nickel was removed by suction filtration. The liquid was distilled quickly without fractionation until all but a trace of volatile base had been removed. The distillate, 2 liters, was made just acid to methyl orange with hydrochloric acid and evaporated to dryness. The last traces of water were removed by azeotropic distillation with isopropyl alcohol. The dry salt was decomposed with a solution of 34 g. (1.48 moles) of sodium in 350 ml. of methanol. This quantity of sodium was equivalent to the base present in the distillate from the reaction mixture as determined by titration. The mixture was flash distilled to give a solution of the organic bases in anhydrous methanol. This was distilled under reduced pressure through a 60-cm. ring-packed column.

There were two main fractions: (1) 40 to 45° at 30 mm.; (2) 70 to 74° at 20 mm. The first was diamine, weight 40 g., yield 41%, purity 92%, determined by titration with hydrochloric acid to a methyl orange end-point; the second was amino alcohol, weight 21 g., yield 25% (on a 100% basis), purity, 102% by titration. The two amines were separated by crystallization but no further investigation of the amino alcohol mixture was made.

Separation of *meso*- and DL-2,3-Diaminobutane.—A part of the diamine from the reduction of dimethylglyoxime was neutralized in aqueous solution with hydrochloric acid. The solution was evaporated to dryness to yield 13.2 g. of the dihydrochloride, equivalent to 7.7 g. of diamine. Fractional crystallization from methanol and aqueous methanol gave 3.7 g. of dihydrochloride having a constant solubility of 0.9 g. per 100 ml. of methanol at 22°. The more soluble solid from the mother liquors had a solubility of 7 g. per 100 ml. Comparison with the approximate solubilities of the dihydrochlorides of the diamines from the reactions of the imines with ammonia showed that the less soluble solid is the salt of the *meso*- and the more soluble, that of the DL-isomer.

Reduction of 3-Nitro-2-butanol.—Hydrogenation with a platinum oxide catalyst but at a lower pressure (48 to 6 pounds) than described by Johnson and Degering,[22] who, however, used a Raney nickel catalyst, was carried out in batches. In a typical run, to 17.9 g. (0.15 mole) of 3-nitro-2-butanol in 100 ml. of ethanol 0.225 g. of catalyst was added and hydrogen introduced up to 48 pounds pressure. After 22 hours the pressure had dropped to 6 pounds. The combined reaction mixture from a total of 143.2 g. (1.20 moles) of 3-nitro-2-butanol was found to contain, by titration, 0.72 mole of basic material. By a process of extraction, and distillation at 20 mm., 22.8 g., 21% yield of product, distilling at 64–70°, mostly at the higher temperature, was obtained. This corresponds to DL-*threo*-3-amino-2-butanol, b.p. 70° (20 mm.); the *erythro*-isomer boils at 75.5° (20 mm.).

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[22] K. Johnson and E. F. Degering, *J. Org. Chem.*, **8**, 7 (1943).

PASADENA, CALIFORNIA RECEIVED JULY 24, 1951

[CONTRIBUTION NO. 1608 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY]

Stereochemistry of the Reaction of 2,3-Epoxybutane with Alcohols

BY G. K. HELMKAMP AND H. J. LUCAS

The *trans*-opening of the oxide ring of 2,3-epoxybutane by methyl and ethyl alcohols shows that a Walden inversion accompanies each of the reactions. Enantiomorphic 2-methoxy-3-ethoxybutanes have been prepared from D(+)-2,3-epoxybutane merely by changing the order of reagents in the steps: oxide to monoether to diether. Comparing *erythro*- and *threo*-ethers of 2,3-butanediol, refractive indices and densities are higher for *erythro*-isomers if hydrogen bonding is possible, otherwise *threo*-isomers have the higher values. Anomalous relationships have been observed among rotations of optically active *erythro*- and *threo*-ethers.

The reaction of 2,3-epoxybutane with a number of compounds, for example, water,[1] acetic acid,[2] hydrohalic acids[3,4,5] and ammonia,[6] has been shown to proceed with a *trans*-opening of the ring. The assumption of a *trans*-opening with methanol has been made by Winstein and Henderson,[7] in their study of the participation of the methoxy group in reactions at an adjacent carbon atom. These authors believe that a *trans*-opening of the oxide ring accompanies also the reaction of cyclohexene oxide with methanol.[7,8]

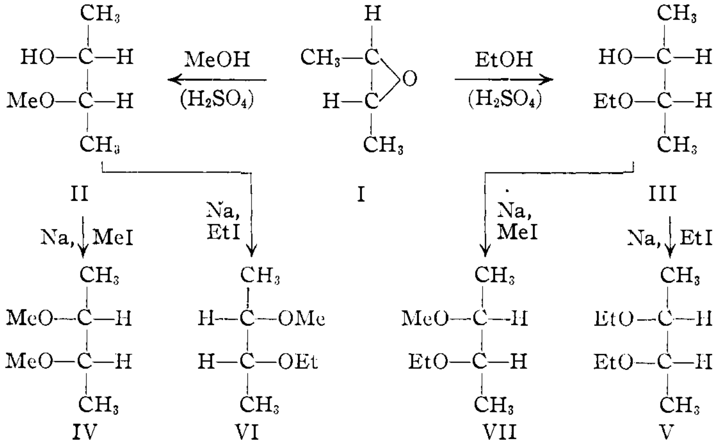

Fig. 1.—Proof of *trans*-opening of the epoxide ring with alcohols.

In the present work it has been found that methyl and ethyl alcohols cause *trans*-openings of the oxide ring of D(+)-2,3-epoxybutane (I) Fig. 1. This has been established by converting the monoethers that result from the ring openings, *viz.*, L(+)-*erythro*-3-methoxy-2-butanol (II) and L(+)-*erythro*-3-ethoxy-2-butanol (III) into the corresponding symmetrical diethers by a Williamson synthesis which is expected not to cause any stereochemical change. These diethers lack optical activity and thus have the *meso*-(*erythro*)-configuration; they are, respectively, *meso*-dimethoxybutane (IV) and *meso*-diethoxybutane (V). Since the oxide has the *threo*-configuration,[9] the ring openings take place with a single Walden inversion. The conclusion that the inactive diethers have the *meso*-configuration is strengthened by the preparation of diastereomeric diethers (also monoethers)

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[1] C. E. Wilson and H. J. Lucas, THIS JOURNAL, **58**, 2396 (1936).

[2] S. Winstein and H. J. Lucas, *ibid.*, **61**, 1581 (1939).

[3] S. Winstein and H. J. Lucas, *ibid.*, **61**, 1576 (1939).

[4] H. J. Lucas and C. W. Gould, Jr., *ibid.*, **63**, 2541 (1941).

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

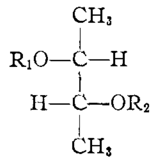
[6] F. H. Dickey, W. Fickett and H. J. Lucas, *ibid.*, **74**, 944 (1952).

[7] S. Winstein and R. B. Henderson, *ibid.*, **65**, 2196 (1943).

[8] S. Winstein and R. B. Henderson, "Heterocyclic Compounds," Vol. 1, edited by R. C. Elderfield, John Wiley and Sons, Inc., New York, N. Y., 1950, pp. 29–30.

[9] H. J. Lucas and H. K. Garner, THIS JOURNAL, **70**, 990 (1948).

from D(−)-2,3-butanediol by the Williamson synthesis (Fig. 2). These all have the D-*threo*-configuration, the same as that of the glycol.[10] They all have physical properties different from the corresponding *erythro*-isomers (Table I), and in addition the symmetrical *threo*-diethers possess optical activity. This shows that the inactivity of the *erythro*-isomers cannot be ascribed to racemization, but must arise from internal compensation.



R_1	R_2	
H	Me	VIII, 3-methoxy-2-butanol
H	Et	IX, 3-ethoxy-2-butanol
Me	Me	X, 2,3-dimethoxybutane
Et	Et	XI, 2,3-diethoxybutane
Me	Et	XII, 2-methoxy-3-ethoxybutane

Fig. 2.—Configuration of *threo*-ethers of D(−)-2,3-butanediol.

The *erythro*-monoethers, II and III, when converted to *erythro*-methyl ethyl ethers by the Williamson synthesis, yield antipodes. The product from II is D(−)-*erythro*-2-methoxy-3-ethoxybutane (VI) and the one from III is L(+)-*erythro*-2-methoxy-3-ethoxybutane (VII). These results are additional proof that alcohols produce a *trans*-opening of the epoxide ring, because a *cis*-opening would give the same product by both procedures and this product would be D-*threo*-2-methoxy-3-ethoxybutane (XII) instead of VI and VII.

Phytochemists may find these results of interest for it indicates that a change in the sign of rotation of some naturally occurring compound might be the result of a change in the order with which reaction steps are carried out in the plant.

Nomenclature and Configurations.—The unsymmetrical ethers (including the mono ethers) of 2,3-butanediol are named with the smaller radical in the 2-position. Thus the family is determined by the configuration of the asymmetric carbon having the higher number[11] which in the case of these ethers is carbon atom C-3.

Optical Purity of the Ethers.—The starting material, D(−)-2,3-butanediol,[12] had an observed rotation, α^{25}D −12.87°, a value 1.0% below a previously observed value[9] of −13.00°, and the oxide prepared from it through the steps previously described[9] had α^{25}D + 46.44°, a value 1.9% below the best previous value[9] of +47.33°. Since purification of D(+)-2,3-diacetoxybutane, one of the intermediates in the oxide preparation, was accomplished by crystallization in the former work[9] but was not attempted here, the greater discrepancy in the oxides is understandable. A purity of 98%, therefore, is believed to represent the maximum optical purity of the oxide and of the ethers prepared from it and from the active glycol.

TABLE I

CONSTANTS OF ETHERS OF 2,3-BUTANEDIOL

	B.p., °C.	Mm.	n^{25}D	d^{25}_4	α^{25}D	$[\alpha]^{25}$D	M.R. Calcd.	M.R. Found	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Crude product Yield, %	Crude product Purity[a], %
II, L(+)-*erythro*-3-Methoxy-2-butanol[b]	79.2	117	1.4098	0.9064	+18.05°	+19.92°	28.45	28.46	57.66	57.33	11.62	11.28	79	99
III, L(+)-*erythro*-3-Ethoxy-2-butanol	83.5	109	1.4106	.8866	+23.53	+26.54	33.08	33.07	60.97	61.01	11.94	11.96	90	90
IV, *meso*-2,3-Dimethoxybutane	108.0	750	1.3890	.8435	0.00	0.00	33.19	33.13	60.97	61.06	11.94	11.71	64	99
V, *meso*-2,3-Diethoxybutane	138.0	745	1.3936	.8190	+ 0.01	+ 0.01	42.43	42.67	65.70	65.92	12.41	12.49	76	79
VI, D(−)-*erythro*-2-Methoxy-3-ethoxybutane	124.0	746	1.3918	.8281	− 6.32	− 7.63	37.81	38.00	63.59	63.54	12.20	12.08	33	86
VII, L(+)-*erythro*-2-Methoxy-3-ethoxybutane	123.8	747	1.3917	.8284	+ 6.34	+ 7.65	37.81	37.98	63.59	63.50	12.20	12.17	70	98
VIII, D(−)-*threo*-3-Methoxy-2-butanol[b]	74.5	113	1.4067	.8983	−24.25	−26.24	28.46	28.52	57.66	57.78	11.62	11.63	86	98
IX, D(−)-*threo*-3-Ethoxy-2-butanol	93.7	173	1.4072	.8773	−32.77	−37.35	33.08	33.17	60.97	61.03	11.94	11.81	87	99
X, D(+)-*threo*-2,3-Dimethoxybutane	111.0	746	1.3905	.8464	+ 2.76	+ 3.26	33.19	33.13	60.97	61.03	11.94	11.86	15	97
XI, D(−)-*threo*-2,3-Diethoxybutane	139.8	747	1.3956	.8267	− 4.07	− 4.94	42.43	42.63	65.70	65.67	12.41	12.22	44	92
XII, D(−)-*threo*-2-Methoxy-3-ethoxybutane	126.2	745	1.3936	.8333	− 0.12	− 0.14	37.81	37.92	63.59	63.85	12.20	12.15	..	..

[a] Based on property of crude (usually α^{25}D) compared to that of purest. [b] Previous values of DL-isomers[7]: *erythro*, b.p. 132.3–132.5° (748 mm.); n^{25}D 1.4107; *threo*, b.p. 126.4–126.5°, n^{25}D 1.4074.

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(10) S. A. Morell and A. H. Auernheimer, THIS JOURNAL., **66**, 792 (1944).

(11) Report of the Committee on Carbohydrate Nomenclature, *Chem. Eng. News*, **26**, 1623 (1948).

(12) The authors are indebted to Dr. G. A. Ledingham, Director, and to Drs. A. C. Neish and J. A. Wheat, of the Division of Applied Biology, National Research Council of Canada, for a supply of the active glycol.

TABLE II

DERIVATIVES OF MONOETHERS

Ether	Derivative	M.p., °C.	Carbon, % Calcd.	Carbon, % Found	Hydrogen, % Calcd.	Hydrogen, % Found	Nitrogen, % Calcd.	Nitrogen, % Found
II	*a*	131.2–131.9[c]					5.13	5.55
II	*b*	56.0–58.0					9.39	9.57
III	*a*	77.8–80.0	71.05	71.11	7.37	7.32		
VIII	*a*	93.6–94.2					5.13	5.46
IX	*a*	73.3–74.1	71.05	71.06	7.37	7.36		

[a] α-Naphthylurethan, prepared according to the directions of T. L. Shriner and R. C. Fuson, "Identification of Organic Compounds," 3rd Ed., John Wiley and Sons, Inc., New York, N. Y., 1948, pp. 163–164. [b] 3,5-Dinitrobenzoate. [c] Previous value for DL-isomer,[7] 111–112°.

Preparation and Yields.—The over-all yield of oxide from glycol through the steps, glycol → diacetate → chlorohydrin → oxide is 45%, compared to 49 and 61.6 previously.[9,13] The reaction of the oxide with an alcohol is best catalyzed with sulfuric acid, for the base-catalyzed reaction proved to be too slow. When the excess of alcohol is tenfold, to minimize side reactions, yields of monoethers are of the order of 80%. The reaction time for ethanol is about twice that of methanol.

Best results in the preparation of *threo*-monoethers from the active glycol are obtained with an excess of glycol (yields are about 85%, based on sodium). The reaction mixture remains homogeneous throughout and sodium iodide does not separate until the glycol is being recovered by distillation at reduced pressure. Recovery of the excess glycol is nearly quantitative and there is no significant change in its optical activity.

The preparation of diethers from monoethers is the least satisfactory and purification is difficult, owing to azeotropic distillation with unreacted monoether. Purification can be accomplished by slow fractional distillation at reduced pressure from molten sodium, two to five times, depending upon the degree of purification, until the rotation of the product reaches a constant value. The yields of pure ether varied from 30 to 55%.

Physical Constants.—These show some interesting relationships. Rotation of D-*threo*-2,3-diethoxybutane is −4.9°, that of D-*threo*-2,3-dimethoxybutane is +3.2° and that of the D-glycol is −13.0°. Reversal of sign from glycol to ether would be expected, since the diacetate and oxide have positive rotations; for that reason the negative rotation of the diethyl ether seems surprising. Another surprising result, that would not be predicted, is the relation between the rotations of the methyl ethyl ethers: that of the D-*threo*-ether is −0.14°, and that of the L-*erythro*-ether is +7.65°. However, this becomes understandable on the basis that in the diethers a D-ethoxy group is negative and a D-methoxy group is positive. Thus the D-*threo*-methyl ethyl ether is slightly negative because the slightly larger value of D-ethoxy outweighs that of D-methoxy; the L-*erythro*-methyl ethyl ether is decidedly positive because the effects of D-methoxy and L-ethoxy work together. The relationships are qualitative only because the conformations of the groups in space, that probably are responsible for reversal of sign of *threo*-dimethyl and diethyl ethers, prevent additive relationships.

There are two relationships among refractive indices and densities. In the monoether series the *erythro*-isomers have the higher values, while in the diether series the *threo*-isomers have the higher values. The presence of the hydroxyl group in the monoether series probably is responsible for this difference. Similar relationships have been noticed previously, but not until now has the significance of a potential bond-forming hydrogen atom been noted. For example, the following *erythro*-compounds have the higher values of refractive index and density: 3-bromo-2-butanol,[3] 3-chloro-2-butanol,[4] 2,3-butanediol, 2,3-butanediamine,[6] 3-amino-2-butanol[6] and *cis*-2,3-buteneimine.[6] The following *threo*-compounds have the higher values: 2,3-dibromobutane,[2,14,15] 2,3-diacetoxybutane,[15] 2,3-dichlorobutane,[4] 2-chloro-3-iodobutane[5] and 2-bromo-3-iodobutane.[5] In one case, that of 3-bromo-2-acetoxybutane the data are conflicting,[2] owing in part to the small spread between values. An exception is noted in the case of the 2,3-epoxybutanes, of which the *cis*-(*erythro*)-isomer has the higher values.[1,3] The rigid structure of the molecule probably is responsible for the exception. Thus for acylic 2,3-disubstituted butanes, the *erythro*-isomer has the higher values for refractive index and density if hydrogen bonding is possible, otherwise the *threo*-isomer has the higher values.

Experimental[16,17]

L(+)-*erythro*-3-Methoxy-2-butanol.—To 2 moles of methanol, freshly distilled from methanol and sodium methoxide, was added 0.08 g. of concd. sulfuric acid and then dropwise, over a period of 0.5 hour, 14.4 g. (0.20 mole) of D(+)-2,3-epoxybutane, $\alpha^{25}\mathrm{D}$ +46.44°, purity 98.1%. The reaction was sufficiently exothermic to initiate boiling. Refluxing was continued for 0.5 hour and the mixture allowed to stand overnight. Solid potassium carbonate was added in amount sufficient to neutralize acid, excess methanol was removed by distillation at 750 mm., and the product collected by distillation at 117 mm.: b.p. 78.5–79.3°; $\alpha^{25}\mathrm{D}$ +17.85°; crude yield 15.8 g. (79%). Two redistillations through a semi-micro fractionating tube gave 11.4 g. (57%); b.p. 79.3° (117 mm.); $n^{25}\mathrm{D}$ 1.4095; $d^{25}{}_{4}$ 0.9064; $\alpha^{25}\mathrm{D}$ +18.05°; $[\alpha]^{25}\mathrm{D}$ +19.92°.

D(−)-*threo*-3-Ethoxy-2-butanol.—To 60 g. of redistilled D(−)-2,3-butanediol ($\alpha^{25}\mathrm{D}$ −12.87°) were added 2.4 g. (0.105 mole) of sodium shavings. After the sodium had dissolved, an excess of ethyl iodide, 28 g. (0.18 mole), was added to the still hot solution (85°). A temperature of about 85° was maintained for about one hour by means of an infrared lamp. The reaction mixture remained homogeneous to this point. The monoether was removed from the excess glycol by distillation at 131 mm.: b.p. 82.3–83.6°; $\alpha^{25}\mathrm{D}$ −32.40°; crude yield 10.71 g. (87%). Two

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(13) P. J. Leroux and H. J. Lucas, THIS JOURNAL, **73**, 41 (1951).

(14) R. T. Dillon, W. G. Young and H. J. Lucas, *ibid.*, **52**, 1953 (1930).

(15) S. Winstein and R. E. Wood, *ibid.*, **62**, 548 (1940).

(16) Only one example of each type of reaction is given. Physical constants and analyses are listed in Table I.

(17) Analyses by A. Elek.

distillations through the semi-micro fractionating tube were necessary to obtain a pure product: b.p. 93.7° (173 mm.); n^{25}_D 1.4072; d^{25}_4 0.8773; α^{25}_D −32.77°; $[\alpha]^{25}_D$ −37.35°.

Excess glycol was recovered by distillation at 7 mm.; weight 47.3 g.; b.p. 69.0–69.7°; α^{25}_D −12.82°; $[\alpha]^{25}_D$ −12.99°. Thus about 93% of the original glycol was accounted for. More important, the rotation was within 0.05° of the original glycol, thus showing that the sodium salt of the glycol does not tend to undergo racemization, even when heated.

meso-**2,3-Dimethoxybutane.**—To 30 ml. of anhydrous ethyl ether were added 2.3 g. of sodium shavings and 5.20 g. (0.05 mole) of L(+)-*erythro*-3-methoxy-2-butanol. After 24 hours hydrogen evolution had virtually ceased, leaving a clear reddish solution along with the excess sodium. The sodium was removed and an excess of methyl iodide, 10.6 g. (0.075 mole) was added. Fairly rapid formation of sodium iodide started after a few minutes. The mixture was heated under a reflux for 2 hours and allowed to stand 3 hours. The ether was removed by distillation, water was added to dissolve sodium iodide, the aqueous phase was shaken twice with portions of the ether previously removed and these were combined with the product. After the solution had been dried with potassium carbonate, distillation was carried out at 750 mm.; b.p. 107.3–108.0°; α^{25}_D +0.03°; crude yield, 3.79 g. (64%). The product was redistilled slowly through a semimicro fractionating tube and from metallic sodium which in the molten state reacted with unchanged starting material: b.p. 108.0° (750 mm.); n^{25}_D 1.3890; d^{25}_4 0.8435; α^{25}_D 0.00°.

PASADENA 4, CALIF.

RECEIVED AUGUST 13, 1951

[CONTRIBUTION NO. 1611 FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, AND FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF SOUTHERN CALIFORNIA]

An Electron Diffraction Investigation of the Structures of the Aminodiboranes $(CH_3)_2NB_2H_5$ and $H_2NB_2H_5$[1,2]

BY KENNETH HEDBERG AND A. J. STOSICK

The structures of N-dimethylaminodiborane, $(CH_3)_2NB_2H_5$, and aminodiborane, $H_2NB_2H_5$, have been investigated by electron diffraction in the gases. The results are in accord with symmetrical structures having fourfold coördination about the nitrogen atom, and may be considered as derived from the diborane (B_2H_6) structure by the simple replacement of a bridge hydrogen atom with the NR_2 group. For $(CH_3)_2NB_2H_5$, assuming the group $H_2B{-}BH_2$ coplanar, the important bond distance and bond angle values with limits of uncertainty are: B–N = $1.55_4 \pm 0.02_6$ Å., C–N = $1.48_3 \pm 0.02_9$ A., B–B = 1.92 ± 0.11 Å. ∠C–N–B = 116.2 ± 1.0°, ∠C–N–C = 111.5 ± 2.5°, ∠B–N–B = 76.4 ± 5.5°, symmetry C_2v (assumed), B–H = 1.25 Å. (assumed), C–H = 1.09 Å. (assumed), ∠H–C–H = 109.5° (assumed), ∠H–B–H = 120° (assumed); the bridge hydrogen atom was neglected. The $H_2NB_2H_5$ investigation indicates that the coplanarity assumed for the group $H_2B{-}BH_2$ and the value 1.25 Å. assumed for $B{-}H_{bond}$ are probably incorrect by substantial amounts; however, these assumptions are unimportant for $(CH_3)_2NB_2H_5$ and do not introduce error into the values of the determined parameters. For $H_2NB_2H_5$ the important distance and angle values are: B–N = $1.50_4 \pm 0.02_6$ Å., B–B = 1.93 ± 0.09 Å., $B{-}H_{bond}$ = 1.15 ± 0.09 Å., ∠B–N–B = 76.2 ± 2.8°, ϵ (the angle between the extension of B–B and the plane of the $-BH_2$ group, the angle increasing as BH_2 rotates away from N) = 15 ± 20°, symmetry C_{2v} (assumed), N–H = 1.02 Å. (assumed), $B{-}H_{bridge}$ = 1.35 Å. (assumed), ∠H–N–H = 109.5° (assumed), and ∠H–B–H = 120° (assumed). The expected B–N–B angle stress and the lesser "electron deficiency" in $R_2NB_2H_5$ as compared to B_2H_6 accounts satisfactorily for the observed distances.

The boron hydrides and their derivatives have held interest for chemists for a long time, an interest arising largely from the fact that many of these substances do not have enough valence electrons to form all of the electron pair bonds which their compositions suggest to be necessary. These substances are especially interesting from a structural standpoint because the spatial arrangements of the atoms in the molecules (which are certainly most important for understanding them) are not at all obvious.

Recently, investigations of the structures of diborane[3] (B_2H_6) and decaborane[4] ($B_{10}H_{14}$) have provided conclusive evidence in support of structures having hydrogen bridges[5] (*i.e.*, protonated double bonds), and in the light of these discoveries it is reasonable to suppose that the hydrogen bridge plays an important role in the "electron deficient" bonding encountered in all the boron hydrides and in many of their derivatives. In 1947 one of us (A. J. S.) proposed that the amino derivative of B_2H_6 might have a structure derived by replacement of one bridge hydrogen atom with a $-NR_2$ group to form in its place a nitrogen bridge, the nitrogen atom forming essentially normal covalent single bonds to each boron atom.[6] Such a structure accounts very satisfactorily for the chemical behavior of these compounds, whereas other structures do not.[7] It was supposed that certain other derivatives of B_2H_6 might have analogous structures. The current investigation arose directly from our desire to test this hypothesis, and for this purpose we selected for study the compounds $(CH_3)_2NB_2H_5$, $H_2NB_2H_5$ and BrB_2H_6. Dimethylaminodiborane had been newly discovered by Burg and Randolph[6a] and, like BrB_2H_5, had not previously been studied by structural

[1] Preliminary results presented at the San Francisco Meeting of the American Chemical Society, April, 1949: A. J. Stosick, Abstracts, Division of Physical and Inorganic Chemistry, p. 26-O.

[2] This work was supported by the Office of Naval Research under contracts N6onr-238-TO-I and N6onr-24423.

[3] (a) W. C. Price, *J. Chem. Phys.*, **16**, 894 (1948); **15**, 614 (1947); (b) K. Hedberg and V. Schomaker, THIS JOURNAL, **73**, 1482 (1951).

[4] J. S. Kasper, C. M. Lucht and D. Harker, *Acta Cryst.*, **3**, 436 (1950).

[5] Discussion of this or apparently related types of structure have been given by many authors. See, for example, W. Dilthey, *Z. angew. Chem.*, **34**, 596 (1921); E. Wiberg, *Ber.*, **69**, 2816 (1936); H. C. Longuet-Higgins and R. P. Bell, *J. Chem. Soc.*, 250 (1943); K. S. Pitzer, THIS JOURNAL, **67**, 1126 (1945); R. E. Rundle, *ibid.*, **69**, 1327 (1947).

[6] See (a) A. B. Burg and C. L. Randolph, *ibid.*, **71**, 3451 (1949), and (b) A. B. Burg, First Annual Summary Report of Investigations on Water-Reactive Chemical Compounds, N6onr-238-TO-I, p. 10 (1947). Essentially the same suggestion has been made independently by E. Wiberg, A. Balz and P. Buchheit, *Z. anorg. Chem.*, **256**, 286 (1948), and Ya. K. Syrkin and M. E. Dyatkina, "The Structure of Molecules," Interscience Publishers, Inc., New York, N. Y., 1950, p. 404; Russian edition published in 1946 describe B_2NH_7 as probably having this structure.

[7] H. I. Schlesinger, D. M. Ritter and A. B. Burg, *ibid.*, **60**, 2297 (1938).