1-(phenylthio)cyclohexane, 96227-50-8; 7-(phenylthio)-1,4-dioxaspiro[4.5]decane, 96227-52-0; 2-cyclohexenone, 930-68-7; 7-(phenylthio)-1,4-dioxaspiro[4.4]nonane, 96227-51-9; cyclopentenone, 930-30-3; (phenylsulfinyl)cyclopentane, 10181-73-4; phenyl sulfide, 19744-72-0; 1-(phenylthio)cyclopentene, 37053-16-0; 1-(phenylthio)-2-(trifluoroacetyl)cyclopentene, 96227-53-1.

Resolution of *d,l*-2,3-Dibromobutane by Enantiomeric Dehydrohalogenation Effected by Brucine. A Refutation of a Contrary Report

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A number of years ago both Lucas[1] and Winstein[2] reported the partial resolution of *d,l*-2,3-dibromobutane which was achieved by taking advantage of the fact that the antipodal dibromobutanes showed a difference in their rates of reaction with brucine. It was suggested by Lucas that the product of the reaction was the quaternary salt of brucine, since in the resolution of propylene bromide the recovered brucine possessed different properties from the original brucine or from brucine hydrobromide and consisted of equal moles of the two reactants. It was demonstrated that this compound was not a simple complex of the two reagents. The rotation, α^{25}_D −2.04° (1 dm), reported by Lucas[1] was almost the same as that reported by Winstein[2] using the same method, α^{25}_D −2.43° (1 dm).

Subsequent to this report a publication appeared[3] which gave a conflicting report of the results of the reaction: "The partial resolution of *d,l*-2,3-dibromobutane with brucine has been described[1,2] resulting in $[\alpha]_D$ +2.5°.[4] Contrary to the earlier statements, this separation does not depend on preferential destruction of one of the enantiomers. Preferential entrapment of the (+)-dibromide in the brucine crystals is the basis of the separation." The genesis of this statement is found in the Experimental Section of the paper[3] and in the Ph.D. disertation of one of the authors.[5] "To *d,l*-2,3-dibromobutane (28.7 g, 0.14 mol) was added brucine (19 g, 41 mmol). The resulting thick paste was allowed to stand for 3 hr. Part of the 2,3-dibromobutane was pumped off under vacuum; in 16 hr, 18.7 g had distilled, α_{365} −23.6°. The brucine and 2,3-dibromobutane residue were dissolved in 10% H_2SO_4 and extracted with ether. Vacuum trap to trap distillation gave recovered dibromobutane α_{365} +48.7°, 7.4 g" (method A).

During the course of the investigation of the bromination of (−)-2-bromobutane with bromine-81 partially active 2,3-dibromobutane was obtained as the major product.[6] Since the realization of partial optical activity in the 2,3-dibromobutane precluded the intermediacy of a symmetrically bridged β-bromoalkyl radical as a mode for the formation of the largely racemic product, it was necessary to investigate the racemization of the active compound under the reaction and isolation conditions. The published results[3] for the resolution were repeated with the exception that the 2,3-dibromobutane was left in contact with the brucine for 48 h, or longer, before distillation.[6] However, only *trans*-2-bromo-2-butene and partially resolved (−)-2,3-dibromobutane were obtained from either the distillate or the brucine entrapped material. It was qualitatively observed that the amount of optical activity in the recovered 2,3-dibromobutane increased with increasing contact time between the brucine and the dibromide, with a concomitant increase in the amount of olefin formed. Since the report by Skell,[3] that the isolated material with a positive rotation (the entrapped material) was in contact with brucine for a total of <19 h, it did not seem reasonable that the same reaction was not observed (albeit, to a greater extent) at only 2 to 3 times that period of time.

Very recently a note appeared which purported to be a refutation of the observation that the resolution was a result of enantiomericly selective dehydrohalogenation.[7] The authors *republished* their original results. They explained the results of the most recent report[6] and those of Winstein[2] and Lucas[1] as resulting from the prolonged contact time between the halide and the brucine and conceded that the olefin reported[6] was a result of dehydrohalogenation.[8]

Since the method of enantiomeric entrapment is of theoretical and potential practical value, it was important to reinvestigate again and in further detail the possibility that the resolution of the halides, in fact, can be achieved by this interesting method.

The reaction was carried out *exactly* as reported[3,5,7] and as recorded verbatom in this publication. The results of this experiment are listed in Table I, method A. It can be seen from the first entry in the table that (−)-2,3-dibromobutane and *trans*-2-bromo-2-butene were obtained from the distillation of the mixture of the racemic mixture of dihalides and brucine. The isolation of the entrapped organic material from the crystal mass, likewise, yielded only (−)-2,3-dibromobutane and *trans*-2-bromo-2-butene. A mixture of all of the organic material (both the distillate and the isolated entrapped material) also showed a negative rotation. Since preferential enantiomeric entrapment was not found but only, as previously reported,[6] enantiomericly selective dehydrohalogenation was observed, an attempt was made to find a relationship between the amount of elimination and the contact time and the optical rotation obtained and the contact time. The reaction was carried out to both shorter and longer contact times and these results are also listed in Table I, methods A and B. The theory that entrapment and not dehydrohalogenation was responsible for the resolution could be disproved by allowing the materials to remain in contact for 2 or 3 h and instead of distilling the material over a 16-h period the crystal mass was triturated with pentane for 2 h (a condition under which dehydrohalogenation does not occur, see first entry method B) and the rotation of the near quantitatively (>98%) isolated dihalide was taken (method B). It was negative, and the product mixture contained the dehydrohalogenation product, *trans*-2-bromo-2-butene. If entrapment was the method of resolution, then no 2-bromo-2-butene should be present and a corequisite must also be true, that the rotation of the mixture would be zero. Since both of these criteria are simultaneously not met, the entrapment theory, although attractive, must not be

(1) Lucas, H. J.; Gould, C. W. *J. Am. Chem. Soc.* **1942**, *64*, 601.
(2) Winstein, S.; Buckles, R. E. *J. Am. Chem. Soc.* **1942**, *64*, 2780.
(3) Skell, P. S.; Pavlis, R. R.; Lewis, D. C.; Shea, K. J. *J. Am. Chem. Soc.* **1973**, *95*, 6735.
(4) The observed rotation reported in ref 2 was α_D −2.43° (1 dm). The report in ref 3 of the *absolute* rotation as positive must be in error.
(5) Pavlis, R. R. Ph.D. Thesis, Pennsylvania State University, 1969.
(6) Tanner, D. D.; Blackburn, E. V.; Kosugi, Y.; Ruo, T. C. S. *J. Am. Chem. Soc.* **1977**, *99*, 2714.
(7) Pavlis, R. R.; Skell, P. S. *J. Org. Chem.* **1983**, *48*, 1901.
(8) Contrary to the report in ref 7. Neither Lucas[1] nor Winstein[2] reported the formation of olefin from the reaction between *d,l*-2,3-dibromobutane and brucine, since it was assumed[1] that the reaction was the formation of the quaternary salt.

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Table I. Treatment of *d,l*-Dibromobutane with Brucine

reactants (g)		contact time (h)			products from distillate, mol % (g)		entrapped products, mol % (g)		$\alpha^{24.5}_{365}$		$[\alpha]^{24.5}_{365}$
d,l-2,3-dibromobutane	brucine	initial	distillation	total	2,3-dibromobutane	*trans*-2-bromo-2-butene	2,3-dibromobutane	*trans*-2-bromo-2-butene	distillate	entrapped	total	combined fractions
Method A[a]												
28.7	19.2	3	16	19	98.4 (8.35)	1.36 (0.07)	95.6 (19.9)	4.4 (0.61)	−22.33	−0.894	−6.11	−5.11
28.7	19.2	48	16	64	73.0 (2.29)	26.9 (0.53)	91.0 (23.1)	8.99 (1.43)	−23.09	−11.90	−12.88	−12.84
14.3[b]	8.5	3	16	19	98.1 (8.50)	1.1 (0.07)	98.1 (5.10)	1.86 (0.097)	−21.97	−4.78		
Method B[a]												
reactants (g)		contact time (h)			products, mol % (g)							
d,l-2,3-dibromobutane	brucine	initial	trituration with pentane		2,3-dibromobutane	*trans*-2-bromo-2-butene					$[\alpha]^{24.5}_{365}$	
14.4	9.64	0	24		100 (14.0)	traces					0	
14.4	9.52	2	2		99.6 (14.2)	0.39 (0.034)					−0.221	
29.5	19.0	3	2		99.4 (28.7)	0.60 (0.11)					−1.20	
14.3	9.49	10	2		99.0 (10.5)	0.98 (0.065)					−1.69	
6.1[b]	3.6	19	2		98.4 (5.7)	1.6 (0.083)					−4.00	
14.4	9.62	40	2		92.7 (11.9)	7.28 (0.59)					−6.96	

[a] See Experimental Section. [b] Dried at 105 °C (anhydrous).

responsible for the resolution of 2,3-dibromobutane. To demonstrate that enantiomeric resolution takes place by dehydrohalogenation, a plot was constructed from the data given in Table I (method B) which shows an excellent correlation between contact time and both the negative rotation of the isolated dibromide (r = 0.99) and the amount of *trans*-2-bromo-2-butene formed (r = 0.96). It can also be seen from these plots that in all cases the longer the contact time the more olefin is formed and that, likewise, the (−) rotation of the isolated dibromide also increases.

It was suggested by a referee that a possible explanation for the failure of the entrapment procedure was due to the fact that the commercially available brucine used may have been one of its hydrates, since brucine crystallizes in both a dihydrated (8.4% H_2O) and tetrahydrated (15.1% H_2O) form,[9] and that he was aware that the hydrated form was not useful as an entrapping agent. The brucine used in this work and in the previously reported work from this laboratory[6] was not the hydrate (see Experimental Section) but did contain 3% residual water. When the commercial brucine was dried and both the procedures were repeated (see Table I, methods A and B) the results did not differ from those obtained with the commercial material. Since the previously reported procedures which claimed successful entrapping experiments[3,5,7] did not mention the source of the brucine used nor did they give any indication of its purity, no explanation for the reported results and the ones obtained in this laboratory is available.

Experimental Section

Materials. Brucine, pure, analytical reagent (Terochem Laboratories, Lot 1220-21) was used without further purification. Analysis showed it to contain 3% water. Anal. Calcd for $C_{23}H_{26}N_2O_4$: C, 70.04; H, 6.64; N, 7.10. Found: C, 67.00; H, 6.44; N, 6.72 (3% H_2O). The sample was dried at 105 °C in vacuo over P_2O_5 for 17 h. Found: C, 70.06, H, 6.59; N, 7.09 (anhydrous).

***d,l*-2,3-Dibromobutane** was prepared from bromine and *cis*-2-butene at −45 °C using Freon 113 as a solvent. The product was obtained by fractional distillation using a 3-ft Teflon spinning-band column: bp 76–77 °C (50 mm) [lit.[10] bp 75.5–76.5 °C (50 mm)]; n^{25}_D 1.5132 [lit.[10] n^{25}_D 1.5126]. GLC analysis (50-m methyl silicone capillary column) showed it to be 99.6% pure with 0.065% *meso*-2,3-dibromobutane as a contaminant.

Instrumentation. Optical rotations were obtained with a 1-dm cell using a Perkin-Elmer 241 polarimeter.[11] NMR spectra, 200-MHz ^1H, were obtained on a Bruker WH-200 FT-NMR spectrometer. GLC analyses were carried out on a Hewlett Packard 5840A gas chromatograph equipped with a flame ionization detector and a 50-m glass SE-30 capillary column.

The Partial Resolution of *d,l*-2,3-Dibromobutane Using Brucine. Two methods were used to investigate the interaction of brucine and *d,l*-2,3-dibromobutane. **Method A.** The procedure previously described[7] and given verbatim in the text was followed exactly. The product mixtures were analyzed by GLC and by 200-MHz ^1H NMR spectroscopy.

The absolute rotations listed in Table I were obtained from samples which contained olefin (0.1–8%) and <1 mol % of diethyl ether (GLC) and therefore were corrected for their concentrations.

Method B. Brucine and *d,l*-2,3-dibromobutane were agitated at room temperature by using a mechanical stirrer for the requisite

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(11) In ref 3 the optical rotations were reported as being obtained on a Rudolph Model 200 photoelectric polarimeter or a Perkin-Elmer F-22 spectropolarimeter. It was at first assumed that the positive rotations reported may have been the result of a misinterpretation of the reading of the instrument since this was possible by using the older model produced by Perkin-Elmer. It appears, that the report[3] was in error since Perkin-Elmer have not produced a Model F-22 spectropolarimeter and since the Rudolph Polarimeter can only be used in tandum with a Model 80 or Model 70 polarimeter.

amount of time (0, 2, 3, 10, or 40 h), after which the solid mass was broken up, 150 mL of pentane was added, and the mixture was mechanically stirred at room temperature for an additional 2 h (for the 0 time experiment the stirring with pentane was carried out for 24 h). The pentane was filtered from the brucine and was washed with an additional 50 mL of pentane, and the pentane extracts were combined. The weight and optical rotation of the solution were measured and the product mixture was analyzed by GLC. The pentane solution was washed with 2 × 50 mL portions of 10% aqueous H_2SO_4 and the pentane was removed by distillation. The weight, volume, and optical rotation of the residue were measured and the product mixture was analyzed by GLC and 200-MHz ^1H NMR spectroscopy.

The absolute rotations listed in Table I were obtained from samples which contained olefin (0.1–2.7%) and <1 mol % of pentane (GLC) and therefore were corrected for their concentrations.

Identification of *trans*-2-Bromo-2-butene. *trans*-2-Bromo-2-butene was identified by comparison of its 200-MHz ^1H NMR spectrum and refractive index with that of the authentic material: ^1H NMR ($CDCl_3$) δ 1.680 (q of d, 3 H), 2.235 (quint., 3 H), 5.628 (q of q, 1 H) [lit.[12] ^1H NMR (CCl_4) δ 1.69 (q of d, 3 H), 2.26 (quint., 3 H), 5.65 (q of q, 1 H)]; n^{25}_D 1.4568 [lit.[10] n^{25}_D 1.4565].

Registry No. *dl*-2,3-Dibromobutane, 598-71-0; brucine, 357-57-3; *trans*-2-bromo-2-butene, 3017-71-8; (–)-2,3-dibromobutane, 49623-63-4.

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Synthesis and Characterization of Novel 1*H*,3*H*-Naphth[1,8-*cd*][1,2,6]oxadiborins

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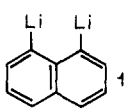
The 1*H*,3*H*-naphth[1,8-*cd*][1,2,6]oxadiborin ring system is a conjugated heterocycle, isoelectronic with the phenalene cation.[1] The only previous mention of this diboryl parent structure was by Letsinger et al.,[2] who synthesized 1,8-naphthalenediboronic anhydride (**2a**) and its ammonia complex. Recently, we observed the 1,3-dimethyl derivative **2d** as an inadvertent oxidation product in the preparation of 1,8-naphthalenediylbis(dimethylborane), "hydride sponge".[3] In this paper, we report the synthesis of compounds **2b–d** via facile substitution reactions starting from **2a**. These compounds are potentially useful as a means of introducing pairs of conformationally defined boron substituents into larger molecular assemblies, besides being novel Lewis acids in their own right.



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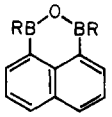

2a, R = OH
2b, R = OMe
2c, R = Cℓ
2d, R = Me

Results and Discussion

Diboronic anhydride **2a** was prepared from 1,8-dilithionaphthalene (1) according to the literature procedure[4] with two modifications: the dilithiate was generated from the more readily obtained 1,8-diiodonaphthalene[5] rather than from 1,8-dibromonaphthalene, and trimethylborate was used instead of tributylborate. The product isolated after recrystallization from Et_2O/petroleum ether was a partial hydrate, according to its elemental analysis.

Compound **2a** was quantitatively converted to dimethyl ester **2b** by reaction with methanol in benzene. The reacting solution was heated at reflux while water was removed from the reflux vapors with molecular sieves and from the pot by azeotropic distillation. Diboronic diester **2b** was transformed into dichloride **2c** by the action of PCl_5 and CCl_4 at reflux; once again, the reaction was quantitative. Compound **2b** was also treated with 5 molar equiv of MeMgBr in $(CH_2)_4O$. The reaction was quenched with 5 molar equiv of $BF_3{\cdot}OEt_2$, leading to the isolation of compound **2d** in 64% yield.

Heterocycle **2d** is the first example of 1*H*,3*H*-naphth[1,8-*cd*]oxadiborin whose substituents are not π-electron donors. It is slightly sensitive to air and decomposes in aqueous acid. The compound displayed irreversible redox potentials at –1.1 V (reduction) and +1.4 V (oxidation) vs. SCE in CH_2Cl_2 containing 0.1 M n-$Bu_4N^+PF_6^-$.

The B–O–B linkage proved to be robust, as attempts to dislodge the oxygen atom with MeOH/AcOH, NaOMe/CH_3I, PCl_5, P_4S_{10}, Lawesson's reagent,[6] MeMgBr, and $C_5H_{11}NH_2$/$PhCH_3$ all failed. Dichloride **2c** was resistant to attack by excess PCl_5 and by $TiCl_4$ in C_6D_5Cl at 130 °C.

When **2d** was treated with C_5H_5N, $C_5H_{11}NH_2$, or quinuclidine, 1:1 addition compounds were formed, as indicated by NMR and IR spectroscopy. The quinuclidine complex was observed in a temperature-dependent 90-MHz ^1H NMR experiment and appeared to be symmetrical or rapidly equilibrating at $T \gtrsim -80$ °C. This is in contrast to the result reported[7] for triethylboroxin, on which quinuclidine was localized at a single boron atom at –20 °C on the 400-MHz time scale. Perhaps the inclusion of the boron atoms in a conjugated system alters the orbital overlap or lowers the electron deficiency of **2d** relative to the boroxin, so that an amine would form a less stable complex with a single boron atom of **2d** relative to the boroxin.

The precursors to compound **2d** are all stable, isolable substances whose orbitals are geometrically defined at the boron atoms, and whose substituents may be easily replaced. As such, they might serve as useful intermediates in the syntheses of oligomeric or polymeric boron Lewis acids.

Experimental Section

1,3-Dimethoxy-1*H*,3*H*-naphth[1,8-*cd*][1,2,6]oxadiborin (2b). Compound **2a** (0.50 g) was dissolved in 25 mL of MeOH and 125 mL of C_6H_6 and the solution was heated for 20 h at reflux under Ar, while removing water from the solvent vapors with molecular sieves. Distillation of the solvents left crude product, which was freed from trace contaminants by crystallization from dry hexane to yield 0.34 g of **2b** as light yellow rectangular prisms, mp 80–82 °C; IR (KBr) 1330 (B–O–B), ^1H NMR (C_6D_6 vs. Me_4Si) δ 3.64 (s, 6, CH_3), 7.35 (d of d, 2, β-H), 7.71 (d of d, 2, $J_{\alpha\gamma}$ = 1.4 Hz, $J_{\beta\gamma}$ = 7.8 Hz, γ-H), 8.38 (d of d, 2, $J_{\alpha\gamma}$ = 1.4 Hz, $J_{\alpha\beta}$ = 6.7 Hz, α-H); ^{13}C NMR (CD_2Cl_2 vs. Me_4Si) 51.13, 125.90, 126.32, 132.01, 132.50, 134.28, 141.87; ^{11}B NMR (CD_2Cl_2 vs. BF_3OEt_2) +29.6; mass spectrum, m/z 226 (M^+). Anal. Calcd for $C_{12}H_{12}B_2O_3$: C, 63.82; H, 5.36; B, 9.57. Found: C, 63.99; H, 5.34; B, 9.71.

1,3-Dichloro-1*H*,3*H*-naphth[1,8-*cd*][1,2,6]oxadiborin (2c). Diester **2b** (0.30 g) and PCl_5 (1.1 g) were added to 6 mL of CCl_4

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