work, one must infer that the acceleration of an oxidation–reduction by electron-releasing substituents is not a valid argument against an ester mechanism.

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Specific Rotations of Pure 2-Bromobutanes. Stereochemistry of the 2-Butanol to 2-Bromobutane Conversion

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There is no satisfactory method for demonstrating the optical purity or for resolving alkyl halides with halogen at the asymmetric center. The purest 2-bromobutane reported in the literature ($[\alpha]^{25}\mathrm{D}$ 28.6°) is now demonstrated to be 28% racemized. Introduction of one deuterium in the 3-position creates a second asymmetric center which serves as an internal standard of configuration, enabling one to define the stereochemical course of reactions without resorting to resolutions. *erythro*- and *threo*-3-deuterio-2-butanols are converted to the bromides with phosphorus tribromide. Comparison of these products with pure *erythro*- and *threo*-3-deuterio-2-bromobutanes indicates the alcohol to bromide conversion occurs without skeletal rearrangement and produces a product which is 85–90% inverted at the carbinol carbon corresponding to 20–30% racemization, the remainder having the same configuration as the alcohol. Thus it becomes possible to estimate $[\alpha]^{25}\mathrm{D}$ for optically pure 2-bromobutane (39.4°), *erythro*-3-deuterio-2-bromobutane (38.9°) and *threo*-3-deuterio-2-bromobutane (39.9°). Racemization is minimized by low reaction temperatures, 2-bromobutane with $[\alpha]^{25}\mathrm{D}$ +32.09° being produced at −15°.

Introduction

Although the specific rotations of the completely resolved haloalkanes are necessary for interpretations of mechanism studies employing these enantiomorphs, there are probably no satisfactory values recorded in the literature. The 2-bromobutanes have been prepared from the resolved 2-butanols by reaction with phosphorus tribromide or hydrogen bromide, and by brominating 2-butylmercuric bromide in pyridine yielding preparations with $[\alpha]^{25}\mathrm{D}$ 28.6°,[4] 26.1°,[5] 28.45°,[6] 28.6°,[7] etc., these being the highest values which appear in the literature. Unpublished experimental results,[8] which will be presented in detail elsewhere, suggested that the pure enantiomers probably have a value of $[\alpha]^{25}\mathrm{D}$ 36°.

Since further resolution of 2-bromobutane is not feasible at present, an alternative means of gaining information about optical purity was conceived. Substitution of a deuterium atom for one of the hydrogens of the $-CH_2-$ introduces a second asymmetric center which serves as an internal standard of configuration. Thus it becomes possible to determine the extent of isomerization during conversion of 3-deuterio-2-butanol to 3-deuterio-2-bromobutane without resorting to resolutions. For example, if *erythro*-3-deuterio-2-butanol is converted to the bromide, the major product might be *threo*-3-deuterio-2-bromobutane, and the extent of isomerization during the conversion would be indicated by the *erythro*-3-deuterio-2-bromobutane content of the product. Since these substances are diastereomerically related, the full array of available physical properties may be used to distinguish these isomers.

Pure samples of *d,l-erythro*- and *d,l-threo*-3-deuterio-2-bromobutanes are available by radical chain additions of deuterium bromide to *trans*- and *cis*-2-butenes, respectively.[9] These bromides can also be prepared from the corresponding *threo*- and *erythro*-3-deuterio-2-butanols, which are available by lithium aluminum deuteride reduction of *meso*- and *d,l*-2,3-epoxybutanes.[6]

Analysis for Diastereomers.—Unfortunately the non-congruous infrared absorption bands (up to 15 μ) of *erythro*- and *threo*-3-deuterio-2-bromobutanes are not sufficiently resolved for convenient determination of extent of intercontamination. However, since alkaline dehydrohalogenations of these substances to the butenes are stereospecific *trans* processes,[9] this reaction was used for two independent methods of analysis.

A. Dehydrohalogenation of the *erythro* isomer yields *trans*-2-butene and 2-deuterio-*cis*-2-butene, and the *threo* isomer yields *cis*-2-butene and 2-deuterio-*trans*-2-butene. A mixture of *erythro* and *threo* yields the four 2-butenes. The *cis*- and *trans*-olefins were separated by vapor phase chromatography. The percentage C_4H_8 in each of them was determined by quantitative infrared analysis and the C_4H_7D content by difference.

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[3] This research was supported in part by a grant from The Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund.

[4] P. A. Levene and R. Marker, *J. Biol. Chem.*, **91**, 405 (1931).

[5] R. Letsinger, This Journal, **70**, 406 (1948).

[6] G. K. Helmkamp, C. D. Joel and H. Sharman, *J. Org. Chem.*, **21**, 844 (1956).

[7] F. R. Jensen, L. D. Whipple, D. K. Wedegaertner and J. A. Landgrebe, This Journal, **81**, 1263 (1959).

[8] G. P. Bean and P. S. Skell.

[9] P. S. Skell and R. G. Allen, This Journal, **81**, 5383 (1959).

B. A primary kinetic isotope effect accounts for the different ratios of 1-, *cis*-2- and *trans*-2-butenes obtained from the 2-bromobutanes. Thus, the ratio of these olefins differs considerably for undeuterated 2-bromobutane and the *erythro*- and *threo*-3-deuterioisomers. In Table I is recorded the ratio of the olefins from these three substances under identical dehydrohalogenation conditions, determined by vapor phase chromatography of the olefinic product. For mixtures of *threo*- and *erythro*-3-deuterio-2-bromobutanes linear interpolations of the observed percentage compositions leads directly to the isomer ratio for the bromides. The isomer ratio for the bromides was calculated independently from the *cis*- and *trans*, and 1-butene percentages, and the three values were in good accord. However, the compositions calculated from the *trans*-2-butene percentages are considered the most reliable because (a) the percentage of this olefin shows the greatest sensitivity to bromide isomer ratio, and (b) this olefin could be determined with greatest accuracy. The results reported below are based on the *trans*-2-butene percentages. To further check this analytical procedure, known mixtures of *threo* and *erythro* compounds were analyzed (Table I), thus demonstrating satisfactory accuracy.

TABLE I

PERCENTAGE COMPOSITION OF THE BUTENES PRODUCED BY DEHYDROHALOGENATION IN 1 *M* POTASSIUM ETHOXIDE IN ETHANOL AT 70°

	1-Butene	*cis*-2-Butene	*trans*-2-Butene
$CH_3CH_2CHBrCH_3$[a]	19.9	21.8	58.3
threo-$CH_3CHDCHBrCH_3$[b]	24.8	9.8	65.4
erythro-$CH_3CHDCHBrCH_3$[b]	35.2	33.4	31.4
Known mixtures of *erythro* and *threo*			
Mixture A[c] Obsd.	25.9	13.1	61.0
Calcd.	26.2	12.9	60.9
Mixture B[d] Obsd.	33.6	31.0	35.4
Calcd.	33.6	30.9	35.5
Unknown mixtures of *erythro* and *threo*			
Sample Ia[e] (high *threo* content)	26.0	11.8	62.2
Sample Ib[e] (high *threo* content)	26.7	11.8	61.5
Sample II[e] (high *erythro* content)	34.4	30.7	34.9

[a] In a different set of experiments the olefin ratios were nearly identical for 2-bromobutane + 2-deuterio-2-bromobutane. [b] The sample of *threo* contained 1.6% undeuterated 2-bromobutane, and the same contamination was assumed for the *erythro*.[6] [c] 12.8% *erythro*, 85.6% *threo*, 1.6% undeuterated. [d] 85.6% *erythro*, 12.8% *threo*, 1.6% undeuterated. [e] Sample IA and IB contained 2.6% undeuterated 2-bromobutane, and the same contamination was assumed for sample II.

General Comments on Syntheses.—The preparations of alcohols and bromides used in this work are summarized in Chart I. The sequence of reactions from the fermentation product (−)-2,3-butanediol[10] to the active alcohols was stereochemically reproducible with variations of optical rotations of no more than ±0.3%. The (−)-2-butanol compared favorably in optical activity with resolved product. The conversion of the alcohols to the halides was highly sensitive to reaction conditions. Values for $[\alpha]^{25}D$ range from 26 to 32°, but careful control of reaction temperature yielded products with variations of about ±0.5%. The radical-chain photochemical addition of DBr to the 2-butenes has been described.[9]

Results

The preparations of alcohols and bromides used in this work are summarized in Chart I. An effort was made to make all reaction variables the same throughout the preparations and the analyses. Infared spectra revealed isomer intercontamination for Ia, Ib and II. It was possible to estimate from the spectra of Ia and Ib that 2.6% of undeuterated 2-bromobutane was present.

Dehydrohalogenation of the 3-deuterio-2-bromobutanes, prepared from the alcohols according to Chart I, yielded 1-, *cis*- and *trans*-2-butenes in the percentages recorded in the last three lines of Table I. Since the undeuterated 2-bromobutane in the deuterated compounds was similar in the samples prepared from the alcohols (2.6%) and the olefin–DBr adducts (1.6%),[9] these differences were ignored in arriving at *threo*:*erythro* ratios. By the linear interpolation described for analytical method B, the compositions of Ia and Ib and II were calculated (Table II).

TABLE II

PERCENTAGE COMPOSITION OF *erythro*- AND *threo*-3-DEUTERIO-2-BROMOBUTANES PREPARED *via* THE ALCOHOLS

Bromide	*threo*-C_4H_8DBr	*erythro*-C_4H_8DBr	*sec*-C_4H_9Br
Sample Ia	88.3	9.1	2.6
Sample Ib	86.4	11.0	2.6
Sample II	10.8	86.6	(2.6)
Analyses of known mixtures			
Mixture A[a]	85.8	12.6	1.6
Mixture B[b]	12.8	85.6	1.6

[a] 85.6% *threo*, 12.8% *erythro*, 1.6% undeuterated. [b] 12.8% *threo*, 85.6% *erythro*, 1.6% undeuterated.

To check the validity of these results, analytical method (A) was used in reverse. The deuterium contents of the *cis*-2-butene and *trans*-2-butene fractions were calculated from the information in Table II and the isotope effects described in Table I. The calculated and experimental values are shown in Table III, and compare favorably, thus increasing the confidence in the calculated isomer percentages listed in Table II.

TABLE III

PERCENTAGE 2-DEUTERIO-2-BUTENE IN THE 2-BUTENE FRACTIONS FROM DEHYDROHALOGENATION OF 3-DEUTERIO-2-BROMOBUTANES

	Sample II		Sample IB	
	cis-	*trans*-	*cis*-	*trans*-
Calcd.	92.0	22.2	34.8	91.5
Found (i.r.)[a]	92.4	22.5	34.5	94.3

[a] Infrared spectrophotometry yields the C_4H_8 content directly and the C_4H_7D content by subtraction from 100. Since the error is expected to be greater for determination of low C_4H_8 content, it would also be greater for the high C_4H_7D.

Mechanism of Racemization.—These results proved that conversions of 2-butanols to 2-bromo-

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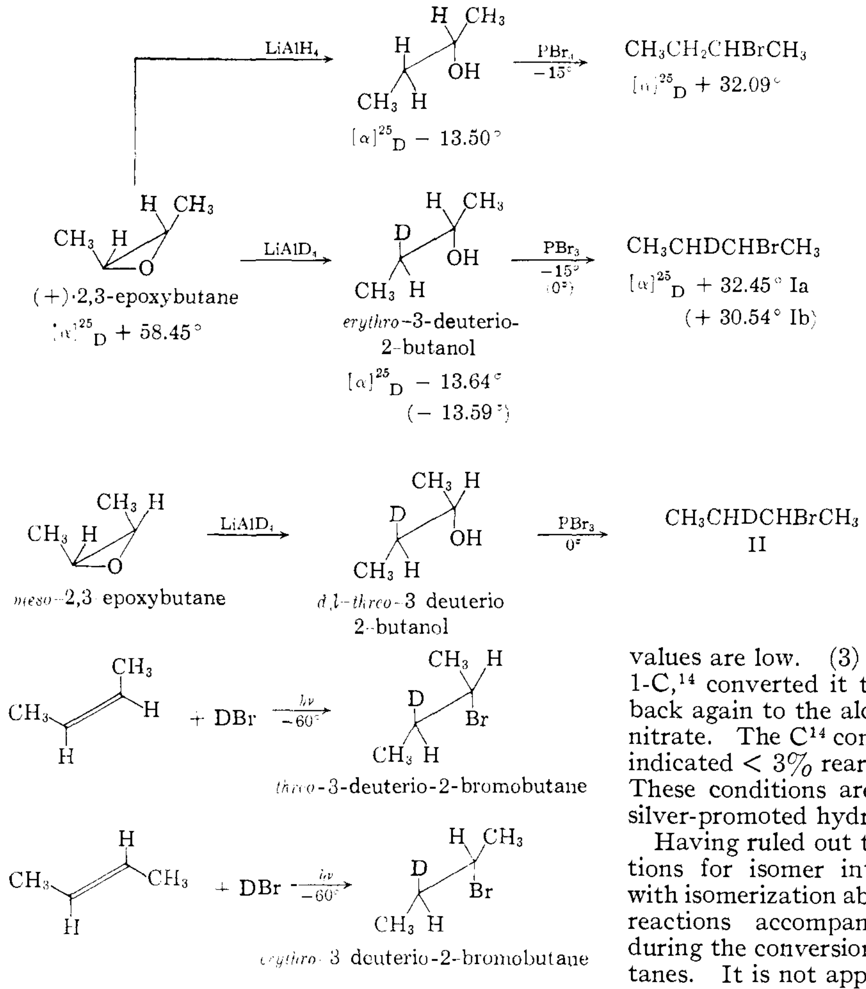
(10) The authors are indebted to Dr. R. W. Watson of the National Research Council of Canada for the culture of N.R.C. No. 42 (3) *Bacillus polymyxa* used for fermentation process.

CHART I



butanes by phosphorus tribromide (Chart I) proceed predominantly with inversion at the reaction center. This proof rests on the assumption that the base-effected elimination reaction is a *trans* process.

These conversions could have been accompanied by (a) racemization at the 2-position, (b) rearrangement of the bromine to the 1-position, and/or (c) the 3-position.

Rearrangement of the bromine to the 1-position can be excluded since it was not possible to detect any 1-bromobutane with vapor phase chromatography, thus providing an upper limit of 0.5%. Further, since dehydrohalogenation could not yield 2-butenes, the determinations of intercontamination of the 3-deuterio-2-bromobutanes from *cis*-, *trans*- and 1-butenes would not have agreed if 1-bromobutanes had been present.

Rearrangement of bromine to the 3-position is virtually excluded by three lines of evidence. (1) This rearrangement would produce some 2-deuterio-2-bromobutane. Dehydrohalogenation of this contaminant would yield 2-deuterio-1-butene as a contaminant in the 3-deuterio-1-butene. Dehydrohalogenation of the 2-butene–DBr adducts yields 3-deuterio-1-butene indistinguishable by infrared spectroscopy from the olefin derived from II. Aside from the differences in the 3.35 and 4.65 μ bands, the infrared spectra of 3-deuterio-1-butene[9] and 1-butene differ in only minor detail. However, since decided differences can be anticipated for the 2-deuterio-1-butene, it follows that this olefin is not one of the dehydrohalogenation products. (2) The 2-butenes from dehydrohalogenation of 2-deuterio-2-bromobutane would be 100% monodeuterio-2-butenes. Since no account was made of this possibility in arriving at the calculated values of Table III, had 2-deuterio-2-bromobutane been present the experimentally found values would have been too high. For example, 3% contamination by this substance would have yielded results 1–2% high. However, except for the least precise determination, the experimental values are low. (3) Shulgin[11] prepared 2-butanol-1-C^{14}, converted it to the bromide with PBr_3 and back again to the alcohol by hydrolysis with silver nitrate. The C^{14} content of the recovered iodoform indicated < 3% rearrangement to 3-butanol-1-C^{14}. These conditions are severe since they involve a silver-promoted hydrolysis.

Having ruled out two of the alternative explanations for isomer intercontamination we are left with isomerization about the 2-position as the major reactions accompanying backside displacement during the conversions of 2-butanols to 2-bromobutanes. It is not apparent that the minor reaction is to be explained by 9–11% of the product being produced by a reaction which proceeds with retention of configuration, or approximately 18–22% being produced *via* a planar intermediate which yields equal quantities of *erythro*- and *threo*-bromides.

The stereochemical results are summarized in Chart II. It is particularly noteworthy that isomer intercontamination occurs to the same extent in both 3-deuterio-2-bromobutanes (Ib and II) prepared under the same reaction condition *via* the alcohols.

Specific Rotations.—Since the extent of isomerization is virtually the same for replacements of the OH in both 3-deuterio-2-butanols, it is probably the same for 2-butanol. Thus the (+)-2-bromobutane prepared from 100% (−)-2-butanol, is 81.4% resolved (Ia) and contains 18.6% racemic material. It follows that the specific rotation of *optically pure 2-bromobutane* is $[\alpha]^{25}D$ 32.09°/0.814 = 39.4°.

If one assumes that optically pure *threo*- and *erythro*-3-deuterio-2-bromobutanes have the same $[\alpha]^{25}D$, then from *threo*-Ib, 30.54°/0.774 yields a value of 39.7° and from *threo*-Ia, 32.45/0.814 yields a value of 39.7° for optically pure *threo*. However, there is a strong reason for expecting the

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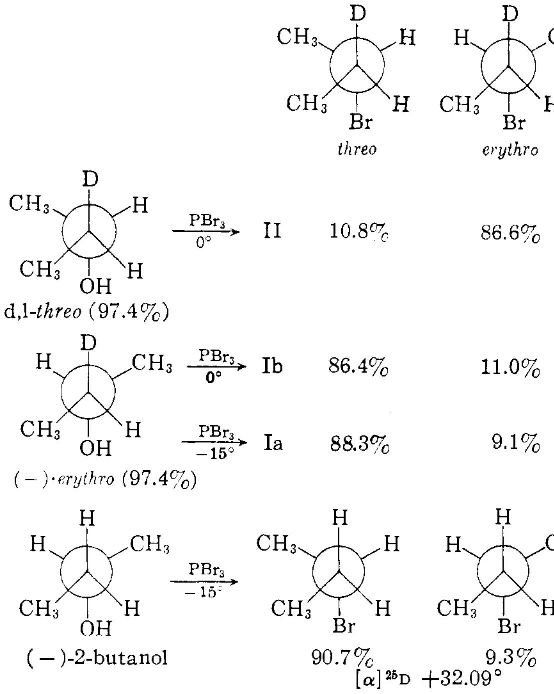
(11) A. T. Shulgin, THIS JOURNAL, **77**, 2338 (1955).

CHART II



threo- and *erythro*-bromides to have different [α]'s, since both substances have one carbon of identical configuration and the other of opposite configuration. Taking into account the 2.6% undeuterated 2-bromobutane (which is assumed to be 18.6% racemized for Ia and 22.6% for Ib), the [α]D's for pure *threo* ($T°$) and for pure *erythro* ($E°$) are related to the [α] observed as

$$\text{obsd. } [\alpha] \times 100 = (\%\text{ resolved } C_4H_9Br) \times 39.4° + (\%\ \textit{threo}) \times T° + (\%\ \textit{erythro}) \times (-E°)$$

Since there is no other function relating $T°$ and $E°$, we have assumed that the [α]D for the optically pure undeuterated bromide is the mean of $E°$ and $T°$, or $(E° + T°)/2 = 39.4°$. Thus from the data for samples Ia and Ib, respectively, we can arrive at values $[\alpha]^{25}_D$ 39.9°, 39.5° for *threo*-3-deuterio-2-bromobutane and $[\alpha]^{25}_D$ 38.9°, 39.3° for pure *erythro*-3-deuterio-2-bromobutane. These differences between [α]'s for the undeuterated, *erythro-* and *threo*-3-deuterio-2-bromobutanes is within the expected range.

Although it has been necessary to make some unsupported assumptions in arriving at these values for specific rotations, no assumptions or experimental uncertainties are apparent which would result in errors greater than 1–2°.

Experimental

Previously described methods were employed for the synthesis of (−)-2,3-butanediol,[12] (+)-2,3-epoxybutane,[13,14] meso-2,3-epoxybutane,[12] (−)-2-butanol,[15] (+)-2-bromobutane,[6] (−)-*erythro*-3-deuterio-2-butanol,[6] (+)-*threo*-3-deuterio-2-bromobutane,[6] *d, l-threo*-3-deuterio-2-butanol[12] and *d,l-erythro*-3-deuterio-2-bromobutane.[12]

The apparent significant variable in the homogeneous reaction between PBr_3 and the alcohols was temperature. Some of the available data are indicated in Chart I.

Pure, *d,l-erythro-* and *d,l-threo*-3-deutero-2-bromobutanes were prepared by radical–chain photochemical additions of deuterium bromide to the 2-butenes.[9]

***erythro*-3-Deuterio-2-butanol.**—Over a one-hour period 20 g. (0.28 mole) of D-2,3-epoxybutane was added to solution of 2.9 g. (0.28 equiv.) of lithium aluminum deuteride in 150 ml. of dry ether. The reaction mixture was refluxed an hour after addition then neutralized with dilute HCl. After the aqueous phase was washed twice with ether, the organic phases were combined, dried over K_2CO_3, and distilled twice through a spinning band column: b.p. 98.5 ± 0.2° (737 mm.), α^{25}_D −11.09°, $[\alpha]^{25}_D$ −13.64°, yield 15 g. (72%).

***threo*-3-Deuterio-2-bromobutane.**—To 5.0 g. (0.067 mole) of well stirred *erythro*-3-deuterio-2-butanol at −15° was added 6.8 g. (0.075 equiv.) of redistilled PBr_3 at such a rate that the temperature remained between −14 and −16°. After the addition, stirring was continued for two hours as the temperature was allowed to rise to 0°. This temperature was maintained during the addition of about 10 ml. of water with vigorous stirring. The organic phase was washed with water, 5% $NaHCO_3$ and water, then dried over $CaCl_2$ and distilled: b.p. 90.0 ± 0.2° (735 m.m), α^{25}_D + 40.93°, $[\alpha]^{25}_D$ + 32.45°, yield 5.0 g. (55%).

Preparative Vapor Phase Chromatographic Separation of the Butenes.—The butenes from the dehydrohalogenation of the *threo-* (I) and *erythro-* (II) isomers were separated by vapor phase chromatography. The 1-butene fraction was separated and collected at −195° using 15 feet of dipropylene glycol dibenzoate 30% on firebrick at 25° and a flowrate of 45 ml. of helium per minute. The *cis-* and *trans*-2-butene fractions were collected together from the column and were separated and collected pure by passing them through a 9-foot column of benzyl cyanide saturated with silver nitrate, 40% on firebrick, at 25° and a flow rate of 28–30 ml. of helium per minute. All of the fractions collected were passed through one of the two above columns and collected a second time at −195° to ensure their purity.

Quantitative Determination of *cis-*, *trans-* and 1-Butene.—The relative amounts of butenes present in the gas samples obtained from the dehydrohalogenation of the bromides were determined from the relative areas under the peaks obtained when the gas samples were passed through a 15 ft. by 10 mm. column packed with 30% dipropylene glycol dibenzoate on firebrick at 25° and a helium flow rate of 45 ml./minute. This method agreed to within 0.2% with the results obtained from analyses of known synthetic mixtures.

Dehydrohalogenation of 3-Deuterio-2-bromobutanes. Method A.—A mixture of 0.10 ml. (0.914 mmole) of each of the deuterated bromides and 5.00 ml. of 1 *M* potassium ethoxide in absolute ethanol was sealed in glass tubes and maintained at 70 ± 5° for two hours. At the end of the reaction period the tubes were cooled to −78°, opened, and the gases were purified by distillation *in vacuo* through a −78° trap. The pure *threo* isomer (from DBr + *cis*-2-butene) yielded 0.892 mmole of purified butenes, 24.8% 1-butene, 9.8% *cis*-2-butene and 65.4% *trans*-2-butene. The pure *erythro* isomer (from DBr + *trans*-2-butenes) yielded 0.880 mmole of purified butene, 35.2% 1-butene, 33.4% *cis*-2-butane and 31.4% *trans*-2- butene. Sample Ia yielded 0.857 mmole of purified butenes, 26.0% 1-butene, 11.8% *cis*-2-butene and 62.2% *trans*-2-butene. Ordinary 2-bromobutane under similar treatment yielded 0.856 mmole of purified butenes, 19.9% 1-butene, 21.8% *cis*-2-butene and 58.3 % *trans*-2-butene.

Method B.—A mixture of 1.00 ml. (9.14 mmoles) of sample II and 50 ml. of 1 *M* potassium ethoxide in absolute ethanol was maintained at 70 ± 5° under a water condenser for two hours, the evolved gases being swept from the top of the condenser to a −130° trap (frozen pentane). At the end of the reaction period the gases were swept from the reaction flask into the −130° trap. The gases were purified by distillation *in vacuo* through a −78° trap. Quantitative vapor phase chromatographic analysis on the purified gas (5.1 mmoles) indicated its composition to be 34.4% 1-butene, 30.7% *cis*-2-butene and 34.9% *trans*-2-butene. Sample Ib (9.14 mmoles) under similar conditions yielded 6.47 mmoles of purified butene, 26.7% 1-butene, 11.8% *cis*-2-butene and 61.5% *trans*-2-butene.

Similar dehydrohalogenations of pure *erythro* and *threo* isomers (from DBr + 2-butene isomers) were reported earlier,[9] yielding 25.1% 1-butene, 8.9% *cis*-2-butene and 66.0%

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[12] G. K. Helmkamp and N. Schnautz, *J. Org. Chem.*, **24**, 529 (1959).

[13] H. J. Lucas and C. W. Gould, Jr., THIS JOURNAL, **63**, 2541 (1941).

[14] H. J. Lucas and H. K. Garner, *ibid.*, **72**, 2145 (1950).

[15] P. J. Leroux and H. J. Lucas, *ibid.*, **73**, 41 (1951).

trans-2-butene and *erythro* yielding 35.4% 1-butene, 34.3% *cis*-2-butene and 30.3% *trans*-2-butene.

Known mixtures of *threo*, *erythro* and ordinary bromides from DBr + 2-butenes were dehydrohalogenated under similar conditions. Synthetic mixture A (9.14 mmoles) containing 85.6% *threo*, 12.8% *erythro* and 1.6% undeuterated 2-bromobutane yielded 5.63 mmoles of purified butenes, 26.6% 1-butene, 12.4% *cis*-2-butene and 61.0% *trans*-2-butene. Mixture B (9.14 mmoles) containing 12.8% *threo*, 85.6% *erythro* and 1.6% ordinary-2-bromobutane yielded 6.0 mmoles of purified butenes, 34.3% 1-butene, 30.3% *cis*-2-butene and 35.4% *trans*-2-butene.

Since method A involved total olefin recovery, it is apparent that a small fractionation error is inherent in method B. These latter results were subjected to a small correction to eliminate the fractionation error.

Rate of Dehydrohalogenation.—A crude determination of the rate of dehydrohalogenation of 2-bromobutane was carried out by dehydrohalogenation of 1.00 ml. (9.14 mmoles) of 2-bromobutane in 50 ml. of 1 *M* potassium ethoxide in absolute ethanol at 70 ± 2°. During the reaction 0.004-ml. samples were taken from the reaction flask and analyzed by vapor phase chromatography with a 10′ Apiezon column at 66° and 60 ml. of helium per minute. The amount of unreacted bromide was determined by its peak area compared to the bromide peak area of a sample taken before the reaction was started. The reaction proceeded as follows: 16 min., 56.5%; 29 min., 69.8%; 45 min., 84.2%; 65 min., 95.6%. The second-order rate constant is $5.0 \times 10^{-2} \pm 0.5$ l. mole^{-1} min.$^{-1}$.

Analysis for Deuterium Content.—Deuterium analysis on the butenes separated by vapor phase chromatography was carried out by determining the amount of undeuterated olefin present in each of the *cis*- and *trans*-2-butene fractions from their infrared optical densities at 14.90 and 10.37 μ, respectively, compared to an optical density *vs.* pressure curve[9] constructed for pure *cis*- and *trans*-2-butenes.

A 35.9-mm. sample of *cis*-2-butene from sample Ib had an optical density at 14.90 μ of 0.222 which corresponds to 23.5 mm. or 65.5% of *cis*-2-butene in the sample. The remaining 34.5% was attributed to 2-deuterio-*cis*-2-butene. A *trans*-2-butene sample, 109.0 mm., from the same bromide had an optical density at 10.37μ of 0.071 which corresponds to 6.25 mm. or 5.7% *trans*-2-butene in the sample. The remaining 94.3% was attributed to 2-deuterio-*trans*-2-butene.

A 65.5-mm. sample of *cis*-2-butene from sample II had an optical density of 14.90 μ of 0.050 which corresponds to 5.0 mm. or 7.6% *cis*-2-butene in the sample. The remaining 92.4% was attributed to 2-deuterio-*cis*-2-butene. A *trans*-2-butene sample, 77.0 mm., from the same bromide had an optical density of 0.679 at 10.37 μ which corresponds to 56.5 mm. or 77.5% *trans*-2-butene in the sample. The remaining 22.5% was attributed to 2-deuterio-*trans*-2-butene.

All spectra were determined in a 5.0-cm. gas cell *vs.* a NaCl plate using a Perkin-Elmer model 21 infrared recording spectrophotometer.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

A Systemized Method of Calculating Dipole Moments and Internuclear Distances in Bicyclic Molecules

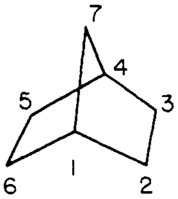
BY C. F. WILCOX, JR.

RECEIVED JUNE 18, 1959

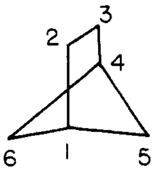
This paper presents tables from which internuclear distances and dipole moments of bicyclo[2,2,1]heptane, bicyclo[2,2,1]-hexane, bicyclo[1,1,1]pentane and their derivatives can be rapidly calculated. Although the models used to derive these tables are highly simplified, calculations and arguments are presented which strongly suggest that more sophisticated treatments would yield essentially identical results.

Introduction

For about fifty years numerous chemists have been interested in the chemistry of molecules which, like bicyclo-[2,2,1]heptane (I) possess strained rings. Recently, several groups of workers have prepared derivatives of the more highly strained bicyclo[2,2,1]hexane (II).[1-3] It appears possible that the still more highly strained bicyclo[1,1,1]-pentane system (III) may also be synthesized.[3]



II



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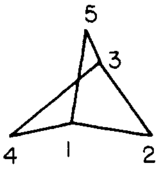

III

The potential availability of derivatives of these three rigid bycyclic systems with the same functional groups offers an opportunity to observe how reaction rates and products change with the varying geometry and strain of the parent system. Among the questions which necessarily will be raised by such future investigations are the essentially geometrical ones of the internuclear separation of two given substituents and the expected dipole moment of some derivative. The purpose of this paper is to anticipate these questions and provide answers in a generalized and systematic form. Tables will be presented from which internuclear distances between any two atoms and dipole moments of simple derivatives of the three hydrocarbons can be calculated rapidly.

Derivation of the Tables.—The formal calculation of internuclear distances and dipole moments is most easily approached by vector methods.[4] The distance between two points (nuclei) is simply the scalar magnitude of the vector joining these points so that this problem reduces itself to a knowledge of the coördinates of the atoms in question. From these coördinates one can immediately write down the vector joining the atoms and, after performing some simple arithmetic, obtain its scalar magnitude (internuclear separation). Similarly, the dipole moment of a molecule is, to the usual ap-

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(1) L. Horner and E. Speitschka, *Ber.*, **88**, 934 (1955).

(2) T. H. Colby, Ph.D. Dissertation, University of Washington, 1957.

(3) J. Meinwald and P. Gassman, page 14-O of Abstracts, 135th Meeting of the American Chemical Society, Boston, Mass., April 6–10, 1959.

(4) For an example of the utility of vector methods see E. J. Corey and R. A. Sneen, THIS JOURNAL, **77**, 2505 (1955).