

The Stereochemistry of Electroreductions.

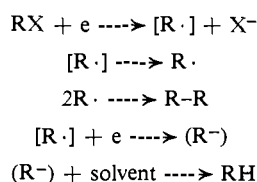
I. Cyclopropyl Halides¹

Raymond Annino, Ronald E. Erickson, John Michalovic,² and Bruce McKay²

Contribution from the Department of Chemistry, Canisius College,
Buffalo, New York. Received May 12, 1966

Abstract: The electrochemical behavior of optically active 1-bromo-2,2-diphenylcyclopropanecarboxylic acid, its methyl ester, and 1-bromo-1-methyl-2,2-diphenylcyclopropane is reported. Reduction of the acid or its methyl ester yields products of partially inverted configuration, whereas the reductions of the carboxylate ion and 1-bromo-1-methyl-2,2-diphenylcyclopropane proceed with partial retention of configuration. The stereochemical results correspond closely with those observed in zinc metal reductions of the same compounds. They are readily interpreted in terms of a mechanism involving initial attack by the electrode or metal surface on the halogen side of the carbon-halogen bond.

In recent years there has been a great deal of interest shown in the mechanism of the electroreduction of the carbon-halogen bond. Elving and Pullman's generalized reaction mechanism scheme follows³



where $[\text{R}\cdot]$ and (R^-) represent electrode complexes. In view of the large potential gradient in the immediate vicinity of the electrode, about 10^7 v/cm,⁴ the initial step in this mechanism has been assumed to be attack of the electrode on the carbon atom of a polarized carbon-halogen bond.³

Controlled-potential electrolyses of benzyl halides have given evidence for the involvement of both carbanions and radicals as intermediates; carbonation of the electrolyzed benzyl chloride has yielded phenylacetic acid,⁵ whereas 4,4-dinitrobibenzyl has been isolated from the electrolysis of *p*-nitrobenzyl bromide.⁶

Many mechanistic implications have been drawn by correlating changes in polarographic half-wave potentials with changes in structure. Streitwieser and Perrin,⁷ by use of linear free energy relationships, have shown that the transition state for the polarographic reduction of substituted benzyl chlorides possesses considerable radical character. Lambert⁸ correlated half-wave potentials of alkyl halides with SN2 reactivity and more recently has proposed that in certain sterically hindered bridgehead halides, an ionic process of dissociation to carbonium ions may be the potential-determining step.⁹

Sease, Chang, and Groth¹⁰ have suggested that in bridgehead halides, and perhaps in all halides, initial attack occurs on the halogen atom. Zavada, *et al.*,¹¹ have questioned the validity of any comparisons of homogeneous reaction kinetics with half-wave potentials. They report the same half-wave potential for a number of simple monobromides which have widely different rates of homogeneous substitution reaction under both SN1 and SN2 conditions. Recently these same authors criticized the homolytic mechanism of Sease, *et al.*, on the basis that the half-wave potentials found for large-ring bromides bear no relation to the monomolecular rate constants obtained from solvolysis experiments, and they continue to classify correlations of half-wave potentials with SN2 reactivities as "superficial."¹²

Zuman, in a recent review on the polarography of alicyclic compounds, notes that there is little or no correlation of either SN1 or homolytic mechanisms with half-wave potentials for a whole reaction series but calls the correlations with SN2 reactivity "relatively good."¹³

Although the work in this laboratory concerned with the reduction of carbon-halogen bonds is incomplete, the above controversy prompts us to publish some of our most recent findings.

In an effort to distinguish between a displacement on carbon and a displacement on halogen, either of which may involve free radical or carbanion intermediates, the stereospecificity of the reduction of carbon-halogen bonds at asymmetric carbon atoms is now being investigated.

A set of optically active cyclopropyl bromides was selected for the initial stereochemical study for the following reasons. (1) Cyclopropyl carbanions invert at a very low rate;¹⁴ thus, it may be possible to observe stereospecific reactions even if the electrode complex dissociates to free carbanion before reaction with a

(1) The support of this work by the National Science Foundation is gratefully acknowledged.

(2) Abstracted in part from the M.S. thesis of J. M. and the senior thesis of B. M.

(3) P. J. Elving and B. Pullman, *Advan. Chem. Phys.*, **3**, 1 (1961).

(4) G. J. Hoijtink, *Rec. Trav. Chim.*, **76**, 885 (1957).

(5) S. Wawzonek, R. C. Duty, and J. H. Wagenknecht, *J. Electrochem. Soc.*, **111**, 74 (1964).

(6) G. Klopman, *Helv. Chim. Acta*, **44**, 1908 (1961).

(7) A. Streitwieser, Jr., and C. Perrin, *J. Am. Chem. Soc.* **86**, 4938 (1964).

(8) F. L. Lambert and K. Kobayashi, *ibid.*, **82**, 5324 (1960).

(9) F. L. Lambert, A. H. Albert, and J. P. Hardy, *ibid.*, **86**, 3155 (1964).

(10) J. W. Sease, P. Chang, and J. L. Groth, *ibid.*, **86**, 3154 (1964).

(11) J. Zavada, J. Krupicka, and J. Sicher, *Collection Czech. Chem. Commun.*, **28**, 1664 (1963).

(12) J. Krupicka, J. Zavada, and J. Sicher, *ibid.*, **30**, 3570 (1965).

(13) P. Zuman, *Talanta*, **12**, 1337 (1965).

(14) H. M. Walborsky and F. M. Hornyak, *J. Am. Chem. Soc.*, **77**, 6026 (1955); H. M. Walborsky and F. M. Hornyak, *ibid.*, **78**, 872 (1956); H. M. Walborsky, Y. A. Youssef, and J. M. Motes, *ibid.*, **84**, 2465 (1962); F. J. Impastato and H. M. Walborsky, *ibid.*, **84**, 4838 (1962); H. M. Walborsky, F. J. Impastato, and A. E. Young, *ibid.*, **86**, 3283 (1964); D. E. Applequist and A. H. Peterson, *ibid.*, **83**, 862 (1961).

proton source. (2) If a free radical of appreciable lifetime is formed, racemization would be expected to occur since cyclopropyl radicals are known to invert rapidly.^{15,16} (3) If a carbonium ion is formed, rearranged products would be expected since cyclopropyl carbonium ions are not stable.¹⁷ (4) A suitable set of optically active compounds, 1-bromo-2,2-diphenylcyclopropanecarboxylic acid and its derivatives, are well characterized and their corresponding reduction products have been configurationally related.¹⁸

During the course of this investigation it became obvious that some chemical reduction model would be useful and a number of reductions with zinc were also carried out.

Experimental Section

General. Polarographic analysis was used to obtain potential-control conditions for the electrolysis of larger amounts of material at the massive mercury electrode. Temperature was not controlled and varied from 22 to 24°. Half-wave potentials and the αn values reported were obtained directly from the recorded polarograms.

Initially, lithium chloride or tetrabutylammonium bromide was used as the supporting electrolyte, but in acid solution the polarographic waves were not sufficiently resolved from the hydrogen discharge to allow precise control of the electrochemical reaction during controlled potential electrolysis. It was found that in the presence of acetic acid, as the concentration of the electrolyte salt was increased, the polarographic wave merged with that of the hydrogen discharge. This was also reflected in the large-scale electrolysis experiments (especially with the acid, which is somewhat more difficult to reduce than the ester) by a decrease in the optical purity of the final product. The use of tetraethylammonium bromide in later experiments alleviated this difficulty.¹⁹

It was soon found that over the long period of time required in the large-scale electrolyses (3–6 hr) the aqueous calomel electrode fiber connection increased in resistance owing to precipitation of the salt by diffusion of ethanol into the junction. An isolated platinum or silver wire was henceforth used as a reference electrode, and a polarogram *vs.* this reference established the necessary control voltages for large-scale electrolysis. However, for purposes of comparison all potentials are recorded *vs.* the aqueous saturated calomel electrode (aqueous sce).

Materials. Tetrabutylammonium bromide (TBABr), polarographic grade, was obtained from Southwestern Chemical. Eastman White Label tetraethylammonium bromide (TEABr) was recrystallized several times from ethanol before use. Both Fisher Certified Grade lithium chloride and undenatured 95% ethanol were used without any further purification.

The 1-bromo-2,2-diphenylcyclopropanecarboxylic acid (Ia), its methyl ester (Ib), and 1-bromo-1-methyl-2,2-diphenylcyclopropane (Ic) were synthesized and resolved according to the published methods.^{14,18}

Apparatus. A three-electrode system was used in all experiments together with a Sargent Model XV polarograph and the *iR* compensator of Annino and Hagler.²⁰ The cell assembly consisted of three separate compartments connected by sintered-glass disks of fine porosity. One of the outer compartments contained the platinum sheet anode, and the other, a reference electrode such as aqueous saturated calomel (Beckman fiber or hole type), platinum, or silver wire. The middle or sample compartment was used for

the dropping mercury electrode (dme) and all three contained inlet tubes for passing nitrogen through or over the solution.

A small cup was suspended from a 3-mm o.d. glass rod passing through the rubber stopper which positioned the dme. This allowed the determination of *m* for the capillary at the potential where the diffusion current had reached its limiting value. A number of capillaries were used during the course of the research. Their characteristics were in the range of *m* = 1.2–1.4 mg/sec and *t* = 3.2–4.7 sec at 81-cm pressure.

High-purity dry nitrogen (Linde Air Products) was first saturated with ethanol before passing into the polarographic or large-scale electrolysis cells.

Controlled-potential electrolysis experiments were carried out in a double-diaphragm cell described by Meites.²¹ Since a bare wire reference electrode would probably change potential as the electrolysis proceeded, it was isolated from the sample compartment by sealing it into a 4 × 110 mm fine-porosity Pyrex immersion tube (Corning Catalog No. 39535) which contained the ethanolic solution of the electrolyte. The whole reference electrode assembly was then placed in the sample compartment. Constant effective potential was maintained with a potentiostat similar in design to that described by Lamphere.²² However, it was necessary to match the low impedance control loop of this system with that of the isolated reference electrode by placing a cathode-follower (Health operational amplifier system Model EU-19) in series with the reference electrode.

The servo-mechanical coulometer described by Meites²¹ was used to establish the number of electrons involved in the electrolysis.

Infrared spectra were recorded either on a Perkin-Elmer Model 21 or a Beckman IR-4 double beam recording spectrophotometer. Samples were prepared and scanned as Nujol mulls or as neat liquids between sodium chloride crystals.

Nuclear magnetic resonance (nmr) spectra were recorded on a Varian A-60 recording spectrometer as approximately 15% solutions in chloroform-*d* (CDCl₃).

Optical rotations were measured on an O. C. Rudolph & Sons polarimeter, Model 80. All measurements were made in chloroform solution using a 10-cm cell.

Polarographic Analysis. Portions (25 ml) of 0.1 *M* electrolyte in 95% ethanol were pipetted into each cell compartment, and oxygen was removed by passing nitrogen through the solution for 30 min. A 1.00-ml portion of 0.0100 *M* ethanolic solution of the compound to be analyzed was added and the solution was polarographed (at 0.1 v/min) under a nitrogen atmosphere. All data were obtained directly from the recorded polarograms (0.1 v/in.) using the maximum values of the diffusion current. The value of αn was obtained from the slope of a plot of $\log i/(i_d - i)$ or $\{[\log i/(i_d - i)] - 0.546t\}$ *vs.* *E*_{DME} as recommended by Meites and Israel.²³

Controlled-Potential Electrolysis. Approximately 60 ml of electrolyte solution was added to the cell and purged with nitrogen. The mercury pool solution interface was kept in motion with a mechanical stirrer. To establish that the current-voltage characteristics of the system were those expected from previous polarographic analysis with the same reference electrode system, the residual current was recorded at a number of control potentials and the upper potential limit (before significant supporting electrolyte discharge) was noted. The sample (0.3–0.5 g), dissolved in a minimum amount of ethanol, was then added, and after additional purging, the electrolysis was run at the appropriate control voltage until the current decayed to background.

Product Analysis. Distilled water (300–400 ml) was added to the electrolysis solutions along with 5 ml of concentrated hydrochloric acid. The solution was extracted with ether or benzene, dried, evaporated *in vacuo*, and weighed. Yields are in Table II. The material was then taken up in 10 ml of chloroform, and its optical rotation was determined. An nmr spectrum was obtained on the same material after evaporation and redissolution in CDCl₃. For the polarimetric data reported in Tables II and III, the nmr spectra indicated the absence of starting material and the presence of only the normal reduction product.

The nmr spectra of reactants and products were easily distinguished. Compounds Ia, b, and c all had two doublets centered at δ 2.72 and 2.05, 2.78 and 2.02, and 1.95 and 1.65 ppm, respectively (due to geminate cyclopropyl hydrogens), while Ic also had a singlet (methyl protons) at δ 1.72 ppm in the region of interest.

(21) L. Meites, *ibid.*, 27, 1116 (1955).

(22) R. W. Lamphere, *ibid.*, 23, 258 (1951).

(23) L. Meites and Y. Israel, *J. Am. Chem. Soc.*, 83, 4903 (1961).

(15) D. E. Applequist and A. A. Peterson, *J. Am. Chem. Soc.*, 82, 2372 (1960).

(16) A. M. Walborsky, *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), 23, 75 (1962).

(17) C. A. DePuy, L. G. Schnack, J. W. Hauser, and W. Wiedemann, *J. Am. Chem. Soc.*, 87, 4006 (1965).

(18) H. M. Walborsky, L. Borash, A. E. Young, and F. J. Impastato, *ibid.*, 83, 2517 (1961).

(19) F. L. Lambert and K. Kobayashi, *J. Org. Chem.*, 23, 773 (1958), have noted that chlorobenzene is polarographically reducible when tetraethylammonium bromide is used as the supporting electrolyte but not when tetrabutylammonium bromide is used. An earlier paper by J. J. Lothe and L. B. Rogers, *J. Electrochem. Soc.*, 101, 258 (1954), reports that the nature and concentration of the electrolyte as well as the dielectric constant of the solvent have a marked effect on the polarographic behavior of carbon tetrachloride.

(20) R. Annino and K. J. Hagler, *Anal. Chem.*, 35, 1555 (1963).

The nmr spectra of products IIa and IIb were similar in the cyclopropyl hydrogen region, each showing three sets of quartets centered at δ 2.41, 2.1, and 1.58 ppm for IIa and δ 2.52, 2.15, and 1.58 ppm for IIb. The spectrum of IIc was considerably more complex but an intense doublet (methyl on cyclopropane ring) at δ 0.92 ppm was useful for analytical purposes.

Infrared spectra for all products were comparable to those reported in the literature.¹⁸

Typically, 0.219 g [$\alpha_D -114 \pm 3^\circ$ (CHCl₃), lit.¹⁸ $-112 \pm 2.5^\circ$] of Ia in 95% ethanol which was 0.02 M in sodium hydroxide and 0.1 M in lithium chloride was electrolyzed and worked up in the manner described above. Compound IIa (0.152 g, 91% yield) was isolated and its optical rotation was determined [$\alpha_D +71.8 \pm 2^\circ$ (CHCl₃), lit.¹⁸ $+230 \pm 5^\circ$]. Since (-)-Ia has been configurationally related to (+)-IIa,¹⁸ retention (31%) had occurred.

Zinc Reductions. Initial experiments were carried out with zinc-acetic acid under refluxing conditions. This procedure yielded racemic mixtures. The data reported in Table III were obtained with the following procedures.

In Acetic Acid. The compound (0.5 to 0.6 g) was added to 20 ml of glacial acetic acid containing 4.0 g of zinc, and the mixture was stirred magnetically at room temperature for 2 days. The solution was filtered, the zinc-zinc acetate precipitate was washed with glacial acetic acid, and 100 ml of water was added to the filtrate. If the product was the 2,2-diphenylcyclopropanecarboxylic acid, it precipitated at this point and was collected. In the case of the ester or the 1-methyl-2,2-diphenylcyclopropane, the aqueous solution was extracted with ether, dried over MgSO₄, and evaporated to yield the product, which was then examined as reported above under Product Analysis.

In Ethanolic KOH. 1-Bromo-2,2-diphenylcyclopropanecarboxylic acid or the 1-bromo-1-methyl-2,2-diphenylcyclopropane (0.5–0.6 g) was added to 10 ml of ethanol containing 1 g of KOH and 5 g of zinc, and the mixture was stirred for 18 hr in the case of the acid and 30 hr in the case of the methylbromo compound. The solution was filtered, washed, acidified, and treated as above to obtain the products.

Results and Discussion

The polarographic data for the reduction of all of the cyclopropyl compounds are summarized in Table I. The ester produced a well-developed, diffusion-

Table I. Polarographic Data for 1-Bromo-2,2-diphenylcyclopropanecarboxylic Acid, Methyl 1-Bromo-2,2-diphenylcyclopropanecarboxylate, and 1-Bromo-1-methyl-2,2-diphenylcyclopropane

Electrolyte	Compound	$E_{1/2}^a$	αn^b	I^c
0.1 M TEABr } 0.17 M } acetic acid	Ia	-1.11	0.40	3.4
	Ib	-1.10	0.42	3.8
0.1 M TEABr } 0.01 M NH ₃ or } 0.01 M NaOH	Ia	-1.72	0.35	2.5
	Ib	-1.10	0.42	3.8
0.1 M LiCl } 0.1 M LiCl	Ib	-1.20	0.40	3.7
	Ia	-1.67	0.55	2.4
0.01 M NH ₃ or } 0.01 M NaOH	Ib	-1.20	0.40	3.8
	Ib	-1.30	0.33	3.9
0.1 M TEABr	Ic	-2.3		

^a *V*_s. aqueous saturated calomel electrode. ^b Slope of a plot of $\log i/(i_d - i)$ vs. $E_{DME} = -0.0542/\alpha n$. ^c Diffusion current constant = $i_d/m^{2/3}t^{1/6}C$, where i_d is the limiting value of the diffusion current (maximum currents).

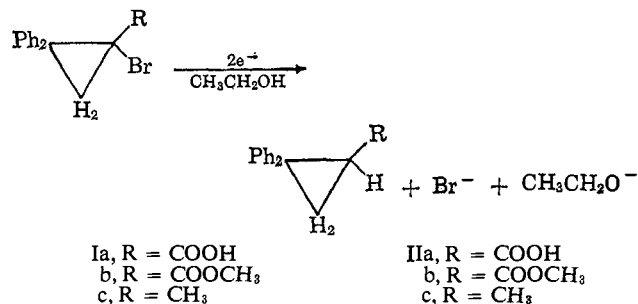
controlled polarographic wave whose diffusion current constant, I , was consistent with a two-electron reduction. Plots of $\log i/(i_d - i)$ vs. E_{DME} were linear over the range 0.1–0.9*i*_d in the presence of LiCl or TEABr. The diffusion current was somewhat erratic, however, when TBABr was used as the supporting electrolyte, and an increase in the apparent half-wave potential as well as a decrease in the slope of the wave was noted.

Since no effort was made to correct for changes in double-layer structure, the values of αn may not be significant.²⁴ However, if one assumes a reasonable value for α , 0.4 to 0.6, the results are consistent with the addition of one electron in the rate-determining step. Since the half-wave potential of the ester does not vary with pH, protonation must occur after the addition of the electrons.

The polarogram of the acid in neutral unbuffered solution consisted of two badly resolved waves which probably reflected the separate reductions of the unionized and ionized forms. That they were not separate one-electron waves was shown by electrolysis at a controlled effective voltage of -1.27 v vs. aqueous sce. The number of coulombs used to reduce the current to the background value was less than that required for a two-electron reduction. A polarogram of the resulting solution revealed only one reduction wave at -1.67 v vs. aqueous sce, corresponding to the anion of the acid. Further electrolysis at -1.67 v vs. aqueous sce yielded two electrons for the total reduction process. Another sample was electrolyzed at -1.27 v vs. aqueous sce, and the solution was acidified and extracted with ether. The nmr spectrum of the material obtained after evaporation of the ether indicated a mixture of the unreduced acid and the normal reduction product to be present.

The polarographic wave of 1-bromo-1-methyl-2,2-diphenylcyclopropane was not resolved from the supporting electrolyte discharge when TBABr or LiCl was used as the electrolyte. This interference was also noted in the large-scale electrolysis of this compound where racemic products were formed. However, in the presence of TEABr as supporting electrolyte polarographic resolution was adequate and it was possible to select a control potential for the large-scale electrolysis where background interference was minimized.

The significant results for the electrolysis of the cyclopropane compounds at the massive mercury electrode are summarized in Table II, and the reductions with zinc, in Table III. Initial experiments with compounds Ia, b, and c were carried out on racemic materials. In all cases, coulometric analysis indicated an uptake of two electrons and the reduction products (IIa, b, c)



were obtained in high yield. No dimeric or rearranged products were detected. Thus there is no direct chemical evidence for the presence of either a free radical or a carbonium ion intermediate in this particular electroreduction.

(24) An explanation for the effect of the nature and concentration of electrolyte on the slopes and half-wave potentials of electron transfer controlled waves has been offered by W. H. Reinmuth, L. B. Rogers, and L. E. I. Humelstadt, *J. Am. Chem. Soc.*, **81**, 2947 (1959). For an earlier paper which reviews double-layer effect and electrochemical kinetics, see M. Breiter, M. Kleinerman, and P. Delahay, *ibid.*, **80**, 5111 (1958).

Table II. Electrolytic Reduction of 1-Bromo-2,2-diphenylcyclopropanecarboxylic Acid, Methyl 1-Bromo-2,2-diphenylcyclopropanecarboxylate, and 1-Bromo-1-methyl-2,2-diphenylcyclopropane

Compound	% inversion	% retention	Electrolyte			$E_c,^a$ v	% yield
			Salt (0.1 M)	Acetic acid, M	OH ⁻ , M		
Ia	26		TBABr	0.04-0.17	0	-1.2 to -1.4	90-96
Ia	35		TEABr	0.17	0	-1.1 to -1.2	86
Ia	30		LiCl	0.17	0	-1.2 to -1.5	86-90
Ia		31		0	0.02-0.05	-1.7	91
Ia		38	TBABr	0	0.02	-1.7	85
Ib	43			0.17-0.34	0	-1.1 to -1.5	85-90
Ib	35		TEABr	0.17	0	-1.2	73
Ib	30		LiCl	0.17-0.34	0	-1.3 to -1.4	86
Ib	56		TBABr	0	0.02	-1.6	87
Ib	46		TEABr	0	0	-1.3 to -1.6	86-95
Ib	34		LiCl	0	0	-1.3 to -1.5	95
Ic		21	TEABr	0	0	-2.2	73-80

^a E_c = effective potential at which material was electrolyzed, reported vs. aqueous sce.

Table III. Zinc Metal Reduction of 1-Bromo-2,2-diphenylcyclopropanecarboxylic Acid, Methyl 1-Bromo-2,2-diphenylcyclopropanecarboxylate, and 1-Bromo-1-methyl-2,2-diphenylcyclopropane

Compound		% inversion	% retention	% yield
Ia	Glacial acetic acid, room temp, 48 hr	21		61
	10% KOH-ethanol, room temp, 18 hr		26	82
Ib	Glacial acetic acid, room temp, 48 hr	15		68
	Neutral ethanol and zinc, 48 hr	11		95
Ic	10% KOH-ethanol, room temp, 30 hr		21	80

Early experiments with optically active Ia yielded configurationally inverted IIa and the initial assumption was that an S_N2 -like mechanism was operative, followed by either an S_E2 reaction on the electrode complex (III), or protonation of the inverted (but stable) carbanion (IV) after diffusion into the body of the solution (see Figure 1).

However, as seen by the complete set of data in Table II, the actual mechanism may be considerably more complex.²⁵

The most significant data of Table II are the predominant retentions of configuration observed in the reductions of Ic, and of Ia in basic solution. An over-

(25) As discussed in the Experimental Section, both the polarographic behavior and the optical purity of the products are affected by the composition and concentration of the supporting electrolyte. In the presence of 0.5 M LiCl-0.18 M HOAc in ethanol, Ia or b can be reduced to racemic IIa and b, or in some cases (at high control potentials) to IIa and b with slight retention. In these cases it is proposed that, in addition to direct electrochemical reduction, some of the compound is reduced by the *in situ* hydrogen generated at the electrode surface. This reaction might be expected to proceed with retention of configuration if one can draw the analogy between it and reduction by hydrogen at active surfaces.^{26, 27}

(26) (a) H. O. House, "Modern Synthetic Reactions," W. A. Benjamin, Inc., New York, N. Y., 1965; (b) J. H. Brewster, *J. Am. Chem. Soc.*, **76**, 6361 (1954).

(27) E. Ott, and K. Kramer, *Ber.*, **68**, 1655 (1935), have reported that α -chloro- α -phenylpropionic acid is reduced by zinc-acetic acid with inversion of configuration while reduction with Pd-H₂ proceeds with retention. These results have been discussed by J. H. Brewster, *J. Am. Chem. Soc.*, **78**, 4061 (1956), where it is proposed that a direct attack on the bromine atom by the zinc surface produces a carbanion which is then protonated from the rear before it can escape the shielding action of the metal.

all retention in terms of the " S_N2 -type" inverting addition of electrons shown in Figure 1 requires a double inversion, *i.e.*, a second inversion, of the intermediate carbanion followed by protonation from the side not shielded by the electrode, before diffusion into the body of the solution. This, however, is more likely to occur with Ia and Ib than with Ic and Ia anion (resulting from Ia in basic solution), since the carboxyl and carbomethoxy groups would be expected to lower the barrier to inversion. The carbanions from Ia anion and Ic are more likely to hold their (inverted) configurations until protonated in the body of the solution. The experimental observations are clearly in contradiction to such an " S_N2 -type" mechanism. In addition, the parallel stereochemical results obtained with zinc metal reduction of those compounds, and the known fact that cyclopropyl bromides are quite unreactive under S_N2 conditions, are strong arguments against the use of the S_N2 mechanism.

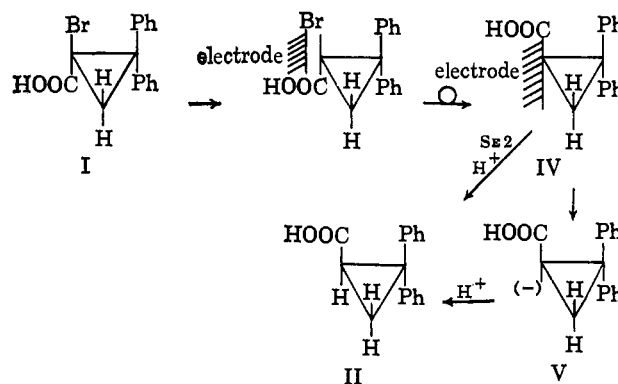


Figure 1.

A general reaction scheme is shown in Figure 2. It is given to aid in the following discussion and is not meant to represent an exact physical picture of the electroreduction.

The two main proposals which are offered to explain the stereochemistry of the process are: (1) that an initial attack by the electrode occurs on the same side of the molecule as the bromine atom to give an electrode complex with the same configuration as the reactant; and (2) that the over-all stereochemistry is determined by a

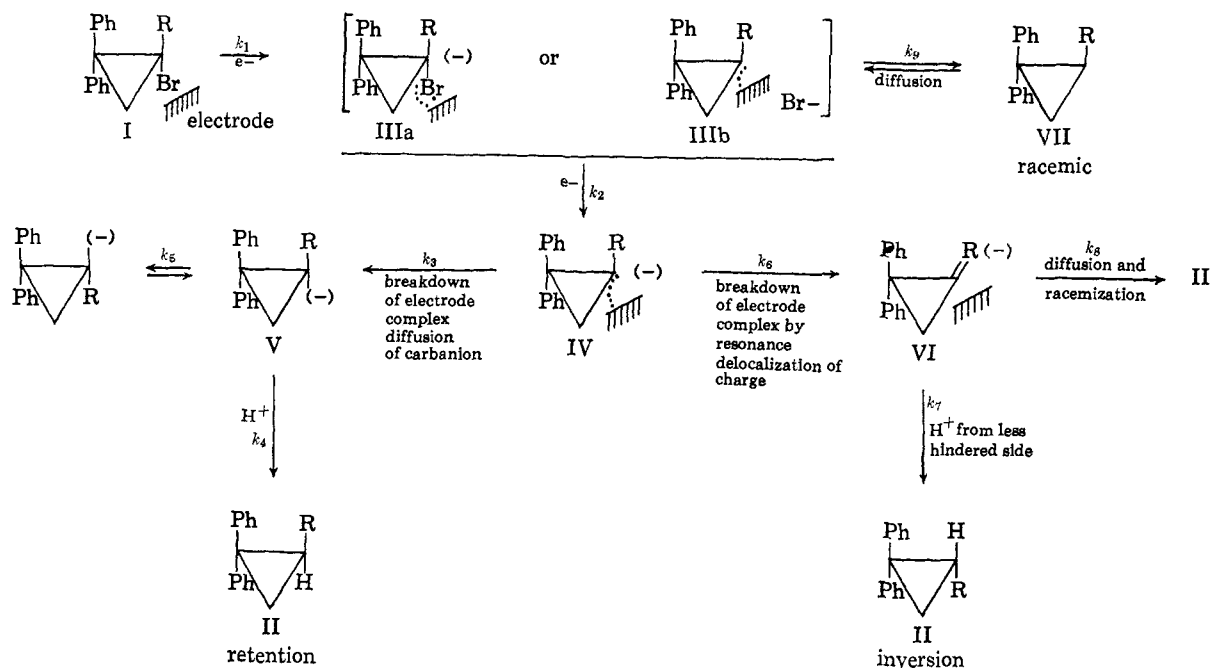


Figure 2.

stereoselective reaction of the free or electrode-shielded carbanion with solvent or proton.

For all compounds, k_1 is the rate constant for the addition of the first electron to give either IIIa or IIIb. The addition of another electron to the electrode complex (IIIa or IIIb) yields the carbanion electrode complex IV. At this point it is proposed that two different pathways may be operative. If R is methyl or carboxylate ion the dissociation of the electrode complex yields carbanion, V, which is then protonated. The optical purity of the product depends on the stability of V toward inversion. Since k_5 is expected to be smaller than k_4 ,^{15,16} when R is methyl or carboxylate ion, a significant amount of retention is found. When R is carboxyl or carbomethoxy, either a planar carbanion VI is formed, or the carbanion inverts rapidly relative to the proton uptake. If the carbanion moves completely away from the electrode, solvent attack might occur with comparable ease from either side and racemic product is formed. To the extent that carbanion VI is protonated before it can diffuse into the body of the solution, inverted product is formed. The observed case is apparently somewhere between these extremes.

According to this hypothesis, racemization may also occur by dissociation of the electrode complex (IIIb) to give the planar free radical VII.²⁸

It is apparent from the polarographic half-wave potentials that the carboxy and carbomethoxy groups

(28) The radical VII might also have dimerized before diffusion back to the electrode. However, this second-order process is expected to depend on the current density used in the electrolysis (L. Meites, "Techniques of Organic Chemistry," Vol. I, Part IV, A. Weissberger, Ed., Interscience Publishers, Inc., New York, N. Y., 1960, p 3309), and apparently was not an important side reaction in this work.

are assisting in the reduction. This is not inconsistent with the proposed mechanism since the p orbital of the carbonyl carbon may stabilize the developing one-electron orbital by partial overlap. Although this contribution is probably not as important with the anion of Ia, it may explain why this anion is reduced at a more positive potential than Ic.

The use of zinc reductions as a model was chosen because they represent a heterogeneous reaction involving electron transfer from a metal surface. Inspection of Tables II and III shows the stereospecificity of zinc reductions and electroreductions to be identical. This correlation may be fortuitous since Ib does not react with zinc under basic conditions and Ic does not react with zinc and acetic acid under the mild conditions employed. Zinc is generally believed²⁶ to attack the halogen atom in carbon-bromine bond reductions. If one replaces the electrode surface in Figure 2 with a zinc surface, the mechanism is consistent with the results reported in the literature²⁷ and in Table III.

Thus for cyclopropyl halides, at least, the mechanism of electrolytic reductions may be much more closely related to metallic reductions than SN1 or SN2 processes.²⁹

Acknowledgment. The authors wish to thank J. E. Van Verth for his helpful discussions regarding the mechanism presented herein and the State University of New York at Buffalo for the use of their polarimeter.

(29) Since cyclopropyl halides are known to be extremely unreactive in normal SN2 processes, the mechanistic scheme hypothesized here, involving initial attack on the same side of the molecule as the halogen atom, may not be operative in all cases. We are extending our stereochemical studies to other systems and continuing work on possible correlations between electroreductions and metal reductions.