cluded; the others either parallel those shown or were conformations of higher energy. At about 3 Å the "benzene-ethylene complex" (experimental ethylene-benzene bond angles and lengths, depicted as Exp't in Figures 2 and 3) has the lowest energy of all the conformations studied. In the stepwise bond-breaking process, the C_1–C_7 bond length was arbitrarily chosen to be twice as long as the C_2–C_8 value. Both singlet (^1S) and triplet (^3T) electronic states were studied.

Similar analyses were performed on compound **1**. The experimental geometry of dihydrobarrelene (**3**) was used to fix the ring geometries. The conformation of the methoxycarbonyl groups used was the one with the carbonyl groups colinear with C_1–C_4 and the C_7–C_1–C_9–O_{10} dihedral angle equal to 45°. The results of these calculations, shown in Figure 3, parallel those for compound **3**.

To test whether the retrodiene reaction was allowed under the conservation of orbital symmetry concept,[19b] we performed both extended Hückel[19a] and CNDO/2 calculations for ethylene-ethylene and ethylene-butadiene cycloaddition reactions. The two methods gave a slightly different ordering of energy levels but otherwise the same results were obtained. Similar CNDO/2 analyses were performed on both compounds **3** and **1**. The occupied reactant molecular orbitals (MO) were composed predominantly of linear combinations of benzene and ethylene MO's, of which the bonding product MO's were the major contributors, thus confirming the allowableness of the concerted retrodiene reaction of **3** and **1**.

Registry No.—**1**, 41894-67-1; **2**, 41894-68-2; dimethyl cyclohexa-1,3-diene-1,4-dicarboxylate, 1659-95-6.

Electrochemical Reduction of (+)-(2*S*,4*S*)-2,4-Dibromopentane

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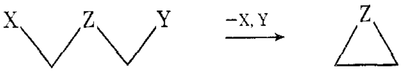
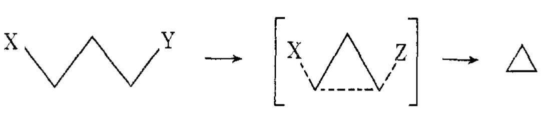
Electrochemical reduction of *meso*- and *dl*-2,4-dibromopentane (**2**) in dimethyl sulfoxide affords in each case roughly equal amounts of *cis*- and *trans*-1,2-dimethylcyclopropanes (**7** and **8**, respectively). The results are interpreted in terms of a stepwise reduction mechanism, *via* a γ-halo carbanion (**13**). (−)-(2*R*,4*R*)-2,4-Pentanediol was prepared by resolution of the racemic diol; the diol was then converted by means of phosphorus tribromide in pyridine into (+)-(2*S*,4*S*)-**2**. Electrochemical reduction of this material afforded (−)-(1*R*,2*R*)-**8** of high optical purity, demonstrating that cyclization of **13** occurs *via* a semi-W transition state. The reduction of *dl* and optically active **2** by a number of chemical reductants was also examined.

There exists a wide variety[2] of reactions which amount to overall 1,3 elimination of two substituents with formation of a carbon–carbon bond, *i.e.*

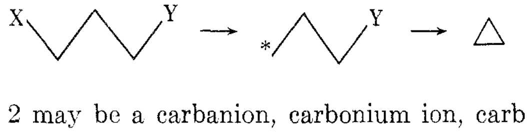


Z = carbon or a heteroatom

Generally, mechanisms proposed for such reactions have fallen into two classes, concerted (eq 1) or stepwise (eq 2). The carbon denoted by an asterisk in

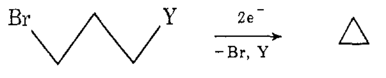


(1)



(2)

eq 2 may be a carbanion, carbonium ion, carbene, or radical; at any rate, a discrete intermediate intervenes on the way to product, while in the concerted mechanism the bonds to X and Y are both breaking as the new bond is forming. A great deal of recent evidence[3] has demonstrated that a number of such reactions formerly thought to be concerted actually proceed in stepwise fashion. Indeed, there does not now appear to exist any authentic example of a concerted 1,3 elimination.[3] In this light, we were attracted to a number of recent reports that electrochemical reduction of compounds of general structure **1** affords cyclopropanes in good

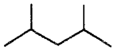


(3)

1, Y = Br, Cl, $^+N(CH_3)_3$

yields,[4] and especially to the suggestion that certain of of these reductions—primarily open-chain compounds—proceed by a concerted mechanism.[4]

We describe herein evidence that electrochemical reduction of the open-chain dibromides *meso*- and *dl*-2,4-dibromopentane (**2**) actually proceeds stepwise, *via* an intermediate γ-halo carbanion.[5] Further, we present the first unequivocal demonstration of the stereochemistry of cyclization of an acylic γ-halo carbanion. The study consisted of an analysis of the products, including stereochemistry, of the electrochemical reduction of *meso*- and *dl*-2,4-dibromopentane (**2**) and of (+)-(2*S*,4*S*)-**2**. Reduction of **2** by chemical reductants was also briefly investigated.



2

Results

Synthesis.—*meso*- and *dl*-2,4-dibromopentane (**2**) were prepared by an improved modification of the

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[1] (a) Excerpted in part from the Ph.D. thesis of W. E. B., Wesleyan University, 1972. (b) A portion of these results have been communicated in preliminary form: A. J. Fry and W. E. Britton, *Tetrahedron Lett.*, 4363 (1971).

[2] A. Nickon and N. H. Werstiuk, *J. Amer. Chem. Soc.*, **89**, 3914 (1967), and many references therein.

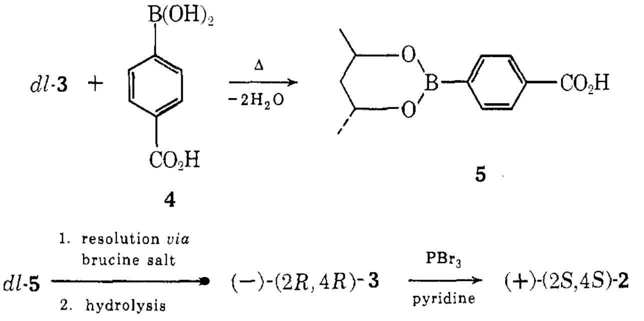
[3] (a) F. C. Bordwell, *Accounts Chem. Res.*, **3**, 281 (1970); (b) L. A. Paquette, *ibid.*, **1**, 209 (1968).

[4] (a) M. R. Rifi, *Collect. Czech. Chem. Commun.*, **36**, 932 (1971); (b) M. R. Rifi, *Tetrahedron Lett.*, 1043, (1969); (c) M. R. Rifi, *J. Amer. Soc.*, **89**, 4442 (1967).

[5] It is well established that electrochemical reduction of alkyl halides involves carbanion intermediates: (a) A. J. Fry and R. G. Reed, *J. Amer. Chem. Soc.*, **94**, 8475 (1972); (b) J. L. Webb, C. K. Mann, and H. M. Walborsky, *ibid.*, **92**, 2042 (1970).

method of Pritchard and Vollmer.[6] This method consists of sodium borohydride reduction of acetylacetone, conversion of the resulting mixture of *meso*- and *dl*-2,4-pentanediol (**3**) to the corresponding sulfite esters, separation of the latter by fractional distillation, and final saponification. Treatment of either *meso*- or *dl*-**3** with phosphorus pentabromide in pyridine afforded the corresponding dibromide **2**, contaminated in each case with a few per cent of the other isomer. The dibromides were purified by preparative vpc before each experiment. Optically active **2** of known absolute configuration was obtained by the method shown in Scheme I. Azeotropic removal of water from a benzene mixture of *dl*-**3** and *p*-carboxyphenylboronic acid (**4**) afforded racemic *trans*-4,6-dimethyl-2-*p*-carboxyphenyl-1,3,2-dioxaborinane (**5**) in quantitative yield. After resolution *via* its brucine salt, optically active **5** was converted into (−)-(2*R*,4*R*)-**3** by vigorous hydrolysis in aqueous sodium hydroxide.[7] The configuration of the diol produced by this sequence follows from the fact that conversion of alcohols to bromides by phosphorus pentabromide in pyridine occurs with inversion of configuration[9] and from the proof of configuration below of the resulting dibromide **2**, which was obtained from **3** in the usual manner. After purification by preparative vpc the dibromide exhibited $[\alpha]^{25}\text{D}$ + 102° ($CHCl_3$) and $[\alpha]^{25}_{540}$ 126°. Its absolute configuration was established by partial reduction with triphenyltin hydride in hexane to a mixture of pentane, 2-bromopentane (**6**), and unreacted **2**. After isolation by preparative vpc, **6** exhibited $[\alpha]^{25}\text{D}$ + 45.5 ± 2.7°. Since it is known that (+)-**6** has the *S* absolute configuration,[10] (+)-**2** must have the 2*S*,4*S* absolute configuration.

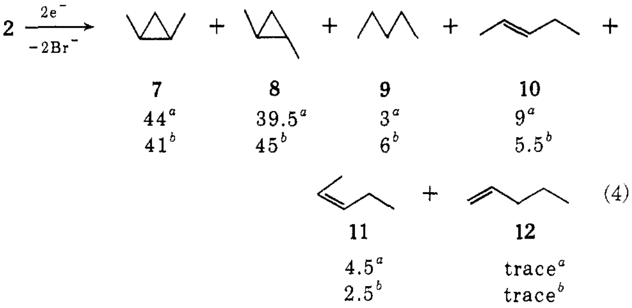
SCHEME I



Dibromide **2** must be of high optical purity. Hudson[10b,c] has reported $[\alpha]^{25}\text{D}$ −52.6 (neat) and −53.4° (MeOH) for (−)-**6**. Furthermore, the specific rotation of a single neat sample of **6** has been measured as +48.2° at 25° and +49.5° at 20°.[11] Thus the rotation of **6** is both solvent and temperature dependent, and the optical purity of the sample prepared from **2** is consequently somewhat uncertain; assuming that Hudson's material was optically pure, that prepared in the present study must be between 87 and 96% optically pure. Results obtained upon electrochemical reduction of this material (*vide infra*) suggest that its optical purity actually lies near the upper end of this range.

Electrochemical Data.—All electrochemical experiments upon *meso*- and *dl*-**2** and upon **6** were carried out in dimethyl sulfoxide (DMSO) containing 0.1 *M* tetraethylammonium bromide (TEAB). Each compound exhibited a single polarographic wave, which appeared at −1.90, −1.91, and −2.09 V (*vs.* sce) for *meso*-**2**, *dl*-**2**, and **6**, respectively. The two dibromides exhibited severe polarographic maxima, which could be eliminated using drop times of 0.5 sec produced by a mechanical drop timer, allowing accurate measurement of the half-wave potential. Because of these maxima, however, diffusion current constants ($I_d = i_d/Cm^{2/3}\cdot t^{1/6}$)[12] could not be computed.

Controlled-potential electrochemical of the diastereomers of **2** was carried out at −2.2 V. The results are summarized in eq 4. These figures represent relative yields but are identical within experimental error with absolute yields: the absolute yield of the mixture of hydrocarbons **7**–**12** is 100 ± 5%. Coulometry indicated the consumption of 2.0 ± 0.1 Faradays/mol of **2**, as expected.[5]



^{a} Per cent yield using *dl*-**2**. ^{b} Per cent yield using *meso*-**2**.

Vpc analysis of the solution as electrolysis proceeded demonstrated the buildup and decay of three substances of similar retention time fomed in roughly equal proportions. Identification of these materials, which had disappeared by the end of the electrolysis, was impossible since even at their maximum concentration they were present in amounts too small for isolation. The retention time of the largest peak corresponded to that of **6**, a likely intermediate (see Discussion).

Addition of water (1.0 *M*) to the electrolysis medium before reduction of *meso*-**2** resulted in a measurable, but small, effect upon the product composition: **7** (41.5%), **8** (49.5%), **9** (6%), **10** (2.5%), **11** (1%), and **12** (no detectable amount).

The electrochemical reduction of (+)-(2*S*,4*S*)-**2** was carried out in the same manner as that of *dl*- and *meso*-**2**. The hydrocarbon products were extracted from the electrolysis mixture with cold heptane and analyzed by vpc. Because of the small scale upon which electrolyses were carried out, the heptane extracts were analyzed directly by polarimetry without attempting to isolate *trans*-1,2-dimethylcyclopropane (**8**) from the mixture. This procedure is justified by the facts that none of the other products is chiral and that these products account quantitatively for all of the dibromide

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[6] J. G. Pritchard and R. L. Vollmer, *J. Org. Chem.*, **28**, 1545 (1963).

[7] This sequence was modeled after a related resolution reported by Agosta.[8]

[8] W. C. Agosta, *J. Amer. Chem. Soc.*, **89**, 3926 (1967).

[9] W. Gerrard, *J. Chem. Soc. C*, 741 (1946).

[10] (a) J. H. Brewster, *J. Amer Chem. Soc.*, **81**, 4575 (1959); (b) H. R. Hudson, *Synthesis*, **1**, 112 (1969); (c) H. R. Hudson, B. A. Chaudri, and D. G. Goodwin, *J. Chem. Soc. C*, 1329 (1970).

[11] Norse Laboratories, private communication, July 1972.

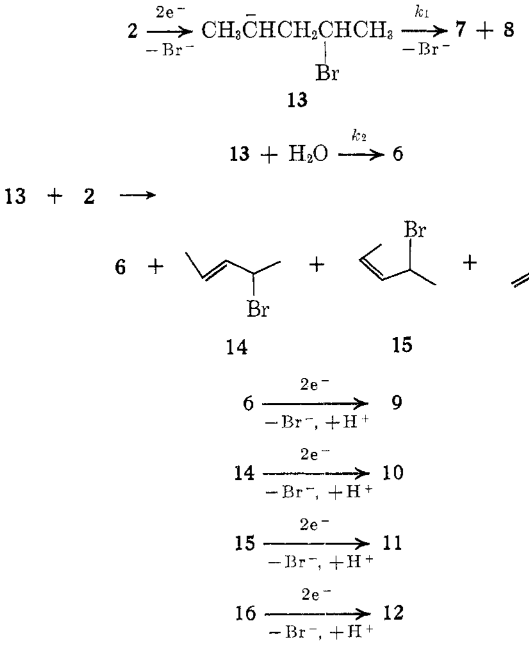
[12] A. J. Fry, "Synthetic Organic Electrochemistry," Harper and Row, New York, N. Y., 1972, pp 71–73.

reduced; *i.e.*, there are no nonvolatile products. After correction (using the results of the vpc analysis) for a small amount of **8** lost by volatilization, the specific rotation of **8** produced in the electrolysis was determined to be $[\alpha]^{25}\text{D}$ −46 ± 2°. Doering and Kirmse[13] have shown that (−)-**8** has the 1*R*,2*R* absolute configuration and have presented a convincing argument that the specific rotation of optically pure **8** is ±46°. The high value for the rotation of **8** obtained in the electrolysis is the basis for the conjecture (*vide supra*) that the starting dibromide (+)-**2** was of high optical purity.

Discussion

Isolation of almost identical mixtures of **7** and **8** from electrolysis of either *dl*- or *meso*-**2** provides essentially definitive proof[14,15] that electrochemical reduction of 1,3-dibromides to cyclopropanes proceeds in stepwise fashion and not concertedly as had previously[4] been claimed. The formation of products **7–12** in the reduction may be rationalized by the sequence of reactions shown in Scheme II. The formation of unsaturates

SCHEME II



10–12 and pentane (**9**) strongly implicates a carbanion, presumably **13**, in the reduction. The conclusion appears almost inescapable that this carbanion lies on the reaction pathway for cyclization and that the loss of stereochemical identity occurs at the carbanion stage. Addition of water (1.0 *M*) to the electrolysis medium has only a slight effect upon the total yields of cyclopropanes. This is qualitatively a good indication that cyclization of **13** to **7** and **8** is quite efficient, but it is difficult to attach any quantitative significance to it. The experiment implies that the ratio $k_1/k_2[H_2O] >> 1$ (where k_1 is the rate of cyclization of **13** and $k_2[H_2O]$ is the pseudo-first-order rate of protonation of **13**, at $[H_2O] = 1.0\ M$). It would be interesting to know k_1, but, since water is a very poor proton donor in dipolar aprotic solvents such as dimethylformamide (DMF) and DMSO,[17−20] it is not possible to use data measured in other solvent systems to estimate k_2.

The results of electrochemical reduction of *meso*- and *dl*-**2** led to the conclusion that reductive cyclization of 1,3-dibromides is not concerted, but stepwise *via* carbanion **13**. Reduction of (+)-(2*S*,4*S*)-**2** then permitted a definitive answer to another question of considerable current interest, *i.e.*, the stereochemistry of cyclization of γ-halo carbanions.[3b,21] Two extreme geometries may be envisaged for the cyclization, semi-W and semi-U,[2] depending upon whether the bromine atom of the γ-halo carbanion is displaced with inversion or retention, respectively. Results from a number of previous studies suggest that the preferred geometry is semi-W; however, all such cases have involved either more or less rigid cyclic systems or γ-halo anions in which the central atom is a heteroatom.[2,3] Either of these factors might affect the course of cyclization in an unsuspected way, hence our interest in the stereochemistry of cyclization of **13**, an all-carbon, open-chain γ-halo carbanion. Scheme III illustrates the stereochemical course of cyclization of **13** by both pathways, recognizing that inversion of configuration at the carbanion carbon and rotation about single bonds must both be taken into account. It is seen that the semi-W path will produce a mixture of *cis*- and (1*R*,2*R*)-*trans*-1,2-dimethylcyclopropanes, while cyclization by the semi-U path affords a mixture of *cis*- and (1*S*,-2*S*)-*trans*-cyclopropanes. In the event, the *trans*-1,2-dimethylcyclopropane obtained in the electrolysis was the 1*R*,2*R* enantiomer, of high optical purity (100 ± 5%) (see Results). Thus cyclization of **13**, and presumably γ-halo carbanions in general, does indeed occur preferentially in semi-W fashion, *i.e.*, with inversion as do the more constrained polycyclic and heterocyclic analogs previously studied.

Some comment upon the evidence previously presented[4a,b] in favor of the view that reduction of compounds such as 1,3-dibromopropane is concerted may be appropriate. The claim for concertedness is based upon certain polarographic criteria and upon the failure of water to quench the electrochemical reduction of

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[13] W. von E. Doering and W. Kirmse, *Tetrahedron*, **11**, 272 (1960).

[14] Interconversion of *dl*- and *meso*-**2** does not occur at a measurable rate under the electrolysis conditions.

[15] The *caveat* might be raised (and was by a referee of our preliminary communication) that concertedness could be preserved through conversion of *meso*-**2** into **7** and **8** by separate concerted paths (and likewise for *dl*-**2**). This would require the coincidence that the activation energies of two related overall paths of greatly differing stereoelectronic requirements be approximately equal. We regard this possibility as artificial and very unlikely and reject it as unnecessarily complex. We are here invoking the logical principle known as Occam's Razor which, despite recent criticism,[16] appears to remain a useful tool as long as it is recalled that it merely advises one, given several explanations of a set of facts, to select the simplest explanation *consistent with the known facts*. As the phrase in italics here suggests, new facts may at any time compel new and more complex interpretations in a given system.

[16] P. G. Gassman and F. J. Williams, *J. Amer. Chem. Soc.*, **94**, 7733 (1972).

[17] J. R. Jezorek and H. B. Mark, Jr., *J. Phys. Chem.*, **74**, 1726 (1970).

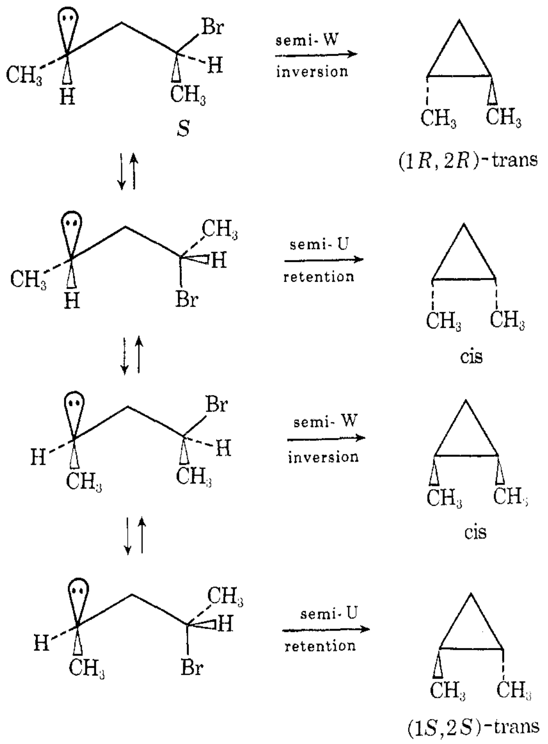
[18] Proton transfer rates appear to be lower in DMSO than in DMF. Thus, on the polarographic time scale the radical anion of 9,10-diphenylanthracene is not protonated in DMSO–phenol solutions,[19] but is readily protonated in DMF–phenol.[20] Furthermore, the only effect of water (2.8 *M*) on the polarographic reduction of 9,10-diphenylanthracene in DMSO is to *lower* the diffusion current because of increased viscosity of water–DMSO solutions over DMSO itself.[19]

[19] L. L. Chung and A. J. Fry, unpublished results.

[20] K. S. V. Santhanam and A. J. Bard, *J. Amer. Chem. Soc.*, **88**, 2669 (1966).

[21] (a) B. M. Trost, W. L. Schinski, F. Chen, and I. B. Mantz, *J. Amer. Chem. Soc.*, **93**, 676 (1971); (b) S. J. Cristol and A. R. Dahl, *ibid.*, **92**, 5670 (1970).

Scheme III



1,3-dibromopropane to cyclopropane.[4a,b] The latter could well be due simply to rapid cyclization of an intermediate γ-halo carbanion[22] analogous to **13** and indeed this possibility was recognized.[4b]

The arguments from polarographic data adduced in favor of concertedness for certain reductions take the following form. Rifi has said that. . . those dibromides which give cyclic products upon electrolysis[23]. . . have a more positive value [of $E_{1/2}$] than those[24] which give open-chain hydrocarbons. The lower but reproducible value is considered to be an indication of a concerted mechanism in the formation of cyclic compounds,[4b] and, also, . . . how well developed the central (*i.e.*, new carbon–carbon) bond is in the transition state will be reflected in the half-wave potential of the dihalide.[4a] If no other effect could possibly account for the fact, *e.g.*, that 1,3-dibromopropane and 3-bromopropyltriethylammonium bromide are ~0.2 and 0.8 V easier, respectively, to reduce than a 1,5- or 1,6-dibromide, the inferences drawn by Rifi from these data would be both reasonable and justified. In fact, however, there are a number of other factors which can contribute to the observed differences. For example, the inductive effect of one bromine upon the other must be considered. Using the data of Lambert,[25] we calculate that the reduction potential of 1,3-dibromopropane should be more positive than that of 1,5-dibromopentane by 0.17 V; the observed difference is 0.23 V. Rifi has rejected inductive effects as a source of the observed differences because 1-bromo-3-chloropropane is somewhat harder (0.13 V) to reduce than 1,3-dibromopropane, an order opposite to that expected on the basis of inductive effects, and because 3-bromopropyltriethylammonium bromide is easier to reduce than can be accounted for on the basis of inductive effects alone. Neither of these arguments is convincing, however. First, it has recently been discovered that reduction potentials of 1,3-dibromides measured at a mercury cathode are markedly affected by adsorption[26] and may in fact differ by as much as 0.4 V from the same potentials measured at platinum. Thus small differences in expected potentials may be associated with adsorption phenomena. Since alkyl bromides are more strongly adsorbed at mercury than chlorides, one would expect 1,3-dibromopropane to be shifted positive by this adsorption effect more than the corresponding bromo chloride. By the same token, the reduction potential of 3-bromopropyltriethylammonium bromide cannot be directly compared with that of the 1,3-dibromide or indeed any other neutral mono- or dibromide, since it is well known that quaternary ammonium ions undergo strong specific adsorption at a mercury surface.[27] Furthermore, inclusion of a charged electroactive substance in the electrical double layer will shift the position of the outer Helmholtz plane, causing a change in its measured reduction potential (relative to related neutral compounds) of unknown but probably large magnitude.[27] It must also be pointed out that mechanistic conclusions based upon variations in the value of α, the electrochemical transfer coefficient, are equally invalid in the face of demonstrable adsorption effects, since the latter phenomenon itself is sufficient to induce significant changes in α even in a series of closely related compounds.

Chemical Reductants.—The reduction of *dl*- and (+)-**2** by several chemical reductants was studied briefly, to determine whether reductive cyclization occurs and, if so, its stereochemistry. Reduction of (+)-**2** by sodium naphthalenide in 1,2-dimethoxyethane afforded a mixture of hydrocarbons **7–12**, along with some unreacted **2**. After isolation of the volatile fraction and polarometric analysis, the rotation of **8** produced in the reaction was calculated as −62 ± 15°, indicating that cyclization occurs with inversion as it should, since carbanion **13** must be an intermediate in the reduction.[28] The wide error limits on this result are associated with the small scale upon which the reaction was run, with the consequence that measured rotations were small, though real and reproducible.[29] When the optically active dibromide was allowed to react with a large excess of lithium aluminum hydride in ether, pentane was the major volatile product. However, when the mole ratio of (+)-**2** to lithium aluminum hydride was 1:1 the volatile products (total yield 50%) consisted of approximately equal amounts of hydrocarbons **7–11**. The optical rotation of the product mixture was zero within experimental error,

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[22] This would parallel the difficulty of quenching cyclopropane formation found in the present work and would be consistent with the common observation that water is a poor proton donor in dipolar aprotic solvents.[5a,17,18]

[23] *E.g.*, 1,3-dibromopropane and 3-bromopropyltriethylammonium bromide.

[24] *E.g.*, 1,5-dibromopentane and 1,6-dibromohexane.

[25] F. L. Lambert, *J. Org. Chem.*, **31**, 4184 (1966).

[26] O. R. Brown and E. R. Gonzalez, *J. Electroanal. Chem.*, **43**, 215 (1973).

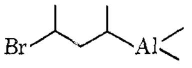
[27] D. M. Mohilner, *Electroanal. Chem.*, **1**, 241 (1966).

[28] (a) J. F. Garst, P. W. Ayers, and R. C. Lamb, *J. Amer. Chem. Soc.*, **88**, 4260 (1966); (b) G. D. Sargent, J. N. Cron, and S. Bank, *ibid.*, **88**, 5363 (1966).

[29] Professor Manfred Schlosser has informed us (private communication, Jan 5, 1973) of his recent proof that reduction of optically active 4,6-dibromononane to *trans*-1,2-dipropylcyclopropane by lithium amalgam[30] also proceeds with inversion.

[30] M. Schlosser and G. Fouquet, *Synthesis*, 200 (1972).

even though, barring unsuspectedly large errors, a small but real rotation should have been observable for the **8** formed in this reaction. The dependence of cyclopropane yield upon hydride concentration could conceivably be explained by formation of an organoaluminum species such as **14**, which could either cyclize



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to **7** and **8** or suffer competitive reduction to **9** by hydride. Alkyllithium intermediates could also account for the observed results.

Reduction of (+)-**2** by triphenyltin hydride has already been mentioned in connection with the proof of absolute configuration of **2**; no more than traces of cyclopropanes were observed. This was also true for the reaction of *dl*-**2** with hexamethylphosphorus triamide[31] which afforded as the major product a single substance whose vpc retention time was identical with that of *trans*-piperylene and which was not investigated further. Reaction of *dl*-**2** with magnesium in ether under nitrogen afforded as the major volatile product (~40% absolute yield) a substance with the same vpc retention time as that of *cis*-2-pentene (**11**). Other products included **8** (20%), **7**, **9**, **10**, and **12**. If the major product is indeed **11**, the preponderance of **11** over **10** is surprising. The reaction may be related to the reported[32] conversion of 1,4-dibromocyclooctanes to cyclooctene upon reaction with magnesium.

Experimental Section

Apparatus.—Polarography was carried out with the aid of a Princeton Applied Research (PAR) Model 170 electrochemistry system. Polarographic drop times were controlled at 0.5 sec with the PAR Model 172 drop timer. Controlled-potential electrolyses were performed using a potentiostat based upon a Kepco KS-120-2.5 programmable power supply. Coulometry was performed by recording the voltage drop across a standard resistor in series with the cell on a Leeds and Northrup Speedomax H recorder equipped with Disc integrator and the digital printer accessory for the integrator. Preparative gc was carried out on a Varian Model 90-P3; analytical gc was carried out on a Varian Model 1200, with flame ionization detector.

***meso*- and *dl*-2,4-Dibromopentane** (**2**).—The synthesis of the isomeric 2,4 pentanediols (**3**) was a modification of that reported by Pritchard and Vollmer.[6] A solution of 400 g of acetylacetone in 1200 ml of methanol was added dropwise to a stirred solution of 100 g of sodium borohydride and 1.0 g of sodium hydroxide in 1 l. of water, while the reaction temperature was maintained between 0 and 10°. After addition was complete, the resulting solution was concentrated to 1500 ml using a rotary evaporator and was then extracted continuously with ether for 15 hr. After removal of ether, distillation afforded 369 g (90%) of a mixture of *dl*- and *meso*-**3**. The diols were separated and converted into the corresponding bromides (**2**) in ~80% yield by the literature procedure.[6] Each dibromide was contaminated by a few per cent of the other isomer; final purification was carried by preparative vpc (15% Carbowax on Chromosorb G, 0.25 in. by 10 ft column). Retention times under these conditions were as follows: *dl*, 16.5 min; meso, 20.5 min. Analytical vpc upon the preparative vpc-purified samples demonstrated that they do not interconvert under vpc conditions.

***p*-Carboxyphenylboronic Acid** (**4**).—*p*-Tolylboronic acid was prepared by a modification of the procedure of Johnson and Bean.[33] A solution of 1.17 mol of *p*-tolylmagnesium bromide in 1100 ml of ether was added dropwise to a solution of 122 g of trimethyl borate in 400 ml of ether at −78° under nitrogen. After addition was complete (~4 hr), the solution was stirred for an additional hour under nitrogen. The temperature was then raised to 0° and the reaction mixture was stirred overnight. The resulting yellow solution was then poured into 700 ml of cold 10% sulfuric acid with vigorous stirring, and the ether phase was separated. The methanol from the aqueous phase was removed at the rotary evaporator, and the aqueous solution was then extracted with three 100-ml portions of ether. The combined ether fractions were dried, the ether was distilled, and the resulting solid was recrystallized from water to afford 109.5 g (69%) of *p*-tolylboronic acid: nmr (CCl_4) AB quartet at δ 7.65 and 7.05 (J = 8 Hz), singlet at 2.15. A thick yellow oil, possibly di-*p*-tolylboronic acid, was removed by filtration during the recrystallization. *p*-Tolylboronic acid (24 g) was oxidized by potassium permanganate according to the method of Michaelis[34] to afford 18 g (61%) of **4**. The nmr spectrum of **4** in DMSO-d_6 consisted of a singlet at δ 7.9 and broad absorption from 4.1 to 6.5.

(−)-(2*R*,4*R*)-2,4-Pentanediol (**3**).—*p*-Carboxyphenylboronic acid (45.0 g) and *dl*-2,4-pentanediol (28.2 g) were added to a flask fitted with a Dean-Stark trap and containing 500 ml of benzene. After 0.5 hr at reflux the theoretical amount of water had been collected. The solution was filtered to remove a small amount of insoluble material. After removal of the solvent (rotary evaporator) and air drying, the yield of *dl*-*trans*-4,6-dimethyl-2-*p*-carboxyphenyl-1,3,2-dioxaborinane (**5**), a white crystalline material, mp 168–183°, was 71 g (97%). Its nmr spectrum consisted of an AB quartet at δ 8.15 and 7.9 (J = 8 Hz) (4 H), multiplets at 4.3 (2 H) and 1.9 (2 H), a doublet at 1.35 (J = 6 Hz, 6 H), and singlet at −0.8 (1 H). This material (35 g) and 50 g of brucine were dissolved in 1 l. of acetone and the solution was refluxed until all crystalline material had dissolved. Concentration and cooling afforded the brucine salt of **5**, mp 127–140°, $[\alpha]^{25}_{540}$ −12° (benzene). After seven fractional crystallizations from acetone using a high recovery diamond pattern,[35] 20 g (50%) of brucine salt was obtained which had mp 129–132° and $[\alpha]^{25}_{540}$ −3.8°. This material was dissolved in hot acetone and to this solution was added a solution of 4.78 g of *d*-tartaric acid in 40 ml of hot acetone. An immediate white precipitate of brucine tartrate formed and was removed by filtration. After removal of acetone at the rotary evaporator and drying, there was obtained 5.40 g of a mixture consisting of optically active **5** contaminated with a small amount of brucine and 2,4-pentanediol. This mixture was added to 15 ml of 20% sodium hydroxide and refluxed for 5 min. The yellow solution was cooled and a small amount of brown oil (brucine?) floating on the surface was removed by pipet. The solution was then saturated with sodium chloride and extracted with four 15-ml portions of chloroform. The combined chloroform fractions were dried and the solvent was removed to afford 2.0 g of (−)-2,4-pentanediol (**3**, 94.5% overall yield from the brucine salt). A portion of this material was distilled *in vacuo;* it exhibited $[\alpha]^{25}\text{D}$ −41.3° ($CHCl_3$).

(+)-(2*S*,4*S*)-2,4-Dibromopentane (**2**).—(−)-2,4-Pentanediol, $[\alpha]^{25}\text{D}$ −41.3° ($CHCl_3$), was converted to the corresponding dibromide in the usual manner.[6] After purification by preparative vpc, optically active **2** exhibited $[\alpha]^{25}\text{D}$ +102° ($CHCl_3$). Another sample prepared in the same way exhibited $[\alpha]^{25}_{540}$ +126°.

Proof of Configuration of (+)-2.—(+)-2,4-Dibromopentane (15 mg) was dissolved in 0.1 ml of heptane. Triphenyltin hydride was injected into this solution in 5-ml portions and the reaction mixture was analyzed at intervals by vpc. The only products were 2-bromopentane (**6**) and pentane (**9**), accompanied by traces of cyclopropanes **7** and **8**. When the concentration of **6** had become greater than that of **2**, the reaction mixture was separated by preparative vpc. Products **6** and **9** were collected as a single fraction. This material was diluted to 1 ml with heptane. Vpc analysis indicated the condentration **6** to be 750 μg/ml. This solution had an observed rotation at the D line of +0.034 ± 0.001°. The specific rotation of this sample of **6** was therefore +45.4 ± 2.7°. Its optical purity and absolute configuration are discussed in the Results section.

Electrolysis of *meso*- and *dl*-2,4-Dibromopentanes.—The electrolysis medium, consisting of 15 ml of a 0.1 *M* solution of tetraethylammonium bromide in DMSO contained in a divided cell of

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[31] B. B. Jarvis, S. D. Dutkey, and H. L. Amonon, *J. Amer. Chem. Soc.*, **94**, 2136 (1972).

[32] M. S. Baird, C. B. Reese, and M. R. D. Stebles, *Chem. Commun.*, 1340 (1971).

[33] R. F. Bean and J. R. Johnson, *J. Amer. Chem. Soc.*, **54**, 4415 (1932).

[34] A. Michaelis, *Justus Liebigs Ann. Chem.*, **315**, 19 (1901).

[35] R. S. Tipson, in "Technique of Organic Chemistry," Vol. 3, A. Weissberger, Ed., Interscience, New York, N. Y., 1956, Chapter 3.

conventional design[36] maintained at 15°, was purged with nitrogen for 15 min. Preelectrolysis was then carried out at −2.2 V (sce)[37] for 15 min, and 20 μl (35.6 mg) of dibromide was then injected into the cell through a serum cap. Vpc analysis was carried out on a $^1/_8$ in × 20 ft Durapak OPN/Porasil C (Waters Associates) column operated at ambient temperature. Retention times of hydrocarbons under these conditions were as follows: *trans*-1,2-dimethylcyclopropane, 14.7 min; pentane, 15.8 min; *cis*-1,2-dimethylcyclopropane, 16.6 min; 1-pentene, 17.3 min; *trans*-2-pentene, 18.2 min; *cis*-2-pentene, 18.9 min.

Vpc Analysis of Electrolysis Mixtures.—It was determined by comparison with standard solutions of the known hydrocarbons that sensitivity factors[39] for pentane, the isomeric pentenes, and the isomeric 1,2-dimethylcyclopropanes in flame ionization vpc are approximately identical (within 2% of each other). Analysis of the gas chromatogram of an aliquot of the electrolysis solution was then carried out by cutting and weighing peaks and comparing the weight of each peak with a calibration chart constructed by injecting a number of standard samples of *trans*-1,2-dimethyl cyclopropane. Integration was by Disc integrator with digital printing accessory when samples to be analyzed by polarimetry were analyzed.

Noninterconvertability of *meso*- and *dl*-2,4-Dibromopentane under Electrolysis Conditions.—Into a 0.1 *M* solution of tetraethylammonium bromide in DMSO was injected 100 μl of *dl*-**2**. This solution was stirred over mercury for 143 min (electrolyses were always complete in much less than 1 hr). Water was added to the solution, the mixture was extracted with pentane, and the pentane was dried and removed *in vacuo*. Vpc and nmr analysis demonstrated the absence of *meso*-**2** or other contaminants. Similar observations were made when the electrolyte was tetrabutylammonium perchlorate.

Electrolysis of (+)-2,4-Dibromopentane.—Electrolysis was carried out as above. After completion of electrolysis, the solution was extracted with four 5-ml portions of cold heptane. This solution was diluted to a known volume (25 ml) and analyzed by vpc immediately before polarimetry. Vpc analysis indicated a concentration of 0.781 mg/ml. The measured rotation was −0.036 ± 0.001° in a 1-dm tube; therefore, $[\alpha]^{25}\text{D}$ was −46 ± 2° for the cyclopropane **8** formed in the reaction.

Reaction of (+)-2,4-Dibromopentane with Sodium Naphthalenide.—(+)-2,4-Dibromopentane (44.5 mg) was added to 1 ml of 1,2-dimethoxyethane (distilled from sodium naphthalenide) under a nitrogen atmosphere. Approximately 1.5×10^{-4} mol of a concentrated solution of sodium naphthalenide in 1,2-dimethoxyethane was injected slowly into the dibromopentane solution. *cis*- and *trans*-2-pentene, pentane, cis-1,2-dimethylcyclopropane, and 1-pentane accounted for 28.5% of the dibromide. *trans*-1,2-Dimethylcyclopropane was produced in 20.5% yield based on the dibromide. Trap to trap distillation of the reaction mixture and polarimetric analysis gave an observed rotation of −0.050° after correction for unreacted starting material (see above). The specific rotation that *trans*-1,2-dimethylcyclopropane produced in this reaction was thus −62 ± 9.5° at the sodium D line.

Reaction of *dl*-2,4-Dibromopentane with a Large Excess of Lithium Aluminum Hydride.—Racemic 2,4 dibromopentane (50 mg) was added to a large excess of lithium aluminum hydride in tetrahydrofuran under nitrogen. After 12 hr the solution was analyzed directly by vpc. The major product was pentane, but small amounts of cyclopropanes and pentene isomers were also present.

Reaction of (+)-2,4-Dibromopentane with a Molar Excess of Lithium Aluminum Hydride.—(+)-2,4-Dibromopentane [17.8 mg (7.74×10^{-5} mol)] was added to a solution of 7.7×10^{-5} mol of lithium aluminum hydride in 0.3 ml of ether under nitrogen. After 10 hr the solution was analyzed by vpc. Approximately equal amounts of *cis*- and *trans*-dimethylcyclopropanes, *cis*- and *trans*-2-pentene, and pentane were present (~10% yield of each). The volatile materials were separated by trap to trap distillation and dissolved in heptane. The concentration of *trans*-dimethylcyclopropane in the heptane solution was determined by vpc. If its specific rotation were −46°, it should have produced a polarimetric rotation of −0.015°; in fact the observed rotation was 0.000 ± 0.0001°.

Reaction of *dl*-2,4-Dibromopentane with Hexamethylphosphorus Triamide.—Hexamethylphorous triamide [118 mg (7.18×10^{-4} mol)] was added to a solution of 89 mg (3.5×10^{-4} mol) of *dl*-2,4-dibromopentane in 1 ml of benzene under nitrogen. After 12 hr at room temperature the solution was analyzed by vpc. No cyclopropanes were observable. The major product formed in good yield; it had the same retention time as *trans*-piperylene.

Reaction of *dl*-2,4-Dibromopentane with Magnesium.—*dl*-2,4-Dibromopentane (18 mg) was added to an excess of magnesium and a crystal of iodine in 0.25 ml of ether under nitrogen. After 10 hr the solution was analyzed by vpc. The major volatile product (~40%) had the same retention time as *cis*-2-pentene (**11**). Other products included **8** (20%), **7**, **9**, **10**, and **12**.

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Registry No.—(+)-**2**, 42075-31-0; *meso*-**2**, 1825-11-2; *dl*-**2**, 1625-68-9; (−)-**3**, 42075-32-1; *dl*-**3**, 1825-14-5; **4**, 14047-29-1; *dl-trans*-**5**, 42075-35-4; **5** brucine salt, 42199-85-9; (−)-**8**, 20520-64-3.

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[36] Reference 12, pp 324–326.

[37] Polarographic and electrolysis potentials were measured with the cadmium amalgam reference electrode of Marple,[38] but are reported relative to sce.

[38] L. W. Marple, *Anal. Chem.*, **39**, 844 (1967). This electrode is *ca.* −0.7 V relative to sce.

[39] H. M. McNair and E. J. Bonelli, "Basic Gas Chromatography," Varian Aerograph, Walnut Creek, Calif., 1968, pp 140–143.