Electrochemistry. 5.[1] Products and Stereochemistry of the Electroreduction of 1-Bromo-1-phenylethane and (±)-1-Deuterio-1-bromo-1-phenylethane

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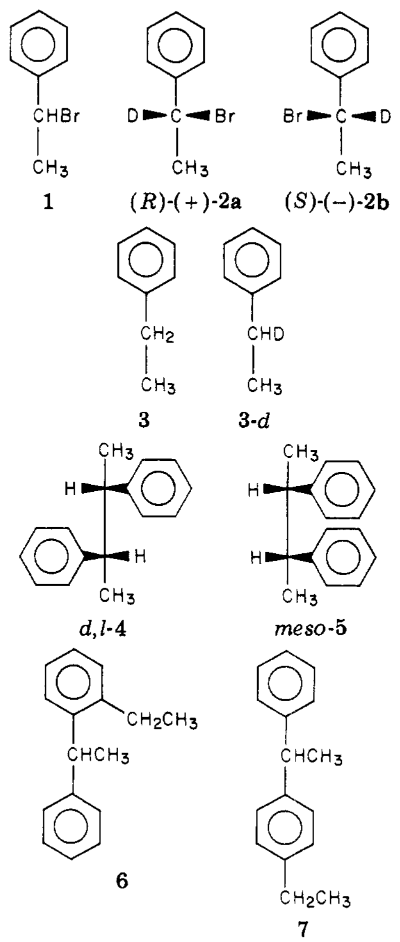
The electroreduction of (±)-1-bromo-1-phenylethane (**1**) and optically active (±)-1-deuterio-1-bromo-1-phenylethane (**2**) at a mercury pool and of **1** at a glassy carbon cathode was studied. Phenylethane (**3**), (±)-2,3-diphenylbutane (**4**), *meso*-2,3-diphenylbutane (**5**), 1-(2-ethylphenyl)-1-phenylethane (**6**), and 1-(4-ethylphenyl)-1-phenylethane (**7**) were obtained from the electroreduction of **1**. The product ratios were strongly potential dependent. Evidence for the existence of a transient organomercury(II) intermediate was obtained. The stereochemical fate of **2a** and **2b** was studied. Exhaustive electroreduction of **2** on a preparative scale led to **3b** with varying optical results. Small net retention or inversion depended mostly on proton-donating ability of the medium. These results are consistent with the presence of an intermediate carbanion. A mechanism which accounts for the formation of dimers **4**–**7** involving an intermediate organomercury(II) species is proposed.

The mechanism of the electroreduction of the carbon–halogen bond has been a topic of interest for four decades.[2] An understanding of this problem bears on the general question of the orientation of a substrate as it approaches a metal–solution interface. S_N1-like[3] and S_N2-like[4] approach, front side approach with inversion,[5] and attack of the electrode from the halogen side of the carbon–halogen bond[6] have all been proposed to represent the geometry of the system during electron transfer. An S_N2-like process is unlikely in view of the ease of reduction of bridgehead polycyclic halides,[6,7] such as 1-bromoadamantane, which has been shown to produce an excellent yield of adamantane[8] and some 1,1′-biadamantyl.[9] This dimer cannot have arisen from an S_N2 mechanism.

Chart I



Reports presently in the literature which describe the stereochemistry of electroreduction of halides represent special cases and do not provide a general answer respecting the stereochemistry of this reaction. Annino and co-workers[10] reported that the reduction of a series of 1-substituted 1-bromo-2,2-diphenylcyclopropanes ranged from 56% inversion to 38% retention of stereochemistry, depending on the substituent. Substituents which could participate in effective resonance stabilization of an intermediate carbanion led to inversion. Other substituents led to retention of stereochemistry, a result characteristic of the cyclopropyl carbanion.[11] Webb, Mann, and Walborsky[12] reported 21–25% retention in configuration for the electroreduction of 1-methyl-1-bromo-2,2-diphenylcyclopropane, a result in agreement with that of Annino and co-workers. Grabowski and Czochralska[5,13] claimed

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[1] Paper 4: J. Casanova and H. R. Rogers, *J. Org. Chem.*, **39**, 3803 (1974).

[2] (a) M. von Stackelberg and W. Stracke, *Z. Electrochem.*, **53**, 118 (1949); (b) J. Casanova and L. Eberson in "The Chemistry of Functional Groups. The Chemistry of the Carbon–Halogen Bond", Vol. 2, S. Patai, Ed., Interscience, New York, 1973, pp 1023-1032; (c) L. Eberson and L. Horner in "Organic Electrochemistry", M. Baizer, Ed., Marcel Dekker, New York, 1973, pp 885–891.

[3] (a) J. Pearson, *Trans. Faraday Soc.*, **44**, 683 (1948); (b) F. L. Lambert, A. H. Albert, and J. P. Hardy, *J. Am. Chem. Soc.*, **86**, 3155 (1964).

[4] (a) P. J. Elving and J. T. Leone, *J. Am. Chem. Soc.*, **79**, 1546 (1957); (b) P. J. Elving and P. Pullman, *Adv. Chem. Phys.*, **3**, 1 (1961).

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[6] J. W. Sease, P. Chang, and J. Groth, *J. Am. Chem. Soc.*, **86**, 3154 (1964); (b) W. F. Carroll, Jr., and D. G. Peters, *J. Org. Chem.*, **43**, 4633 (1978).

[7] J. Zavada, J. Krupička, and J. Sicher, *Collect. Czech. Chem. Commun.*, **28**, 1664 (1963).

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[9] Cf. ref 2b, this paper, citation 152.

[10] R. Annino, R. E. Erickson, J. Michalovic, and B. McKay, *J. Am. Chem. Soc.*, **88**, 4224 (1966).

[11] H. M. Walborsky and J. M. Motes, *J. Am. Chem. Soc.*, **92**, 2445 (1970).

[12] (a) J. L. Webb, C. K. Mann and H. M. Walborsky, *J. Am. Chem. Soc.*, **92**, 2042 (1970); (b) C. K. Mann, J. L. Webb, and H. M. Walborsky, *Tetrahedron Lett.*, 2249 (1966).

[13] (a) B. Czochralska, *Chem. Phys. Lett.*, **1**, 239 (1967); (b) B. Czochralksa, *Rocz. Chem.*, **42**, 895 (1968).

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Table I. Electroreduction of 1-Bromo-1-phenylethane[a,b]

potential, $-V$[c]	products (rel %) 3	4	5	6	7	nF[d]	% yield[e]
0.9	17.6	39.7	40.3	0.4	2.4	1.10	93
1.2	27.9	33.8	33.9	0.8	4.2	1.30	95
1.3	36.0	30.2	30.2	0.6	3.0	1.32	93
1.4	41.0	28.2	28.3	0.7	3.3	1.45	92
1.5	73.0	12.0	12.1	0.9	2.4	1.81	97
1.6	97.0	trace	trace	0.5	2.5	1.91	91
1.7	100.0					2.02	95

[a] On a mercury pool cathode. [b] Dimethylformamide, with 0.2 M tetraethylammonium fluoroborate, 1-2 mM of substrate, at 23 °C. [c] Potentials were measured vs. the saturated calomel electrode. [d] Calculated from digitally recorded coulometric data and the amount of the substrate used. [e] A small percent of styrene (0.1-0.9) and/or 1-phenyl-1-ethanol is included in the total yield.

Table II. Specific Rotations for 1-Deuterio-1-phenylethane in the Electroreduction of Optically Active 1-Bromo-1-(deuterioethyl)benzene at −1.7 V vs. SCE[a]

supporting electrolyte[b]	solvent: acetonitrile $[\alpha]^{27}{}_D$ of 2, deg	acetonitrile $[\alpha]^{25}{}_D$ of 3b, deg	dimethylformamide $[\alpha]^{27}{}_D$ of 2, deg	dimethylformamide $[\alpha]^{27}{}_D$ of 3b, deg
$LiClO_4$	+91.0[c,d]	undetectable	−96.0[c,e]	−0.019 ± 0.004[f]
$(C_2H_5)_4NBF_4$	+91.0[c,d]	−0.076 ± 0.008[f]	+91.0[c,d]	−0.107 ± 0.015[f]
$LiClO_4$			−96.0[c,e]	−0.019 ± 0.004[f]
$(C_2H_5)_4NBF_4$ [h]			+91.0[c,d]	−0.072 ± 0.008[f]
$LiClO_4$ [i]			+87.6[c,g]	−0.086 ± 0.004[f]

[a] Reaction temperatures were 3.5-4.0 °C. [b] 0.2 M. [c] In chloroform, (+) rotation of 2 corresponds to *R* configuration. [d] 82% enantiomeric excess. [e] 86% enantiomeric excess. [f] In chloroform, (−) rotation of 3b corresponds to *R* configuration. [g] 79% enantiomeric excess. [h] Reaction carried out at −1.5 V vs. SCE. [i] Solvent was 0.2 M in 2-methyl-2-propanol.

77–92% inversion of configuration for 2-chloro-2-phenylpropionic acid. This unusual result has been rationalized in several ways,[14] and has recently been challenged by other investigators.[15] Eberson[16] carried out the reduction of optically active 1-chloro-1-phenylethane in dimethylformamide–D_2O and obtained 2% retained configuration in the hydrocarbon product.

It was our objective to examine the stereochemical fate of an optically active simple bromide, unencumbered by structural features which might bias the stereochemistry. Solvolytic stability of secondary bromides rendered these prime substrate candidates, but necessitated the introduction of isotopic hydrogen to preserve chirality. We elected to introduce deuterium into the starting materials, rather than provide it in the solvent pool, due to the uncertainty regarding the primary source of protons in these reactions.[17] For the study we chose optically active 1-deuterio-1-bromo-1-phenylethane. Reactive benzylic and 1-phenylethyl intermediates have been widely studied,[18,19] and our results could be compared readily to others.

Results

Racemic 1-bromo-1-phenylethane (**1**), optically active (±)-(*R*)-1-deuterio-1-bromo-1-phenylethane (**2**), and (−)-(*S*)-1-deuterio-1-bromo-1-phenylethane were prepared as described in the Experimental Section. Working potentials for preparative electroreduction of **1**, **2a**, and **2b** were selected on the basis of polarographic waves observed using a dropping mercury electrode. Three waves were observed for **1**, $E_{1/2}{}^1 = -0.86$, $E_{1/2}{}^2 = -1.32$, and $E_{1/2}{}^3 = -1.36$ V (vs. the saturated calomel electrode). Using a glassy carbon electrode only one wave was observed at −1.45 V (vs. SCE). Addition of 0.2 M 2-methyl-2-propanol did not significantly alter the shape of the polarogram. A proposal for the origin of the three waves in the electroreduction at mercury is considered in the Discussion. Products obtained in the exhaustive electroreduction of **1** are shown in Table I. The yields of product were high and show a smooth transition from one-electron to two-electron product with increasingly negative potential. Organomercurial products were notably absent from these mixtures, but several low potential runs (ca.−1.0 V) carried out below 0 °C underwent chemical decomposition, which involved the deposition of metallic mercury during subsequent extraction of the catholyte with ether. Electroreduction at potentials more negative than the diffusion plateau of the most cathodic wave produced a clean two-electron reduction and yielded phenylethane as the only product. Therefore such a potential, 1.7 V, was selected as the potential for stereochemical studies of compound **2**.

Table III. Stereochemical Results of the Electroreduction of Optically Active 1-Bromo-1-(deuterioethyl)benzene to 1-Deuterio-1-phenylethane at −1.7 V vs. SCE

supporting electrolyte	solvent: acetonitrile	dimethylformamide
$LiClO_4$	racemization	3 ± 1% retention
$(C_2H_5)_4NBF_4$	11 ± 1% inversion	16 ± 2% inversion
$LiClO_4$ [a]		13 ± 1% inversion
$(C_2H_5)_4NBF_4$ [b]		11 ± 1% inversion

[a] Solvent was 0.2 M in 2-methyl-2-propanol. [b] Carried out at −1.5 V.

Reduction of **2** in acetonitrile or dimethylformamide with either lithium perchlorate or tetraethylammonium fluoroborate as supporting electrolyte led to small net retention or inversion, depending on the conditions. Two experiments were conducted to probe the potential de-

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(14) Cf. ref 2b, pp 1026, 1028.

(15) (a) C. M. Fischer and R. E. Erickson, *J. Org. Chem.*, **38**, 4236 (1973) (cf. footnote 2); (b) A. J. Fry and R. G. Reed, *J. Am. Chem. Soc.*, **94**, 8475 (1972), footnote 6.

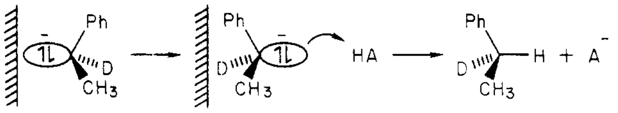
(16) Cf. ref 2b, p 1028, footnote 162.

(17) (a) A. J. Fry and R. G. Reed, *J. Am. Chem. Soc.*, **93**, 553 (1971); (b) *ibid.*, **94**, 8475 (1972).

(18) J. A. Hirsch, "Concepts in Theoretical Organic Chemistry", Allyn and Bacon, Boston, Mass., 1974, pp 33-42.

(19) (a) W. G. Brown and D. E. McClure, *J. Org. Chem.*, **35**, 2063 (1970); (b) F. D. Greene, M. A. Berwick, and J. C. Stowell, *J. Am. Chem. Soc.*, **92**, 867 (1970); (c) K. R. Kopecky and T. Gillian, *Can. J. Chem.*, **47**, 2371 (1969).

Scheme I



pendence of the stereochemistry and the dependence on the proton donating properties of the medium. The specific rotations for 1-deuterio-1-phenylethane are presented in Table II.

Discussion

Table III shows the stereochemical results of reduction under a variety of conditions. When a good proton donor is used as the supporting electrolyte,[1] the solvent seems to have little effect on the stereochemical result. The degree of inversion observed in all cases where the net optical result was inversion is virtually the same, within experimental error, regardless of which solvent was used. Lowering the potential did not seem to affect the stereochemical result. When a poor proton donor or nonproton donor is used as the supporting electrolyte, the solvent may become important in determining the stereochemical outcome, depending upon the interactions of the solvent and supporting electrolyte with the intermediate.

There is evidence that tetraethylammonium ion is a good proton donor toward anionic intermediates.[17] The abstraction of a proton from tetraethylammonium ion leads to the Hoffmann elimination represented as follows:

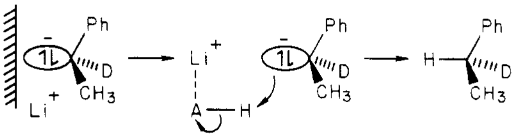
$$R:^- + (CH_3CH_2)_4N^+ \rightarrow RH + CH_2{=}CH_2 + Et_3N$$

In each case where tetraethylammonium ion is used as the supporting electrolyte, the net optical result is inversion. When lithium perchlorate is used as the supporting electrolyte the net optical result ranges from racemization to slight retention. The results seem to suggest that the proton-donating ability of the supporting electrolyte may have decisive effects on the stereochemical outcome. Consistent with this notion is the fact that when 2-methyl-2-propanol is added to the dimethylformamide–lithium perchlorate system the net optical result changes from slight retention to inversion.

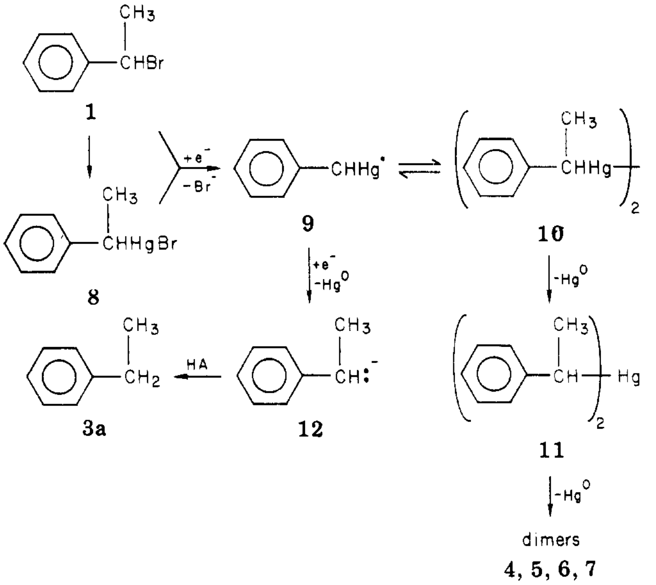
The observed results are consistent with the following mechanism involving a carbanionic intermediate. The first step is the attack on bromine to yield the carbanion of retained configuration.[10] In the case where a good proton donor is used as the supporting electrolyte, such as tetraethylammonium ion or if 2-methyl-2-propanol is present, the carbanion is rapidly protonated from the back side, where it is less sterically hindered. A schematic representation of this process is shown in Scheme I. Racemization which is observed in all cases may occur when desorption of the initial carbanion from the electrode surface allows inversion of configuration before protonation occurs.

In the case where lithium perchlorate is used as the supporting electrolyte, the initial carbanion formed is not protonated rapidly (both dimethylformamide and acetonitrile are relatively poor proton donors). Using Cram's model of ion pairing,[20] the slight retention observed in the DMF/LiClO$_4$ system may be explained by the ion pair formed between the initially formed carbanion of retained configuration and lithium ion adsorbed on the electrode surface. The ion pair, then, desorbs and the carbanion is protonated by front-side attack. Lithium ion provides little steric hindrance toward front-side attack. In addition, it is assumed that the proton donor is positioned for front-side attack by interacting with the lithium ion. A schematic representation of this process is shown in Scheme II. The ion pairing appears not to be important, as evidenced by the small degree of retention observed in the case of dimethylformamide–lithium perchlorate. The proton-donating ability of 2-methyl-2-propanol appears to be more important than the ion pairing in determining the stereochemical result. Racemization is probably due to inversion of the desorbed carbanion prior to protonation. The acetonitrile–lithium perchlorate mixture is no doubt conducive to long-lived carbanions.

Scheme II



Scheme III



Autoracemization of optically active (1-bromo-1-deuterioethyl)benzene under the conditions used for the electrolyses (3.5 °C) proved negligible. In none of the solvent–supporting electrolyte combinations did autoracemization produce more than 3% loss of optical purity. Experimental error is greater than 3%; hence autoracemization was neglected in the final calculations. The results of mass spectrometry showed a deuterium content of 98% at the α position of both phenylmethyldeuteriocarbinol and (α-deuterioethyl)benzene. Hence, Czochralska's "S$_N$2" mechanism[5] interpretation should be viewed with caution.

Regarding the overall mechanism of reduction, a mechanism proposed earlier by Webb, Mann, and Walborsky[12a] and employed by us to rationalize earlier results[21] is most reasonable in the present case. That mechanism is illustrated in Scheme III. Electrocatalytic conversion of the bromide to the mercuribromide salt (8) has been observed in benzylic systems by others[22] and by ourselves. We attribute the variable, most anodic wave ($E_{1/2}{}^1$) to the reduction of 8, whose concentration will be a function of the time of contact between sample and the mercury pool

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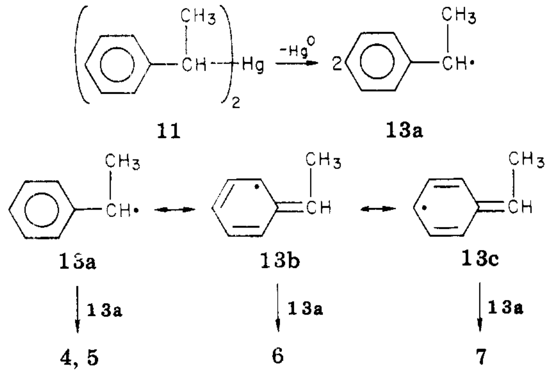
[20] D. J. Cram, "Fundamentals of Carbanion Chemistry", Academic Press, New York, 1965, p 154.

[21] J. Casanova and H. R. Rogers, *J. Am. Chem. Soc.*, **96**, 1942 (1974).

[22] L. B. Rogers and A. J. Diefenderfer, *J. Electrochem. Soc.*, 942 (1967).

Scheme IV



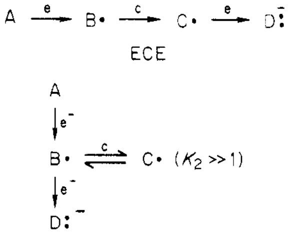
cathode. Dessy has proposed the intermediacy of mercury(I)[23a] species and mercury(I) radicals (**9**) adsorbed on metal surfaces have been proposed.[23b] Heaton and Laitinen have proposed a very similar mechanism for methylmercuric halide reduction,[23c] and adsorbed intermediates such as **9** have been confirmed by Brown and Taylor.[23d] Symmetrization via mercury(I) dimers (**11**) has been proposed by Butin and co-workers.[24]

As indicated in the Results, three polarographic waves were observed for the reduction of 1-bromo-1-phenylethane. The most anodic wave ($E_{1/2}{}^1 = -0.86$ V) was variable in height, depending on the time interval between the assembly of the reduction cell and the actual measurement. We attribute this wave to the one-electron reduction of electrocatalytically produced mercuribromide **8** to mercury(I) radical **9**. The second wave ($E_{1/2}{}^2 = -1.32$ V) would then be due to the direct one-electron reduction of starting material **1** to mercury(I) radical **9**. $E_{1/2}{}^3 = -1.36$ V represents the reduction of **9** to carbanion **12**. Since direct reduction of **1** to **9** and subsequent reduction of **9** to **12** are at very similar potential at mercury, it is not surprising that reduction at a glassy carbon cathode, which cannot involve organomercurial intermediates, should show a single wave.

When reduction is carried out at a mercury cathode, it is further evident that a thermally unstable organomercurial compound is present, since mercury metal was observed in workup of low temperature, low potential reductions of the bromide. Such an observation corresponds to the conversion of the primary one-electron reduction product **11** to dimers **4**, **5**, **6**, and **7** (see Table I). Organomercurials are often observed in low potential reductions of bromides for which the mercury(II) dimer is expected to be stable,[21,25] but are absent in those bromides for which the mercury(II) dimer would be thermally unstable.[26]

It is interesting to note the complete absence of a meta-substituted head-to-tail dimer among the products. Such a dimer was actively sought. This result clearly implies that the dimers are formed by radical–radical recombination and not by a radical substitution process. The proposed mechanism for dimer formation is shown in Scheme IV. Depending on the mode of recombination, dimers **4**, **5**, **6**, and **7** will be produced. Similar results for dimers **4** and **5** have been observed. Small amounts of dimers observed in the reduction at a glassy carbon cathode may be the result of coupling of carbon-bound radicals.

Scheme V



The mechanism of Scheme III accounts for all of the observations which we have made in this study, and accounts for electrochemical mechanism that has been frequently proposed[12a,21] for organic halide electroreductions in the following way: if it can be asserted that mercury(I) dimer **10** is electroinactive and that the equilibrium constant connecting it to **9** is large, then to the extent that **9** is removed from electrochemical reactivity by dimerization it will *appear* that the first electron transfer produces an electroinactive product. This is converted to an electroactive product (**9**) by a (slow) chemical reaction. Compound **9** can then react electrochemically. The process described above may be illustrated as shown in Scheme V.

Experimental Section

General. Melting points and boiling points are uncorrected. Melting points were taken on a Thomas-Hoover Capillary Melting Point Apparatus and on a Fisher Digital Melting Point Analyzer Model 355. Proton NMR spectra were recorded on a Varian Model A-60 spectrometer using carbon tetrachloride solutions with internal Me_4Si. Infrared spectra came from a Beckman IR-33 spectrophotometer using neat samples. Liquids were analyzed and isolated by GLC on a column of silicone oil SE-54, 10% on firebrick, $^1/_4 \times 5$ ft, using a Varian Aerograph Chromatograph Model A-700. Optical rotations were determined on a Perkin-Elmer Polarimeter Model 241 equipped with the thermostat and jacketed cells (1.02-mL volume). Mass spectral data came from a Varian CH-5 mass spectrometer. Thin-layer chromatography was performed on 5 × 20 cm silica gel plates (IB-F flexible sheets) using hexane as a solvent. Spots were visualized with UV light. Electrolyses were performed using a PAR Model 373 Potentiostat–Galvanostat. Electroreductions were followed coulometrically using a PAR Model 379 Digital Coulometer while the chronoamperometric curve was recorded on a Simpson Multirecorder 605. Polarographic data were recorded using a PAR Polarographic Analyzer Model 174-A equipped with a Houston Instrument 2000 Recorder. All chemicals used in syntheses were reagent grade and solvents used in polarimetric studies were spectrograde.

Racemic 1-Bromo-1-phenylethane (1). Commercial acetophenone was distilled under reduced pressure: bp 80 °C (10 mm); NMR δ 2.60 (s, 3, $-CH_3$), 7.92 (m, 5, $-C_5H_6$). The ketone was converted to the 1-phenyl-1-ethanol using lithium aluminum hydride in diethyl ether (79%): bp 50 °C (0.24 mm); NMR δ 1.27 (d, 3, $-CH_3$), 4.27 (s, 1, -OH), 4.58 (q, 1, >CHOH), 7.13 (s, 5, $-C_6H_5$); IR ν 3500 cm^{-1} (OH). The corresponding bromide was obtained by the previously reported procedure[27] (61%): bp 31 °C (0.1 mm) [lit.[27] bp 31 °C (0.1 mm)]; NMR δ 1.94 (d, 3, $-CH_3$), 5.05 (q, 1, >CHBr), 7.20 (m, 5, $-C_6H_5$).

(+)-(*R*)-1-Deuterio-1-bromo-1-phenylethane (2a) and (−)-(*S*)-1-Deuterio-1-bromo-1-phenylethane (2b). The reduction of acetophenone with $LiAlD_4$ (Ventron Alfa Products, 98% isotopic purity) in anhydrous diethyl ether gave 1-deuterio-phenyl-1-ethanol (69%): bp 62 °C (0.2 mm); NMR δ 1.28 (s, 3, $-CH_3$), 4.41 (s, 1, -OH), 7.14 (s, 5, $-C_6H_5$); IR ν 3500

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[23] (a) R. E. Dessy, W. Kitching, T. Psarras, R. Salinger, A. Chen, and T. Chivers, *J. Am. Chem. Soc.*, **88**, 460 (1966); (b) R. Benesch and R. E. Benesch, *ibid.*, **73**, 3391 (1951); (c) R. C. Heaton and H. A. Laitinen, *Anal. Chem.*, **46**, 547 (1974); (d) O. Brown and K. Taylor, *Electroanal. Interfacial Electrochem.*, **50**, 211 (1974).

[24] (a) K. P. Butin, A. N. Kashin, A. B. Ebshler, V. V. Strelets, I. P. Beletskaya, and O. A. Reutov, *J. Organomet. Chem.*, **39**, 39 (1972); (b) O. A. Reutovand and K. P. Butin, *ibid.*, **99**, 171 (1975).

[25] (a) J. Grimshaw and J. S. Ramsey, *J. Chem. Soc. B*, 60 (1968); (b) O. R. Brown, H. R. Thirsk, and B. Thorton, *Electrochim. Acta*, **16**, 495 (1971).

[26] W. F. Carroll, Jr., and D. G. Peters, *J. Org. Chem.*, **43**, 4133 (1978).

[27] R. O. Hutchins, D. Masilamani, and C. A. Maryanoff, *J. Org. Chem.*, **41**, 1071 (1976).

cm^{-1} (OH). From mass spectral data the deuterium content was calculated as 0.98 atom of D per molecule.

The (−)-1-deuterio-1-phenyl-1-ethanol (**3a**) and (+)-1-deuterio-1-phenyl-1-ethanol (**3b**) were prepared from the racemic mixture by the method of Kenyon.[28a,b] Deuterated alcohols were converted to hydrogen phthalate esters by the treatment with an equimolar amount of phthalic anhydride in dry pyridine. The (±)-1-deuterio-1-ethyl hydrogen phthalate was obtained after recrystallization of the oily reaction residue in glacial acetic acid at 6 °C during 5 days (88%): mp 106–108 °C (lit.[28b] mp 108 °C). The treatment of the (±)-hydrogen phthalate with brucine in acetone yielded corresponding brucine salts.[28a] Several recrystallizations in acetone gave (−)-1-deuterio-1-phenyl-1-ethyl hydrogen phthalate brucine salt (22% yield, mp 151–153 °C), while repeated recrystallizations of the residue from mother liquors resulted in (±)-1-deuterio-1-phenyl-1-ethyl hydrogen phthalate brucine salt (11%, mp 102–104 °C, lit.[28b] mp 105 °C). Optically active hydrogen phthalates were obtained after decomposition of corresponding brucine salts in 1 N HCl at room temperature during 5 h and purification in carbon disulfide solutions.[28a,b] (−)-1-Deuterio-1-phenylethyl hydrogen phthalate (18%): mp 84–86 °C (lit.[28b] mp 86 °C); $[\alpha]^{21}{}_{5461}$ −20.3° (*c* 2.96, C_6H_6) [lit.[28b] $[\alpha]^{22}{}_{5461}$ −19.9° (C_6H_5)]. (±)-1-Deuterio-1-phenylethyl hydrogen phthalate (9%): mp 83–85 °C (lit.[28a] mp 81–82 °C); $[\alpha]^{22}{}_{5461}$ +19.2° (*c* 2.26, C_6H_6). The hydrolyses of both hydrogen phthalates in a warm alkaline 95% ethanol followed by the extraction with ether and distillation under reduced pressure gave optically active alcohols. (−)-1-Deuterio-1-phenyl-1-ethanol (**3a**) (7%): bp 49–51 °C (0.25 mm) [lit.[28b] bp 93 °C (14 mm)]; $[\alpha]^{25}{}_{D}$ −56.9° (*c* 1.33, chloroform) (lit.[27]). (+)-1-Deuterio-1-phenyl-1-ethanol (**3b**) (4%): bp 48–51 °C (0.2 mm) [lit.[28a] bp 98–99 °C (20 mm)]; $[\alpha]^{23}{}_{D}$ +55.8° (*c* 2.72, chloroform) (lit.[27]).

Both alcohols were converted to the corresponding optically active bromides by the treatment with PBr_3 in anhydrous ether and pyridine at −45 °C.[27] Reaction mixtures were taken in pentane and after the usual workup the solutions were concentrated under vacuum on a rotary evaporator at ice bath temperature. The liquid residue was distilled under high vacuum. The (−)-1-deuterio-1-phenyl-1-ethanol gave (+)-1-deuterio-1-phenyl-1-ethyl bromide (10%): bp 33 °C (10 mm) [lit.[28] bp 33.5–35 °C (0.07–0.08 mm)]; $[\alpha]^{27}{}_{D}$ +91.0° (*c* 2.09, chloroform) [lit.[29] (calcd) $[\alpha]^{27}{}_{D}$ 111.5° (*c* 2.00, chloroform)]. The (+)-1-phenyl-1-ethanol yielded (−)-1-deuterio-1-phenylethyl bromide (3%): bp 32.5 °C (0.05 mm) [lit.[27] bp 33.5–35 °C (0.07–0.08 mm)]; $[\alpha]^{27}{}_{D}$ −96.0° (*c* 2.08, chloroform). The optical purity of both enantiomers was calculated on the basis of the highest optical rotation reported in the literature[30] as 81.6% for **2a** and 86.1% for **2b**.

Electrolysis Experiments. The electrolytical cell used during this work with a mercury pool as a cathode was essentially the same as that used previously.[1,21] During electroreductions on a mercury cathode a constant stream of dry nitrogen was passed through the cell. The constant temperature in the cell was achieved by means of a water bath (ambient temperature) or an ice bath (0 °C). Mercury was Bethlehem grade. It was recycled as described previously[1] and distilled under vacuum prior to use.

The exhaustive electrolyses on a glassy carbon were made using a glassy carbon crucible, 8 cm o.d. (Beckwith Co.), both as a cell and a working electrode. A copper wire net surrounding the crucible was used for electrical connections to the cathode. Connections to the counterelectrode and an agar bridge which was in contact with an external saturated calomel electrode were the same as previously reported.[1] Anodic and cathodic compartments were separated by a ceramic bucket. Catholyte was stirred magnetically. Both compartments were purged with dry nitrogen prior to electroreduction. The glassy carbon crucible was placed in a larger container through which dry nitrogen was passed during the reduction maintaining the nitrogen atmosphere in the cell.

All components of both electrochemical cells were dried in an oven at 110 °C prior to use. Ceramic buckets were fired overnight at 700 °C after extraction with acetone in a Soxhlet extractor.[31] Supporting electrolytes tetraethylammonium fluoroborate and lithium perchlorate were electrochemical grade and were dried under vacuum prior to use. Dimethylformamide and acetonitrile were used as solvents in large scale electrolyses and polarographic analyses. Purification of DMF was described previously.[1] Commercial acetonitrile was stirred for 48 h over calcium hydride and distilled. Repeated stirring of the distillate over phosphorus pentoxide and redistillation (the fraction boiling at 80 °C was collected) gave polarographically pure solvent.

The catholyte was prereduced in all runs at the potential 0.1 V more cathodic than the working potential. The background current was compensated with the digital coulometer and 1–2 mmol of substrate was added to the cathodic compartment. Electrolyses were carried out until the final current reached the background level. The catholyte was diluted with water and extracted with 3 × 50 mL of redistilled trichlorofluoromethane (Freon-11, Matheson Gas Products). The combined organic extracts were washed with water (5 × 50 mL) and saturated salt solution (2 × 25 mL). After drying over magnesium sulfate for 16 h, the Freon was distilled using a short Vigreaux column. The workup and product isolation were done at +6 °C.

Product Analysis. Electroreductions of the compound **1** gave at the working potential −1.7 V on mercury and at −1.6 V on a glassy carbon cathode a single liquid product: NMR (t, 3, $-CH_3$), 2.68 (q, 2, $-CH_2-$), 7.23 (s, 5, $-C_6H_5$); GLC t_R = 135 s (155 °C column, 240 °C injector, 251 °C detector, He 75 mL/min, filament current 100 mA, chart speed 90 s/in.). The identity of the sole product was established on GLC by comparison to the authentic sample of phenylethane (**3**).

Electrolyses of **1** at less cathodic potentials (at −1.6 to −0.9 V on mercury) yielded a mixture of liquid and solid products showing a complex NMR spectrum. GLC analyses showed a peak corresponding to **3** and four additional peaks (t_R = 1014, 1122, and 1458 s). The same array of products was observed using a glassy carbon electrode at −1.2 V, although the proportion was different.

These products were separated and isolated in the order of their t_R values.[32a] *d,l*-2,3-Diphenylbutane (**4**): t_R = 1014 s; lit.[32b] bp 162–164 °C (25 mm); NMR δ 1.24 (m, 6, 2-CH_3), 2.86 (m, 2, 2-CH), 6.96 (m, 10, 2-C_6H_5), in excellent agreement with the values reported previously;[33] the mass spectrum showed *m/e* 210 (M^+, 41%). *meso*-2,3-Diphenylbutane (**5**): t_R = 1122 s; mp 124–126 °C (lit.[32b] mp 126–127 °C); NMR δ 1.00 (m, 6, 2-CH_3), 2.79 (m, 2, 2-CH<), 7.13 (s, 10, 2-C_6H_5), in full accord with the literature;[33] the mass spectral data gave *m/e* 210 (M^+, 45%). 1-(2-Ethylphenyl)-1-phenylethane (**6**): t_R = 1266 s; lit.[34] bp 165 °C (20 mm); NMR δ 1.12 (t, 3, $-CH_2CH_3$), 1.59 (d, 3, $>CHCH_3$), 2.59 (q, 2, $-CH_2CH_3$), 4.32 (w, 1, $C\mathbf{H}CH_3$), 7.08 (m, 9, $-C_6H_5$, C_6H_4); IR[35] 3040 (m), 3000 (m), 2940 (s), 2935 (w), 2850 (m), 1592 (m), 1480 (s), 1439 (s), 1364 (m), 1068 (w), 1040 (w), 1012 (m), 770 (m), 739 (s), 702 (w), 682 cm^{-1} (s); mass spectrum (rel intensities) *m/e* 210 (M^+, 45%), 195 ($C_{15}H_{15}^+$, 59%), 181 ($C_{14}H_{13}^+$, 14%), 166 ($C_{13}H_{10}^+$, 11%), 133 ($C_{10}H_{13}^+$, 5%), 105 ($C_8H_9^+$, 18%), 91 ($C_7H_7^+$, 26%), supports the structural assignment. 1-(4-Ethylphenyl)-1-phenylethane (**7**): t_R = 1458 s; lit.[34] bp 170 °C (20 mm); NMR δ 1.20 (t, 3, $-CH_2C\mathbf{H}_3$), 1.59 (d, 3, $>CHC\mathbf{H}_3$), 2.58 (q, 2, $C\mathbf{H}_2CH_3$), 4.04 (q, 1, $>C\mathbf{H}CH_3$), 7.00 (s, 5, $-C_6H_5$), 7.11 (m, 4, $-C_6H_4$); IR ν[35] 3062 (w), 3040 (w), 3000 (m), 2942 (s), 2902 (m), 2850 (m), 1585 (m), 1492 (m), 1475 (m), 1432 (s), 1398 (w), 1357 (w), 1151 (w), 1035 (w), 1002 (w), 811 (m), 736 (m), 676 cm^{-1} (s); mass spectra (rel intensities) *m/e* 210 (M^+, 57%), 195 ($C_{15}H_{15}^+$, 100%), 181 ($C_{14}H_{13}^+$, 23%), 166 ($C_{13}H_{10}$, 17%), 105 ($C_8H_9^+$, 50%), 91 ($C_7H_7^+$, 19%), in accordance with the proposed structure.

Small amounts of 1-phenyl-1-ethanol (2–9%) and styrene (0.15–0.9%) were observed in electrolyses carried out over a long

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time at lower potentials and/or at low temperature. These materials showed on GLC t_R = 149 and 140 s, respectively. Their identity was confirmed by the comparison to the authentic samples. Products obtained in the electrolysis of **2a** and **2b** were examined analytically on GLC and were assigned by the comparison to the products obtained in electroreduction of 1. The 1-deuterio-1-phenylethane was isolated from GLC, t_R = 680 s (105 °C column, 150 °C injector, 200° C detector, He, 75 mL/min, filament current 100 mA, chart speed 90 s/in.), and was a subject of polarimetric analyses. Reinjection of the sample of the isolated 1-deuterio-1-phenylethane did not show any impurities and its NMR signals δ 1.24 (d, 3, $-CH_3$), 2.67 (m, 1, –CHD–), and 7.23 (s, 5, $-C_6H_5$) were consistent with the structural assignment. From the mass spectrum the deuterium content was calculated as 0.97 atom of D per molecule.

The catholyte in the electroreduction of 1 carried out at 0 °C and at red light was examined by TLC performed at 6 °C and in the absence of light. The spot having R_f value 0.20 was observed by characteristic mercury vapor development under UV light on a fluorescence silica gel plate.[36] The lifetime of the compound was no longer than 30 min under the reported conditions. The catholyte containing 1 in an open circuit cell (at ambient temperature and on visible light) was examined by TLC. It showed a spot with R_f 0.02 exhibiting mercury vapor development by irradiation with UV light.[37] The thermal decomposition of that compound (in dark) on a silica gel plate was complete in 5 h.

Polarographic Measurements. Polarographic analyses were carried out using 10^{-2} mol of tetraethylammonium fluoroborate in DMF. The concentration of 1 was 10^{-4} M. Half-wave potentials are reported vs. the saturated calomel electrode at room temperature. A dropping mercury electrode and a Tokai glassy carbon cathode[14] were used in this work. The half-wave potentials were determined on a mercury electrode as $E_{1/2}{}^1 = -0.86$, $E_{1/2}{}^2 = -1.32$, and $E_{1/2}{}^3 = -1.36$ V. Measurements on a carbon cathode gave one wave, $E_{1/2} = -1.485$ V. The reported data are the average values of five independent runs.

Polarimetric Analysis. The purities of all solvents used in polarimetric measurements were checked by GLC, NMR, and IR. The racemic 1-phenylethane was fractionally distilled. The fraction boiling at 136 °C was used as a solvent in optical rotation analysis on 1-deuterio-1-phenylethane obtained as the reduction product in electrolysis of **2a** and **2b**. Optical rotation was calculated by a previously reported method[38] and employed Mosher's value[39] for the rotation of enantiomerically pure 1-deuterio-1-phenylethane.

A water-jacketed polarimetric cell was allowed to thermostat at the desired temperature at least 1 h prior to analysis. The mercury and sodium lamps were warmed up through the same period of time.

The background readings (using solvent in both sample and reference cell) were recorded from a digital display in sequences of 5 s during 8 min (96 readings). Polarimetric measurements on **2a**, **2b** and electroreduction products were performed in the same manner. The magnitude of the background rotation was in all experiments less than ±0.0006° and was subtracted from the optical rotation obtained in measurement of reduction products.

The possible racemization of **2a** and **2b** during preparative electrolysis was examined polarimetrically. Temperature in the polarimetric cell was held constant at 0 °C as it was in electroreductions of optically active 1-phenyl-1-bromoethanes. A gentle stream of dry nitrogen (precooled to 0 °C) was passed through the polarimetric cave with cells to prevent any cloudiness on cell windows. Optical rotations were recorded on solutions having the same qualitative and molar composition as that of catholyte in the electrochemical cell. Polarimetric data in these experiments were obtained from the same period of time as required for the electrolysis completion and no racemization of **2a** or **2b** was observed.

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Registry No. 1, 38661-81-3; **2a**, 69150-79-4; **2b**, 71927-77-0; **3**, 100-41-4; **3-*d***, 65805-35-8; **3a**, 71886-64-1; **3b**, 71886-65-2; **4**, 2726-21-8; **5**, 4613-11-0; **6**, 71886-66-3; **7**, 71886-67-4; acetophenone, 98-86-2; 1-phenyl-1-ethanol, 13323-81-4; 1-deuterio-1-phenyl-1-ethanol, 71886-68-5; (±)-1-deuterio-1-phenyl-1-ethyl hydrogen phthalate, 71886-69-6; (–)-1-deuterio-1-phenyl-1-ethyl hydrogen phthalate brucine salt, 71886-71-0; (+)-1-deuterio-1-phenyl-1-ethyl hydrogen phthalate brucine salt, 71886-73-2; (–)-1-deuterio-1-phenylethyl hydrogen phthalate, 71886-70-9; (+)-1-deuterio-1-phenylethyl hydrogen phthalate, 71886-72-1.

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[36] (36) Numerous dialkylmercurials synthesized in our laboratory are of identical R_f value and show mercury vapor development under ultraviolet light.

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Electroreduction of α,β-Unsaturated Esters and Amides. 3. Polarographic Comparison of Compounds from Saturated and Unsaturated Alcohols and Amines[1a]

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Polarographic reduction data for a variety of esters and N-substituted amides of cinnamic and phenylpropiolic acids in anhydrous and aqueous acetonitrile are reported. In general, it was found that unsaturation in the alcohol or amine moiety facilitates electroreduction (i.e., decreases the value of $-E_{1/2}$) of the compound as compared to the case for the corresponding methyl and ethyl esters and *N*-methylamides, respectively.

In previous papers[2-10] we described the syntheses of a number of α,β-unsaturated esters of general formula $Ar(C_2)'CO_2CH_2(C_2)Y$ and α,β-unsaturated amides of general formula $Ph(C_2)'CONHCH_2(C_2)Ph$, where the (C_2) and $(C_2)'$

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